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ADVANCES IN THE ENGINEERING SCIENCE OF IMMISCIBLE POLYMER
BLENDS: A POWDER ROUTE FOR DELICATE POLYMER PRECURSORS AND A
HIGHLY RENEWABLE POLYAMIDE/TEREPHTHALATE BLEND SYSTEM.

by

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ABSTRACT OF THE DISSERTATION

Advances in the engineering of immiscible polymer blends:

A powder route for delicate polymer precursors

and a highly renewable polyamide/terephthalate blend system.

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Powder processing of thermoplastic polymer composites is an effective way to achieve a high level of component homogenization in raw blends prior to melt processing, thus reducing the thermal and shear stress on the components. Polymer blends can be prepared that would otherwise not be possible due to thermodynamic incompatibility. Evaluation of this concept was conducted by processing PMMA and HDPE micron sized powders which were characterized using DSC and rheology. Optical microscopy and SEM, showed that high-quality, fine domain sized blends can be made by the compression molding process. Silica marker spheres were used to qualitatively assess the level dispersive mixing. EDS chemical analysis was effective in providing image contrast between PMMA and HDPE based on the carbonyl and ester oxygen. EDS image maps, combined with secondary electron images show that compression molding of blended powder precursors produces composites of comparable homogeneity and

domain size as extrusion processing. FTIR proved valuable when assessing the intimacy of the constituents at the interface of the immiscible domains. The formation of an in-situ, PMMA nano-network structure resulting from solvent extraction and redeposition using DMF was uniquely found on the surface of these immiscible polymer blends. This work has shown that powder processing of polymers is an effective means to melt processed fragile polymers to high quality blends.

Recently, efforts towards the development of sustainable materials have evolved due in part to the increase in price and limited supply of crude oil. Immiscible polymer blending is a paradigm that enables synergistic material performance in certain instances where the composite properties are superior to the sum of the constituents. The addition of PA6,10 to PTT offers an opportunity to increase the bio-based content of PTT while simultaneously maintaining or improving mechanical properties. PA6,10 and PTT are immiscible polymers that can be blended into multi-phase blends with fine domain morphology. Initially, the blend compositions were estimated based on empirical relationships, subsequently the polymers were formulated and extruded. Extensive work was performed via EDS and rheological measuring to identify a co-continuous composition and to assess the validity of the empirical Jordhamo relationship.

Keywords: immiscible, polymers, blends, powders, compression molding, extrusion, PMMA, HDPE, bio-based, capillary rheometry, Jordhamo relationship, power law, PTT, PA6,10, self – assembled, DMF

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PREFACE

This dissertation is comprised of a series of chapters serving as an introduction to the appended publications. The main achievements of this dissertation are presented in the following seven papers. The papers are referenced by their Roman numerals within the text.

- I. G.Giancola and R.L. Lehman, A powder processing route to polymer composites, Materials Research Society, 1209 (2009), YY07-01.
- II. G.Giancola and R.L. Lehman, Micro/nano structure and morphology of multi-phase polymer/oxide composites prepared by polymer melt processing, Materials Research Society, 1297 (2010), 10-24.
- III. G. Giancola, R.L. Lehman and J.D. Idol, Melt processing and domain morphology of PMMA/HDPE polymer blends prepared from powder precursors, Journal of Powder Technology, 218 (2012), 18-22.
- IV. G. Giancola, R.L. Lehman and J.D. Idol, Sustainable polymer composites: Immiscible blends prepared by extrusion of poly(trimethylene terephthalate) & polyamide6,10 with high bio-based content, International Journal of Sustainable Engineering, in press.
- V. Part A: G. Giancola, R.L. Lehman and S. Miller, Phase inversion composition and domain identification by energy dispersive spectroscopy in immiscible blends of poly(trimethylene terephthalate) and polyamide6,10, Journal of Polymer Engineering and Science, in press.

Part B: G. Giancola and R.L. Lehman, Uniquely identifying polymer composite domains using energy-dispersive spectroscopy, Invited article by SPE plastics research online, in press.

VI. G. Giancola and R.L. Lehman, Viscosity and domain morphology in binary immiscible blends of poly(trimethylene terephthalate) and polyamide6,10, Journal of Polymer Engineering, accepted.

VII. G. Giancola and R.L. Lehman, In-situ formation of nano-scale PMMA network structures on the surface of immiscible polymer blends by solvent extraction and redeposition, Journal of Polymer Engineering, in press.

My specific contribution to each publication, as indicated by my position as first author, has been to play the dominant role in conception of the dissertation (60%), performance of the experimental work (95%), interpretation of the results (85%), and authoring of the manuscripts (75%). In addition to the preparation of the manuscripts, I have been the principle editor with regard to revisions and submission to the journals, although Professor Lehman retained the title of corresponding author.

Chapter 1 contains background information on the topic of immiscible polymer blends and then provides an overview of bio-based polymers and the powder processing of polymers. The main purpose of this chapter is to outline the pathway that was laid out for this research and provide the aim of this work. Chapter 2 deals with the materials and experimental techniques in this research. Chapter 3 provided a synopsis of the appended papers with further discussion and conclusions addressed in Chapter 4. Chapter 5 suggests areas where the research that is presented would be applicable based on

published scientific work. Finally, Chapter 6 gives suggestions for future research based on the experiments presented in the appended papers.

1. INTRODUCTION

1.1. Background

The purpose of blending polymers is to generate engineered materials [1]. Materials fall into several classes when they are blended starting with miscible materials such as alloys. Co-polymers encompass a type of blend where the materials are linked at the molecular level, made up of more than one monomer, and occur in different arrangements such as block, alternating, graft or random orders. Furthermore, when complete polymer networks are interlaced on a polymer scale these are dubbed as interpenetrating polymer blends. In the present work, immiscible polymer blends (IMPBs) were explored. These are unique structures in which no formal chemical interaction exists but under optimal conditions the domains are intimately intertwined with optionally some level of secondary bonding such that high performance materials result.

1.2.Immiscible Polymer Blends

IMPBs are materials that are often broken down by their domain sizes in regards to their ultimate applications. If a blend's domain size is greater than 10 μm , applications include structural materials such as railroad ties and I beams [2]. Domain sizes of less than 10 μm can be achieved by using powder precursors as explained in this work and are associated with higher performance engineering blends. Blends with domain sizes less than one micrometer are specialty materials made by draw-down of larger domain blends. Historically, a common misconception is that IMPBs are impractical incompatible materials with poor performance. This thinking is in part attributed to the blends lacking interfacial bonding resulting in poor load transfer. Also, the properties resulting from such blends have been reported as poor and the literature commonly refers to the incompatibility and non-uniform phase structures of such blends [3]. Contrary to this traditional thinking of IMPBs, the AMIPP Polymer Center at Rutgers University has shown that synergistic behavior can be achieved by properly selecting the component polymers, the molecular weight of these polymers, and by using specialized compositional windows and melt processing. Additionally, knowledge of the solubility parameters of the materials being processed together facilitates a successful IMPB.

Binary immiscible blends are characterized by significant differences in the cohesive energy density, the energy of vaporization per unit volume, of the components as measured by the solubility parameter. The solubility parameter denoted by the Greek letter (δ) is the square root of the cohesive energy density. The solubility parameter is a way to apply thermodynamics to characterize the miscibility or immiscibility in a multiple phase system [4]. When a large difference in solubility parameter occurs

between two blend components, the interfacial surface energy is high and a two-phase morphology results.

Hildebrand first presented the idea of solubility being related to the internal energy of solvent and solutes in 1916. Polymeric materials fall into this category. Hildebrand proposed that molecules subjected to the same internal pressure (energy required to vaporize one unit volume of a material) are the most capable of attracting and interacting with each other. In this scenario, the resultant heat of mixing equals zero. The internal energy divided by the molar volume ratio is equal to the cohesive energy density (the energy that binds the molecules in one unit of volume of liquid or solid) [5]. Unfortunately, the molar vaporization energies for polymers are unable to be obtained [4] and therefore an alternative method must be used to determine the solubility parameters. Indirect methods include the swelling and viscosity measurements in an array of solvents as well as calculations based on group contributions [4]. Dependent variables of the solubility parameter include the polarity of the solvents used, the molecular weight of the polymer and density. Commonly the solubility parameter attributed to a specific polymer varies over a range instead of having one set value. Notably, the solubility parameter is dependent on pressure and temperature so each component needs to have its own solubility parameter at a chosen temperature [4]. In the literature tables containing the molar attraction constants (F_i), values needed for calculating the solubility parameter using the contribution method, can be found [4]. These constants are calculated for each chemical group in the polymer repeating unit. There are several different contribution methods including Hoy, Small and Hildebrand. Molar attraction constants are calculated [6] & [7] by applying regression analysis to physical property data for a number of

organic compounds. In this work, the Hoy contribution method was used where the data of 640 organic compounds is available. Equation 1 represents the solubility parameter where δ is the solubility parameter, ρ is the density, ΣF is summation of the molar attraction constants and M is the molecular mass of the repeating unit of the polymer. The units of the solubility parameter in SI are $\text{MPa}^{1/2}$ but can also be represented in $\text{cal}^{1/2}/\text{cm}^{3/2}$.

$$\delta = (\rho \Sigma F) / M$$

Equation [1]

Comparable values in the solubility parameter results in thermodynamically miscible materials. The reason behind this phenomenon is that non-bonded interaction energies are balanced during mixing. There has been a value system assigned to differences in the solubility parameters (in the molten state) to predict the immiscibility of pharmaceuticals, namely drugs and excipients. Compounds with a $\Delta\delta < 7.0\text{MPa}^{1/2}$ are likely to be miscible whereas $\Delta\delta > 10.0\text{MPa}^{1/2}$ tend towards immiscibility [7].

Under properly selected composition and processing conditions the polymers are said to be “mechanically grafted” [8] in what essentially can be visualized as a three dimensional jig saw puzzle of the domains (figure 1).

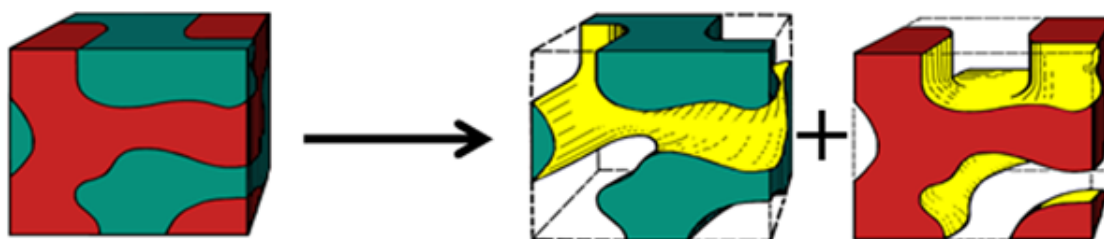


Figure 1. Depicts mechanical grafting. The co-continuous IMPB is shown as the summation of the separated phases revealing the interfacial region.

Although IMPBs lack ligands or other formal bonding between phases, in the co-continuous region the blends possess a tightly interconnected structure that produces optimal mechanical properties and affords efficient load transfer. Within the AMIPP Center immiscible polymer success has been found in a polystyrene (PS)/high density polyethylene (HDPE) system which has been licensed and commercialized. Poly(methyl methacrylate) (PMMA)/poly-L-lactide (PLLA) blends have been processed with biomimetic morphologies (bone scaffold). The advanced polymer center has also conducted research in the recycling of acrylic paint resins.

In the literature immiscible polymer blends of polylactic acid (PLA) and polystyrene have been used in the biomedical field to fabricate tissue engineering scaffolds through the solid state foaming of this IMPB [9]. Not only has the preparation of high performance IMPBs been reported, it is possible to further tailor the engineering properties of such composites with the addition of particulates. This has been demonstrated in the case of enhanced ductility of immiscible blends comprised of high density polyethylene (PE)/polyamide6 (PA6) via the nano-bridge effect of functionalized multi-walled carbon nanotubes [10]. The most recent trend in polymers pertains to renewable materials which focus less on petroleum feedstocks for environmental and cost reasons. In one such instance polymerized soy bean oil has been used as a component of an IMPB with PLLA to produce increased toughness in the PLLA while achieving a bio-based blend [11]. However, minimal research is found in the literature regarding IMPBs generated with either poly(trimethylene terephthalate) (PTT) or polyamide6,10 (PA6,10), and there is no literature on immiscible blends containing these two polymers. Thus, the opportunity presented itself to explore blends of PTT and PA6,10. Furthermore, powder

precursors have not been previously melt processed in a way that achieves comparable morphological results to that of an extruded pellet blend and this concept provided yet another path of research.

Motivation for pursuing research in IMPBs is the production of novel materials with enhanced properties without reverting back to the synthesis stage, an approach that has the potential to lower costs at the industrial level. The goal of such work has been to generate a material with linear and possibly synergistic properties of the components. Blends can also be achieved which exceed the rule of mixtures of the components. This is possible in that IMPBs lack chemical bonding and therefore each component occurs in a separate domain and the properties of these blends are typically additive functions of the constituents [12]. However, properties above the rule of mixtures can be achieved when the processing of the blends results in molecular orientation within domains, thus enhancing properties in the direction of the orientation. Immiscible materials are also not thermodynamically compatible due to entropy constraints resulting from the high molecular weight of the polymers. Through immiscible polymer blending they are able to be processed into successful composites therefore providing a larger pool of neat materials to select from [13]. Immiscible structures are generally observed in three different ways (figure 2) when dealing with constituents “A” and “B”. “A” dispersed in a continuous “B” matrix, “B” dispersed in “A” or a co-continuous matrix of an intertwined and complex morphology of both materials [13].

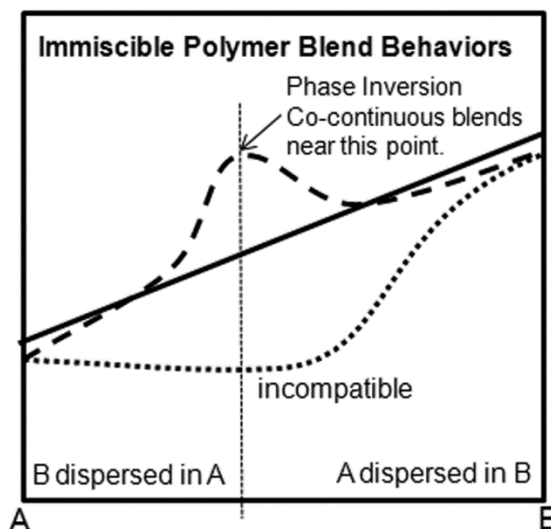


Figure 2. The structures that can result in an immiscible blend when dealing with constituents A and B

The morphological scale of the resulting composites is important and dependent on the application [14]. Typically, fine scale morphologies (on the nano and micron level) are preferred since these types of domains offer enhanced mechanical properties via efficient load transfer mechanisms. Interesting, although these blends lack chemical interactions, the fine structured IMPBs have strong impact on glass transition and crystallization behavior. Ideal polymer blends are homogeneous with good dispersion of the multiple phases present. A co-continuous morphology is generally sought since this compositional region presents a morphology of maximum interconnectivity and interaction between the two phases [15]. To find this region, knowledge of the viscosities of the materials is essential. Co-continuity is dependent on the volume fraction and mixedness of the initial components, processing temperature, shear rates, and the dwell time of the polymer during melt processing [15]. Additionally, the type of processing has direct effect on the final properties produced.

1.3.Bio-Based Polymers

In recent years a global initiative has been to move in the direction of sustainable materials. With the limited supply of fossil fuels in the world, this new and promising area of research has generated interest. The incentives for decreasing the reliance on petroleum based feedstocks are attractive. These sustainable materials are dependent on renewable feedstocks which are often associated with lower costs than petroleum. Bio-based polymers follow the “go green” model of emission reduction and promotion of the necessity of recycling. Synthesis of partially bio-based polymers where substantial segments of the molecule are based on renewable feedstocks has been responsible for the initial success in this area of polymers. Bio-based precursors that are used in the synthesis of renewable polymers include sugar based diols as in the case of PTT and sebacic acid derived from castor oil, a byproduct of the castor seed found in PA6,10. Sometimes it is thought that using renewable feedstocks will infringe on the global food sources, however this is not always the case. Castor oil is extracted from the seed of *Ricinus communis*. Castor plants grow abundantly in tropical or sub-tropical climates [16]. This plant is not a potential food source since it is toxic to humans. As such it is readily available for non-food applications.

Although synthesizing bio-based polymers is an approach for obtaining new materials, it is not always a feasible route to take. Not all polymers can be re-engineered to contain significant renewable content. Therefore another fruitful avenue to pursue is to prepare a blend of a higher bio-based fraction polymer with a lower bio-based fraction polymer to produce a blend that can be used in place of the lower bio-based polymer, ideally with improved properties.

1.4. Powder Processing of Polymers

Typically, thermoplastic immiscible polymer blends are melt processed using conventional techniques such as extrusion and injection molding. These methods are used heavily in commercial processing and rely on high temperatures, high shear rates, and extended dwell time during processing to generate a homogenized blend. The type of processing has strong influence on the resultant blends morphology which in turn govern the resulting properties. Extrusion and injection molding have the potential to generate domain sizes on the micron level from pellet precursors. Most traditional thermoplastic polymers, an example being linear alpha-olefins, have a good ability to withstand commercial processing conditions, although some degree of degradation occurs even in these systems.

Some newer polymers, particularly those used in the cosmetic and pharmaceutical fields, are sensitive to elevated levels of temperature and shear rate. Furthermore these precursors may not be subject to extended processing times and temperatures if they are to retain their specialized properties. Interestingly, some of these polymers have recently become available as fine powders, thus enabling the novel approach of preparing blends from polymer powder precursors to enhance cold mixing and to minimize their thermal degradation during processing. Compression molding is an alternative approach where the processing time at elevated temperatures is low and the shear rate is low. These conditions aid in the preservation of the delicate powder precursors and permit a wider range of polymer blends to be processed. Powder blending also enables polymer blends that are not possible to be produced by melt methods due to unfavorable rheological behavior and solubility parameters. Compression molding suffers drawback in that it has

a short flow path [17] and is absent of high shear mechanical mixing. A resolution to the problems of compression molding is to employ a two stage mixing system. The first stage mixes the polymer powders at room temperature prior to melt processing. The next stage is to compression mold the polymers fusing the polymers into an immiscible polymer blend thus providing a second mixing of the blended polymers at the melt stage. Ample mixing for the powder constituents is provided and since degradation is a function of time, temperature and shear rate, this process minimizes those effects. This novel processing can be applied to blends with widely varying, incompatible, thermal processing properties and immiscible blends which would otherwise not be possible due to thermodynamic issues. The resulting morphologies are comparable to those of extrusion in that they are homogeneous and of micron size (figure 3).



Figure 3. Illustration of the conventional extrusion method in comparison to the two part powder processing method resulting in the same homogeneous, fine-structured blend.

1.5. Aim of the work

This work focused on immiscible polymer blends and was divided into two major sections; powder polymer processing and bio-based polymers. Each section was performed in incremental segments as shown in the appended publications (I-VII).

Polymer powder precursors are new materials that are only now becoming widely available at the industrial level. Initially this work was focused on studying the

availability, and characterization (through differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR)) of raw polymer powders. Once this was explored, a suitable immiscible polymer system (PMMA/HDPE/silica) (SiO_2) was selected for processing. The feasibility of mixing and melt processing (initially through extrusion) of these powders to form a three phase composite was an essential beginning step. A new approach to melt processing polymer powder precursors was sought and employed to satisfy the delicate processing needs of these materials. Furthermore, once it was determined that powder precursors generated immiscible polymer blends, analysis between compression molding of polymer precursors and extrusion of pellets was an essential goal. Analysis of scanning electron microscopy images was aimed at demonstrating that polymer precursors processed by compression molding produced blends with comparable homogenous, fine sized domains similar to blends made by pellet extrusion of the same polymers. Energy dispersive spectroscopy was used for the first time to discriminate between domains of polymers thus providing another useful tool of analysis in an IMPB. Furthermore, a main goal of this work was the assessment of the intimacy of the blends (compression molded and extruded) and the polymer-polymer interactions through FTIR spectroscopy and image analysis. A final step in the powder processing route, (although not an initial intent of this work) was a side avenue that was taken to explore a serendipitous discovery in the PMMA/HDPE powder system – that of a self-assembled continuous, open structured, high surface area, low solids fraction, nano scaled domain network. This network was observed to grow from dissolved blend components on cold fractured surfaces of immiscible polymer blends when reacted with dimethyl formamide.

The research into bio-based polymers was focused initially on an investigation into the use of immiscible polymer blending to improve the bio-based content of a relatively new polymer (PTT), by adding another bio-based polymer (PA6,10) while maintaining or enhancing the engineering and processing properties. Characterization of the materials was necessary prior to melt processing to guide the subsequent processing. Sufficient characterization was completed by using DSC to determine melt behavior, calculation of the solubility parameters for both polymers, and verification of the known viscosity data for the raw materials. The viscosity data were used in conjunction with empirical viscosity/volume fraction relationships to estimate a region of co-continuity and to demonstrate that the two selected polymers could be co-processed by extrusion to produce an immiscible polymer blend. Once it was determined that an immiscible polymer blend could be made from the extrusion of PTT and PA6,10, research shifted to formulating binary blends over the full compositional range with the goal of locating the approximate phase inversion point, assessing the degree of co-continuity in this region and differentiating the domains of the component polymers using EDS. As a final step in this section of the research, extensive viscosity measurements were collected for the binary immiscible polymer system of PTT and PA6,10. The goal of this segment was to describe a way in which viscosity varies over the binary composition range and the applicability of the power law viscosity relationship in two-phase materials. Additionally, the validity of the Jordhamo relationship [18], an empirical rule for identifying the phase inversion composition was assessed for this particular immiscible polymer system.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1. Materials

Polymeric raw materials are typically obtained in pellet form prior to processing. Only recently have bulk amounts of high purity, fine scaled polymer powder for commercial use been made available. To obtain fine sized polymer powders methods such as hammer milling and disk milling were conventionally used. Drawbacks to these methods are contamination of the polymers from the equipment used and other processing limitations. The powdered polymers used in this work were generated via two different avenues. A new cryogenic process of autogenously milling exists which takes pellet precursors and produces micron size particles of equi-axed but irregular shape while an alternate method, emulsion polymerization, produces spherical commercial polymer powders.

The powder portion of this work focused on an immiscible polymer blend of PMMA and HDPE. The acrylic was used in two different forms in several separate studies (Paper I, II & III). The PMMA (Kobo Products: BPA – 500) chosen and explored in Paper I is an emulsion polymerized non-crosslinked material with a mean particle size of 10 μm with a range of 70% between 5-16 μm . The PMMA studied in Paper II, III & VI (Jet Pulverizer: Altuglas V045I) is produced by cryogenic jet-milling of Altuglas V045I pellets. The resulting particles are approximately 10 μm with a blocky equi-axed shape. The PMMA pellets used in Papers III and IV were Altuglas V045I pellets. HDPE is also used in two different forms in Paper II. The pellets used in the conventional extrusion segment of that work were Exxon HD7960. The emulsion polymerized HDPE (Kobo Products: CL-2080) (figure 4) boasts an average particle size of 11 μm with a range of 85% less than 25 μm . It can also be noted that this is a low melting material (105 $^{\circ}\text{C}$).

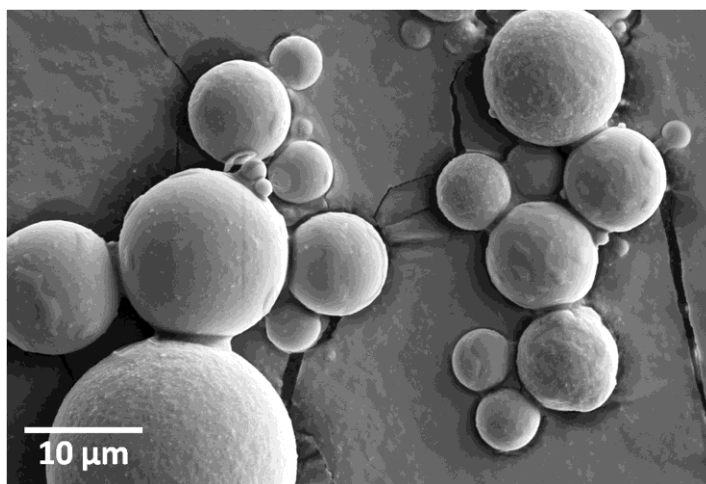


Figure 4. SEM image of emulsion polymerized HDPE (CL-2080); 5kX magnification, working distance 16mm, accelerating voltage 5kV.

In all experiments involving the immiscible blend of PMMA/HDPE, inorganic silica is blended with the component polymers. This SiO_2 additive (Kobo Products: MSS-500/3N) is emulsion polymerized resulting in approximately 5 μm spheres and served as a tool to assess the homogeneity and degree of dispersion in the blends (figure 5).

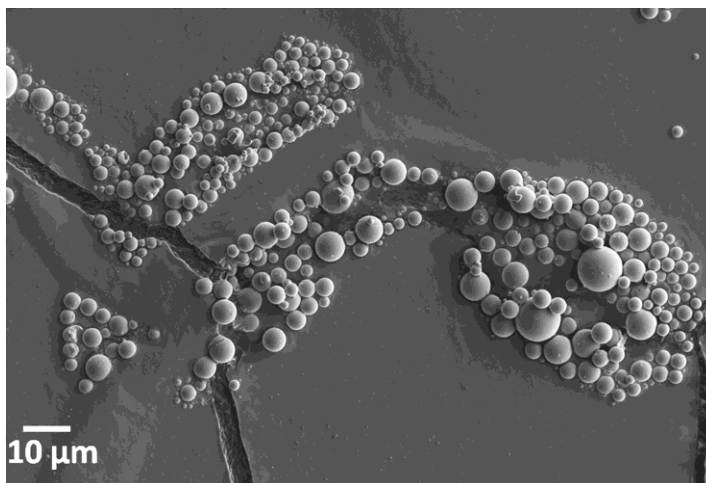


Figure 5. SEM image of emulsion polymerized SiO_2 (MSS-500/3N); 2kX magnification, working distance 16mm, accelerating voltage 5kV.

The two polymeric materials used in the bio-based segment of this work are both in pellet form. PTT and PA6,10 are both obtained by commercial suppliers and are DuPont products. PTT and PA6,10 are semi-crystalline polymers. Visually, the pellets of these materials differ in that the pellets of PTT are opaque and those of PA6,10 are translucent. PTT is a thermoplastic aromatic polyester with 11 carbon atoms in the repeat unit and is derived by reacting terephthalic acid with 1,3 propanediol (trimethylene glycol). This polymer is bio-based due to the diol part of 1,3 propanediol being derived from corn sugar. The renewable fraction is about 36%. The chemical structure of PTT is represented in figure 6.

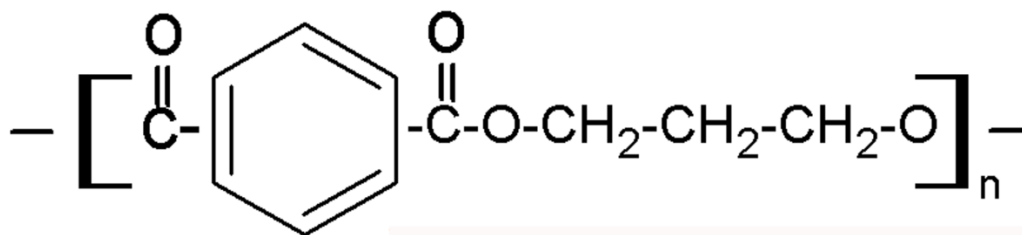


Figure 6. The chemical structure of poly(trimethylene terephthalate).

PA6,10 has 16 carbon atoms in a longer linear backbone with approximately 60% of this polymer originating from renewable sources. The polymer is synthesized by reacting hexamethylenediamine with sebacic acid (dicarboxylic acid) and its chemical structure is shown in figure 7.

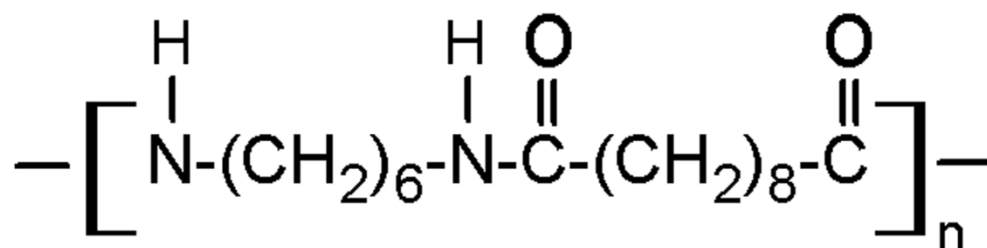


Figure 7. The chemical structure of polyamide6,10

The renewable portion of this polymer is attributed to sebacic acid which is a derivative of castor oil. Castor oil is a byproduct of the castor seed. Castor plants are toxic for human food consumption and are therefore readily available for non-food uses. Table 1. summarizes the materials used throughout the entire thesis.

Material/Product	Form	Supplier	Density (g/cm ³)
PMMA/Altuglas V045I	Powder	Jet Pulverizer	1.15
PMMA/BPA-500	Powder	Kobo Products	1.17
HDPE/ CL-2080	Powder	Kobo Products	0.92
SiO ₂ / MSS-500/3N	Powder	Kobo Products	2.4
HDPE/ Virgin Exxon HD7960	Pellets	Sabic	0.95
PMMA/ Altuglas V045I	Pellets	Sabic	1.15
PTT/ Sorona® 3001	Pellets	DuPont	1.33
PA6,10/ ZYTRSLC3090	Pellets	DuPont	1.08

Table 1. Materials selected.

2.2.Compression Molding

Compression molding is an essential method when melt processing the polymer powder precursors. As discussed, it is necessary to pre-blend the powder precursors as part of the two phase mixing process developed for the powder based composites since only a low level of mixing occurs during the actual melt processing due to the short flow path [17]. The pre-blended compositions are then compression molded, a processing method with low shear rates and short residence times between the platens to limit degradation of these delicate polymers.

A typical procedure for melt processing immiscible polymer powder blends via compression molding is as follows. The components are mixed either until visual homogeneity is reached or by ball milling with about 10 vol.% of approximately 3mm alumina spheres for 10 hours. The alumina spheres are removed by screening after the mixing is complete. The spherical media are used to provide good agitation and promote mixing. The blended compositions are subsequently dried overnight under vacuum at a designated temperature provided by the supplier to eliminate moisture. The blends are

then compression molded with a Carver® press (figure 8) with parallel heated platens maintained at a pre-determined temperature. Polymer powder is added and sandwiched in between room temperature Teflon®- coated steel plates. Approximately 5 g of the blends are used so as to have enough material to form a thin film but to ensure that the polymer does not exude from the edges of the plates. The plates containing the powdered blend are put between the heated platens and placed under a force of 40kN pressed for 150s. The Teflon® plates are removed from the press with the specimen remaining between them and immediately quenched. After the film is separated from the plates, the specimens are cold-fractured and those surfaces are prepared for electron imaging. A precise value of pressure is difficult to determine due to the fact that the polymer is flowing to form a film however the final area of the film is approximately 200 cm² corresponding to a pressure of 2 MPa. The final films are about 250 µm.



Figure 8. The Carver® compression molding press.

2.3.Extrusion

Extrusion is widely used in industry and is a traditional approach to melt processing thermoplastic immiscible polymers blends. This melt processing method is efficient in achieving homogeneous polymer composites by using high levels of shear, at elevated temperatures for extended periods of time. This method has been used extensively in the AMIPP Advanced Polymer Center for developing novel polymer blends. The procedures used to extrude immiscible polymer blends vary depending on the material and the desired morphology and properties. In all cases the equipment used is a Brabender Intellitorque 0.75” 30:1 single screw extruder (figure 9) with various pressure zones and mixing elements. The four controlled heating zones are located over all processing zones; the conveying zone, the transition zone, the metering zone, and the die. Temperatures for these zones vary considerably and are adjusted empirically to enable extrusion. In this work the most critical adjustment was found to be in the temperature of the solids conveying zone such that good wetting of the extruder wall by the polymer was achieved to provide sufficient shear stress for extrusion. Exit temperatures at the die were controlled to give good extrudate surface texture without melt fracture or excess fluidity.

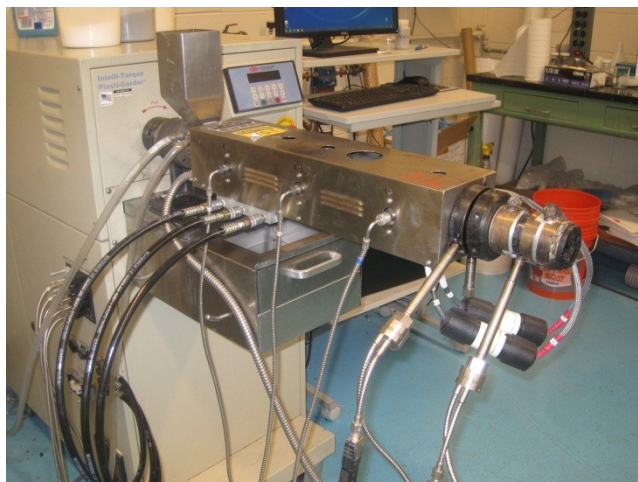


Figure 9. The Brabender Intellitorque Plasticorder with single screw extruder.

In the initial powder precursor experiments extrusion was used in order to demonstrate the formation of immiscible polymer composites from the powders under typical conditions. The polymer powder blends were used to create a densified cake which was subsequently ground into pellets as described in section 3.1. The pelletized mixture was double-extruded. The initial extrudate was prepared at 160 °C with the vent port open to allow any remaining moisture to escape and chopped into pellets, which were returned to the extruder for a second processing at final temperatures of 160 °C, 190 °C, and 220 °C.

As the PMMA, HDPE, SiO₂ spheres system progressed in research, the pellet version was formulated and used as a comparative tool to the compression molded powder system of the same constituents. In this case, the pellets were manually blended until a visually uniform mix was obtained. The PMMA was dried under vacuum at 80 °C before blending. Each composition was double extruded. The initial extrudate was processed with all heating zones set at 200 °C. The extrudate was cooled and pelletized

off-line and then returned to the extruder for a second processing under the same conditions to provide a high level of mixedness.

In the study of bio-based polymer blends, extrusion was the exclusive melt processing technique employed. The processing temperatures for the neat polymers PTT and PA6,10 were about 40 °C different. The compositions which featured high nylon volume fraction often proved difficult to process due to unexpected spikes in the torque. Therefore, the temperature profiles had considerable differences depending on the composition of the blend, and the profile was adjusted empirically online to ensure successful processing. Two critical features of the extruder operation was the maintenance of low temperatures where the pellets were fed and relatively low temperatures in the transition zone to maintain a sufficient level of wall friction. Lastly, close attention was paid to the temperatures at the conveying zone and the die exit temperature was closely controlled to ensure specimens of good quality as indicated by surface finish and the avoidance of melt-fracture. Monitoring at the die was essential to ensure a steady feed of pellets to the die and to avoid problems with excessive fluidity in the die land resulting from the highly shear thinning nature of the polyamide. The extruder was run typically at 100 RPM while processing with a rod extrusion die and a 1/8 inch orifice insert. The temperature of each extruder processing zone was controlled according to a predetermined program. Drying PTT and PA6,10 under vacuum at 120 °C and 80 °C respectively in accordance with commercial recommendations for approximately 12 h was essential to eliminate moisture and subsequent bubbling of the composites. The materials were weighed, manually blended, and held in hermetically sealed glass jars at 80 °C prior to melt processing. Table 2 summarizes the temperature

profiles of the blends that were melt processed via extrusion throughout the thesis. All extruded samples were cryo-fractured in preparation for analysis using the Zeiss Sigma field emission scanning electron microscope (FESEM).

Extruded Blends			
Paper	Materials	Percent(by vol)	Solids/Trans/ Metering/Die (°C)
I	PMMA-BPA-500	30PMMA/55HDPE/15SiO ₂	<i>Double extruded</i>
	HDPE-CL-2080		200/200/200/160
	SiO ₂ -MSS-500/3N		200/200/200/190
			200/200/200/220
II&VI	PMMA-AltuglasV045I	35PMMA/55HDPE/10SiO ₂	<i>Double extruded</i>
	HDPE -ExxonHD7960	45PMMA/45HDPE/10SiO ₂	200/200/200/200
	SiO ₂ -MSS-500/3N	55PMMA/35HDPE/10SiO ₂	200/200/200/200
IV, V & VI	PTT -Sorona [®] 3001 PA6,10-ZYTRSLC3090	0PTT/100PA6,10	230/245/260/275
		10PTT/90PA6,10	215/235/245/250
		20PTT/80PA6,10	215/230/250/245
		30PTT/70PA6,10	215/245/250/260
		40PTT/60PA6,10	230/245/250/260
		45PTT/55PA6,10	240/250/240/250
		50PTT/50PA6,10	230/250/255/235
		55PTT/45PA6,10	220/250/240/250
		60PTT/40PA6,10	230/250/250/245
		70PTT/30PA6,10	180/230/250/245
		80PTT/20PA6,10	200/230/250/245
		90PTT/10PA6,10	215/245/250/260
		100PTT/0PA6,10	235/250/265/280

Table 2. Extrusion profiles.

2.4.Parallel Plate Rheometry

Parallel plate rheometry is a well-known, reliable method for characterizing the viscosity of molten polymers, and has been used extensively as a characterization method in our laboratories for neat materials prior to melt processing. This is an off-line measurement that does not accurately model the shear environment of the extrusion process [18] since shear rates are low ($<1000\text{s}^{-1}$). Furthermore the sample size is small and long residence times are required between the heated plates to run extended shear and temperature scans. The extended exposure to high temperature has the potential to degrade the polymer during the test and also allow the hot polymer to flow out of the aperture.

For all parallel plate rheological testing in this work, a TA AR-2000 rheometer (figure 10) was used with a 25 mm diameter aluminum parallel plate geometry in conjunction with Rheology Advantage Software.



Figure 10. TA Instruments, AR-2000 parallel plate rheometer.

When testing powder specimens, the powder was first compression molded into 25 mm disks and subsequently vacuum dried overnight at supplier recommended temperatures. In preparation for the testing of extruded samples, all extruded blend specimens were chopped into three millimeter pellets and the neat materials were used in their “as received” pellet state. The lower plate was fitted with a melt ring to provide confinement for the testing material. The parallel plates (figure 11) were closed to a one millimeter gap and a stress sweep was performed to define the linear viscoelastic region (LVR).



Figure 11. Parallel plate geometry of the AR-2000 rheometer.

The strain values obtained from the LVR test were used in the time temperature superposition (TTS) oscillatory frequency sweep to obtain shear stress versus shear rate data for the materials at a predetermined temperature profile. The Cox-Mertz transformation was applied to the TTS data and plotted using a logarithmic scale for all viscosity versus shear rate curves.

2.5. Capillary Rheometry

Capillary rheometry is a well-established method to measure the viscosity of nearly all types of polymers and polymer blends. Several standard test methods exist for capillary rheometry as well. Desirable attributes of this rheological method are that the viscous flow in a capillary most closely resembles the nature of flow during extrusion and new material is constantly being measured in the capillary. This is in contrast to the nearly static behavior of the sample in the parallel plate method. The range of shear rates represented by capillary rheometry is low although a single valued shear rate is not possible. Small capillaries were used in this method and thus the error attributed to shear rate averaging is low [19]& [20]. Data can be collected at the high shear rates ($>1000 \text{ s}^{-1}$) typically found in commercial extrusion and injection molding processes.

In this research, capillary rheometry was used to measure the viscosity of the bio-based materials at the end materials and across the full range of blend compositions. All data were collected at 250°C using a Brabender single screw extruder equipped with the capillary die (figure 12a) with a variety of inserts (figure 12b).

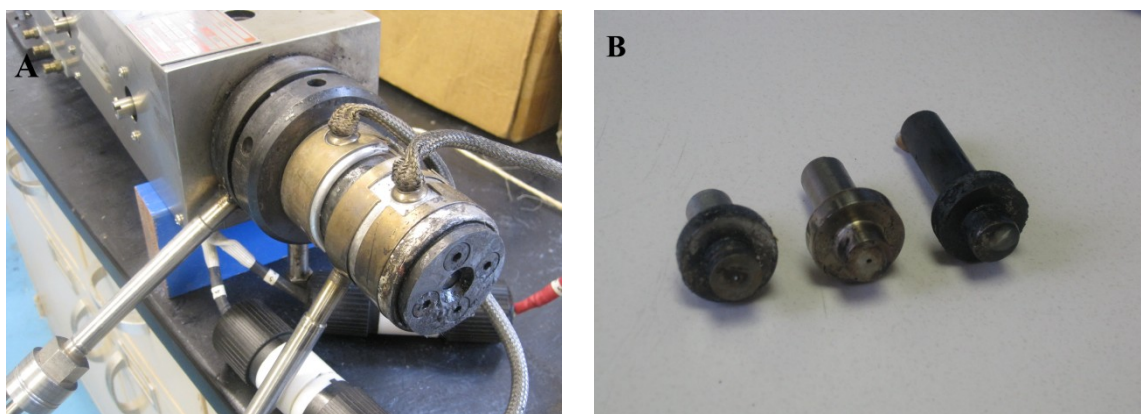


Figure 12a&b. (a)Capillary rheometer; (b) left to right: die inserts 15:1, 20:1 and 30:1.

As a general methodology, different capillary inserts are installed, all being one millimeter in diameter and representing L:D ratios of 15:1 and 30:1. Line-out must then be reached, a process of flow stabilization that occurs before each measurement is made to ensure that the extrudate flow has reached plastication equilibrium. This process usually takes about five minutes to reach such a flow and once achieved, the exiting material from the extruder is collected over a one minute interval. The sample's mass is measured and recorded. Simultaneously during sample collection, the pressure at the capillary entrance is measured by two pressure transducers and the temperature is monitored over four temperature zones. The collection of multiple specimens is necessary for averaging under each condition. The standard test method used in this research is ASTM D5422-09 [20] which calls for repetition of this procedure using two different capillary inserts and at least two extruder drive speeds for the purpose of obtaining shear stress and viscosity values.

Finding the phase inversion composition which ultimately identifies co-continuity is often a difficult process. There are ongoing efforts aimed at developing new techniques to resolve where this region occurs in a polymer system [21]. There are general guiding principles that govern where co-continuity can be found when processing binary immiscible polymer blend systems. An example of such a principle is an empirical relationship called the Jordhamo relationship (equation 2). This principle is based on rheological data of the neat end members and the physical blend does not have to be experimentally prepared to use this mathematical assessment. This equation relates the viscosity (η) of each polymer at the processing temperature to the necessary volume fraction (Φ).

$$\frac{\eta_A}{\eta_B} \cong \frac{\Phi_A}{\Phi_B}$$

Equation [2]

The relationship predicts co-continuity to exist when the volume fraction ratio of the blend is approximately equal to the viscosity ratio at the shear rate and temperature of the extrusion processing. Although this relationship is useful to predict the approximate volume fractions to be used in preliminary extrusion processing, in order to have a comprehensive assessment of any immiscible blend system it is necessary to perform a full rheological evaluation spanning all shear rates and temperatures. Co-continuity does offer advantages in immiscible systems resulting in enhanced structural performance, permeability and thermal conductivity [1]. It must be noted that there has been several instances of improved properties when the droplet-in-matrix morphology is present such as improved impact resistance and tensile properties [1]. The droplet-in-matrix regime is found when one of the polymers in the binary system is dominant, i.e. an over or underestimation of the Jordhamo relationship. If the volume fraction ratio is less than the viscosity ratio then discrete domains of phase A are dispersed in a matrix of phase B. Conversely, if the volume fraction ratio is greater than the viscosity ratio then the domains of B are dispersed in a continuous matrix of A. This relationship is only an approximation considering that experimental data is not a factor. Furthermore, the validity of the Jordhamo relationship obviously depends on the accuracy of the rheological data for the end members, and also when the viscosities are measured at low shear rates. Research has indicated that the Jordhamo relationship overestimates the phase inversion composition when the viscosities are measured at high shear rates [22].

Collecting viscosity at the same processing temperature and shear rate as the extruder creates a problem since polymers are typically shear thinning and therefore the viscosity will vary throughout the processing equipment. Due to this phenomenon, there will be a distribution of phase inversion compositions.

Shear thinning of polymers is modeled through the power law equation shown in equation 3. This model is unique in that it gives the viscosity of a melt as a function of consistency (m) and the power law index (n). Consistency is a highly temperature sensitive parameter and the index measures the shear thinning behavior of the polymer melt. The distinct appearance of temperature and shear parameters in the power law model make it ideal for modeling the shear stress and viscosity behavior of polymer and polymeric blends.

$$\eta = m(T)\dot{\gamma}^{(n-1)}$$

Equation [3]

In this research, as discussed in section 3.6, the power law index of blends cannot be clearly predicted based on the data collected from the end members. The power law index often varies in the intermediate composition region and usually sheds light on the evolving structure of the blends. This is an interesting feature of the power law behavior and was the basis for several conclusions regarding the formation of blends in the PTT/PA6,10 immiscible polymer system. Beyond this system, this finding is likely applicable to many IMPB systems.

2.6. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used extensively throughout this research to assess the morphology of the immiscible polymer blends. In preparation for analysis, the specimens were cryo-fractured, mounted on a stud and coated with either gold or iridium using an Electron Microscopy Sciences (EMS150T ES) coater (figure 13). Coatings of these metals range from 7- 10 μm as a preventative measure against charging effects.



Figure 13. Electron Microscopy Sciences EMS150T ES coater.

The equipment used is a Zeiss Sigma field emission scanning electron microscope (FESEM) (figure 14a&b). Images are typically obtained using an accelerating voltage of 5 kV and an approximately 8.5 mm working distance.

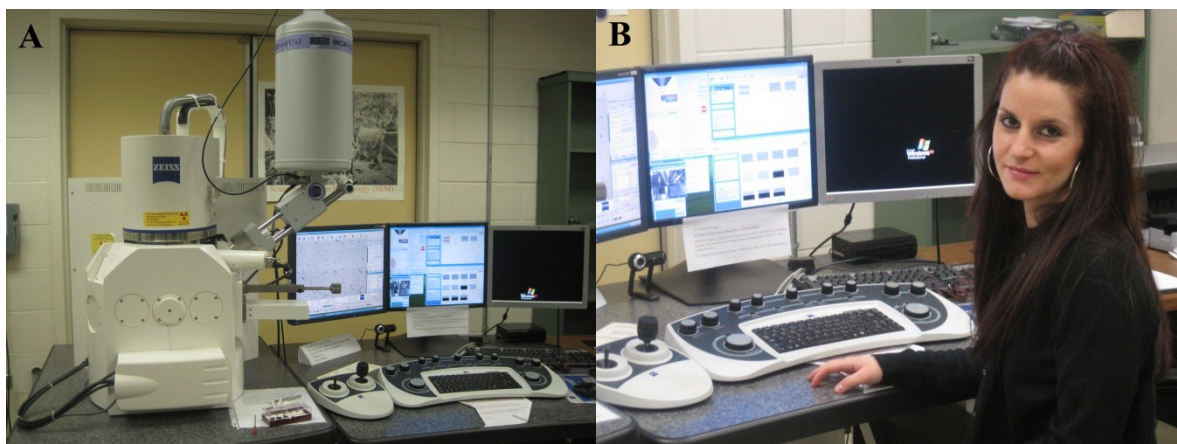


Figure 14a&b. (a)Zeiss Sigma field emission scanning electron microscope used in all electron imaging. (b) Giorgiana operating the FESEM.

Visually, it is possible to narrow down the region of co-continuity based on the SEM images. Incompatible immiscible blends are characterized by the domains of one phase pulling away from the domains of the other phase resulting in a droplet-in-matrix morphology (figure 15).

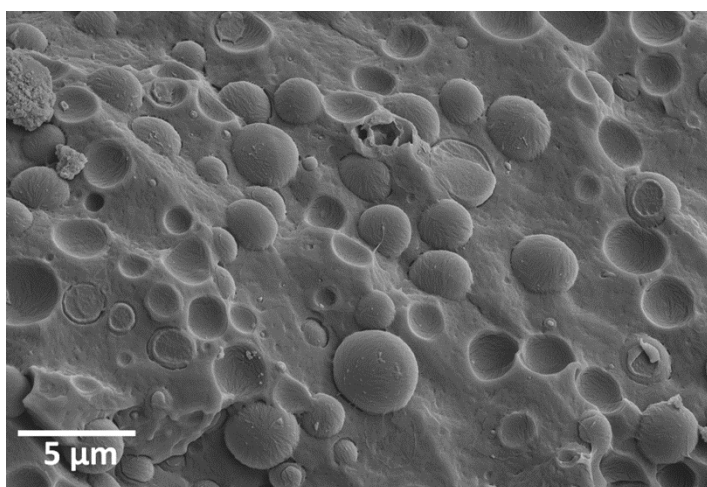


Figure 15. Droplet-in-matrix morphology of 30PTT (by volume); 10 kX magnification, working distance 14 mm, accelerating voltage 5 kV.

As the domains approach co-continuity, typically a fibrous, columnar, semi-dispersed phase parallel to the extrusion axis is present (figure 16). Usually the cross-sections of

the domains are more elongated than those of its composition neighbors and evidence of branching will be present.

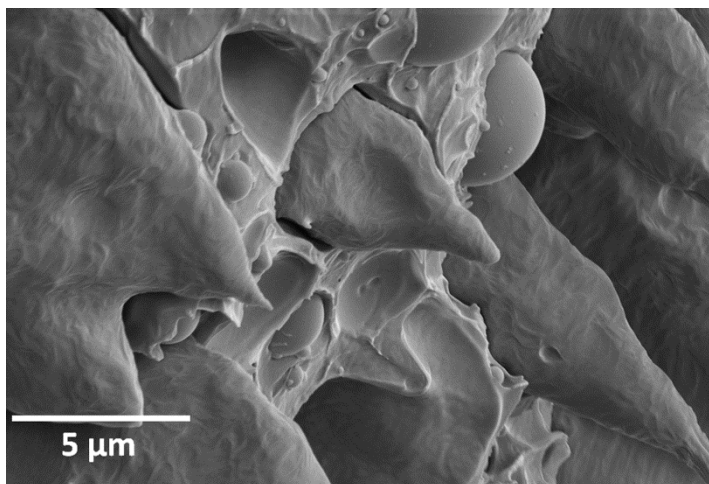


Figure 16. Representation of approaching co-continuity in an extruded blend of 55PMMA/35HDPE/10SiO₂; 15 kX magnification, working distance 16 mm, accelerating voltage 5 kV.

Co-continuity, as observed under the microscope, is characterized by morphology that is highly branched and structures that are intimately intertwined.

Initially, in the powder segment of this work, the raw materials are assessed using optical microscopy and SEM to assess the blend components as well as the mixedness of the generated blend. The three components (PMMA/HDPE/SiO₂) were dyed and identified by color under optical microscopy (figure 17) and also prepared for SEM. The addition of the silica spheres was essential as a tool for visual assessment using SEM to compare the level of dispersion achieved in the powder processing compression molding route in relation to the traditional pellet extrusion method. Furthermore, SEM gives the ability to determine domain sizes achieved via melt extrusion using these techniques.

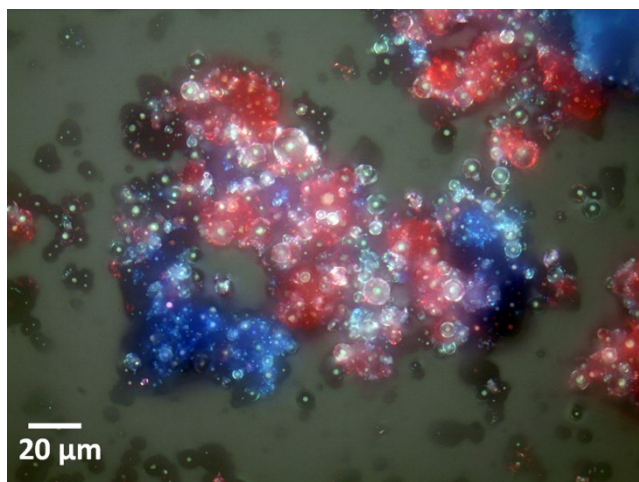


Figure 17. Dyed polymers microspheres of PMMA(red), SiO₂ (blue) and HDPE (white) observed via microscopy; 50X magnification.

SEM images were key in the discovery of the self-assembled nano-network on the surface of the PMMA/HDPE immiscibly binary system. The initial goal of the solvent etching was to confirm domain identification by dissolving the PMMA phase of the system leaving the HDPE. However, when observed under the microscope, the high surface area, low solids fraction, nano scale domain morphology, continuous network was discovered which opened the doors to a new avenue of research.

In the case of the bio-based specimens, solvent extraction of the phases is not used selectively in order to preserve the native nature of the interface and domain sizes are able to be assessed. Furthermore, a rough determination of the components of the binary system can be developed and also the composition where phase inversion exists can be narrowed down through SEM prior to using EDS or solvent etching by evaluating morphologies and domain sizes.

SEM is most useful in the study of not only polymer blends but of composites of all types where the morphology and microstructure are essential to the performance of the material.

2.7. Energy dispersive spectroscopy and Image Analysis

Energy dispersive spectroscopy (EDS) mapping uses standard EDS elemental analysis to fingerprint the image by overlaying elemental maps of the constituents onto the original SEM image to permit chemical identification of individual domains. The EDS analysis was performed using the Zeiss Sigma FESEM with Oxford INCA PentaFETx3 EDS system in conjunction with the Oxford INCA software. Maps were acquired with an accelerating voltage of 3 kV, high current, an increased aperture size to the standard 30 μm and an 8.5 mm working distance. Extended scan times and drift correction were employed to positively identify elements at the submicron resolution. The x-ray signal processing times were set to the maximum values permitted by Oxford INCA in order to minimize noise and improve the x-ray peak resolution which was essential when the element that was being sought was in danger of signal overlap due to close proximity to neighboring elements i.e. nitrogen $K\alpha$ in relation to carbon and oxygen. EDS resolution is much lower than that of the secondary electron images. The best resolution that can be achieved for this system is in the range of 0.5-1.0 μm . Very small domains are not resolved well and subsurface domains can cause confusion in the analysis due to the fact that the signal is generated from the volume and not just the surface. False mapping elements can occur if the signal to noise ratio is not sufficient.

A major finding in this research is the ability to differentiate between polymer domains using EDS. Even with its shortcomings, EDS is a feasible approach to domain identification in IMPBs even when the element has low atomic number and is present in concentrations as low as 10 wt.% [23]. The similarity in the density and chemical composition of the polymers often causes difficulties in determining the identity of specific domains particularly when SEM imaging is used. EDS of polymer with subtle differences is difficult especially when evaluating phase separation in the submicron regime. Polymers are prone to charging due to their high dielectric constants which is further provoked by the high beam currents used to obtain reasonable x-ray counts.

In the powder polymer system of PMMA/HDPE with dispersed particles of silica, EDS was initially used as a tool to identify the inorganic spheres and to assess their level of homogeneity in the blend. Interestingly, this technique was also used to discriminate between the domains of HDPE and PMMA using subtle chemical differences (figure 18). HDPE is a pure hydrocarbon whereas PMMA is rich in oxygen due to its presence in the carbonyl and acrylic ester groups, thus making EDS able to differentiate these phases. This eliminates the need for solvent etching or other physical perturbations of the sample surface to resolve the phase structure. Suitable solvents are often hard to find, particularly in advanced engineered immiscible blends, and etching has the potential to change the structure such that subtle features can be lost. Hence, EDS is a more attractive alternative for phase identification.

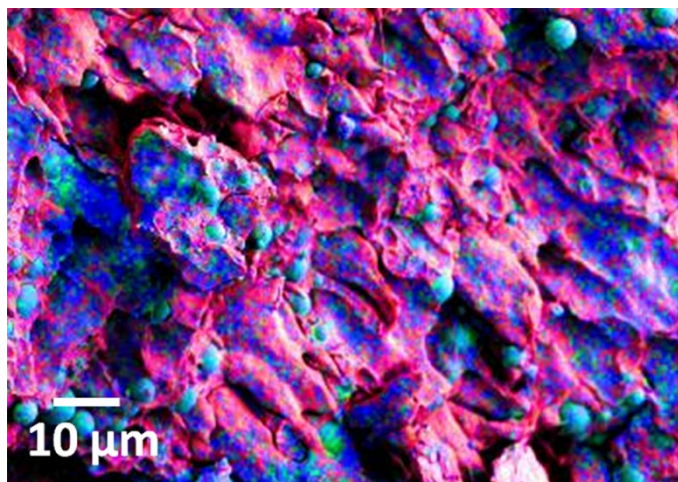


Figure 18. EDS differentiation of PMMA(red), HDPE(blue) and silica domains(green).

In the bio-based portion of this work, EDS was also employed to differentiate the domains of the immiscible blend. Initially, the fact that both polymers (PTT and PA6,10) contained oxygen was thought to preclude EDS from being able to differentiate the respective domains. Indeed, although some success was achieved in differentiating domains based on oxygen, much greater success was achieved when switching to the nitrogen peak. PA6,10 contains significant nitrogen (10.2 wt.%) whereas PTT contains none. Thus, even though the nitrogen signal has low intensity, the contrast between the two polymers is sufficient to enable differentiation via EDS (figure 19).

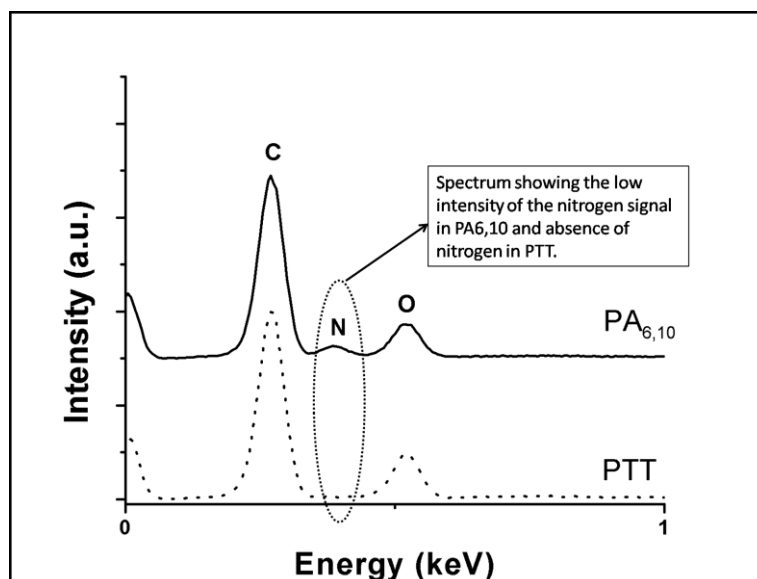


Figure 19. EDS chemical spectrum showing ability for EDS to discriminate polymers based on a 10% concentration of nitrogen in PA6,10.

This approach lead to a greatly improved signal/noise ratio and was critical in the success of this phase of the work. Figure 20a represents the EDS map overlaid on the SEM image of the PTT/PA6,10 blend and figure 20b is the original SEM image of the blend.

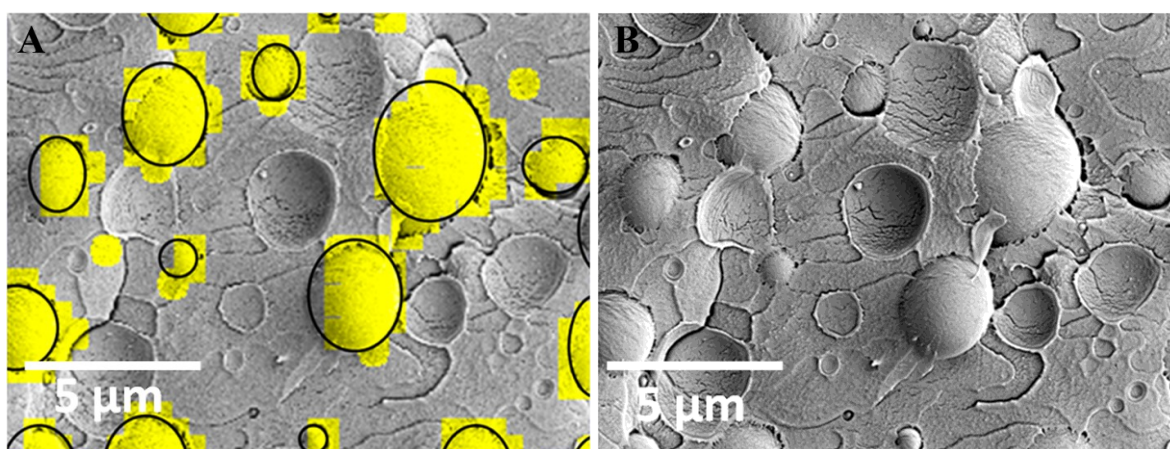


Figure 20a&b. (a) EDS differentiation of PTT and PA6,10(outlined yellow spheres);(b) original SEM image .

Although EDS is not a new technique, this work shows that at high resolution it can be used to differentiate between chemically similar polymers, an often challenging undertaking, and demonstrated its applicability as a new approach to domain identification in immiscible polymer blends.

Image analysis is often used in conjunction with EDS for blends that are dispersed and co-continuous. This methodology involves perimeter tracing of domains, integrating the area traced for each domain and comparing the integrated value with the known volume fraction of the phase in the composite. From these data it is possible to calculate and generate graphs of area and cumulative area curves versus domain size (figure 21a&b).

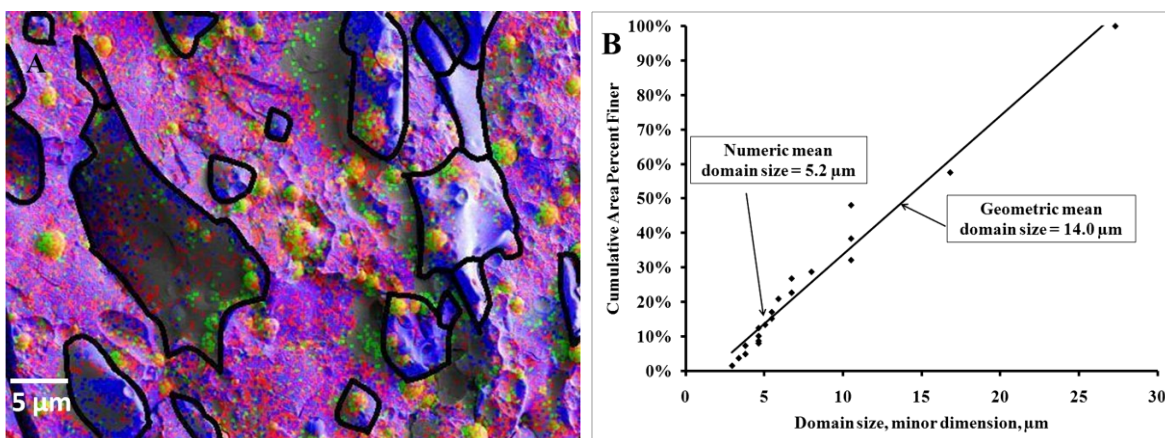


Figure 21a&b. (a) Traced domains on an EDS elemental map overlaid on an SEM image and (b) subsequent area data graphs.

2.8.FTIR

Fourier transform infrared spectroscopy (FTIR) is an essential tool to analyze neat polymers and polymer blends. After acquiring a spectrum of an unknown single material, it can be compared to a known spectrum on file in a library or a reference

spectrum attained in the laboratory. Each material has a unique “fingerprint” which makes identification feasible through band assignments which are available in electronic libraries or in the literature. The position, shape and relative intensities are essential to observe when assigning an appropriate vibrational band assignment [24]. The FTIR spectrum of a compound, in the case of IMPBs, is typically the superposition of the absorption bands of the functional groups [24]. This technique is essential in characterizing polymer blends to assess the intimacy of the polymers at the domain interfaces and the nature of the polymer/polymer interactions.

In this research, all FTIR spectra were acquired using a Perkin Elmer Spectrum RX I FTIR spectrometer in conjunction with a MTEC model 300 photoacoustic detector (figure 22).



Figure 22. The Perkin Elmer Spectrum RX I FTIR spectrometer and MTEC model 300 photoacoustic detector.

The spectrometer was scanned from 600 cm^{-1} to 4000 cm^{-1} with a 150 scan count. The scan count depends on the level of background noise to be eliminated. A higher scan count is essential in discriminating the essential peaks from the noise. All spectra were

normalized and adjusted with background correction. Duplicate and sometimes triplicate scans were conducted to ensure consistency and reproducible results.

FTIR was essential in this research to identify certain characteristics in raw materials prior to blending. This allowed for the finding of unconventional behavior attributed to the raw materials and not the melt processed blend composite as seen in Appendix I [14]. When the emulsion polymerized polymer powders were received, characterization of the material properties was conducted in our laboratory as a crosscheck to the information provided by the supplier. In the initial PMMA/HDPE immiscible blend system, PMMA (BPA-500) was selected for processing. This material failed to fuse under melt processing conditions. FTIR was used to acquire a spectrum for this sample and the spectrum was compared to spectra of known samples of PMMA (figure 23). Although BPA-500 does not appear to show major differences when compared to the reference spectrum, it does show slightly greater absorbance in the 2800-3000 cm^{-1} range (figure 23a) attributed to C-H stretching [14]. Furthermore, reduced absorbance in the 1166-1291 cm^{-1} range (figure 23b) was also observed, attributed to C-O stretching. This behavior is indicative of cross-linking or other structural effects.

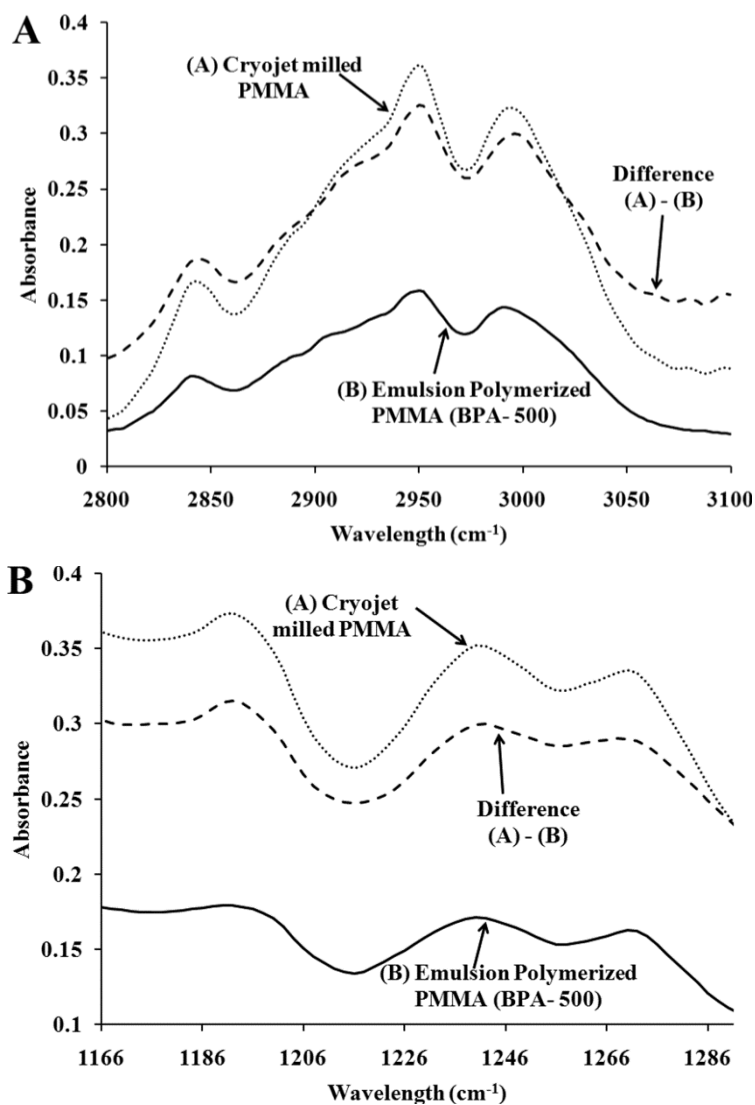


Figure 23a&b. (a) FT-IR spectra of BPA-500, known sample of PMMA and the difference between the spectra; wavelength 2800-3100 cm⁻¹. (b) FT-IR spectra of BPA-500, known sample of PMMA and the difference between the spectra; wavelength 1166-1291 cm⁻¹.

Based on these conclusions, another PMMA powder material was selected and successfully employed in the remainder of the powder segment of this research as discussed in section 3.2.

PMMA is further explored as discussed in section 3.7 with regards to the formation of an in-situ nano-scale PMMA network structure on the surface of the PMMA/HDPE immiscible polymer blends when reacted with dimethyl formamide (DMF) in a solvent extraction/redeposition process. Two types of synthetic PMMA network “surface network” and “solution solids” were generated in the laboratory and were analyzed via FTIR in powder form to learn about the structure of the nano-network. Virgin pellets of commercial PMMA were also analyzed and served as the control. The surface network was generated on the PMMA pellet surface and the solution solids were generated by evaporating the etch solution to dryness in a glass dish. FTIR was successful in determining that the nano-network generated on the surfaces of the IMPBs as well as the networks generated in the lab are comprised of PMMA by revealing nearly identical fingerprints of the control material to the networks found on the IMPBs and generated network material. Although all of the materials showed strong absorbance peaks at 1470 and 1495 cm^{-1} , attributed to the bending asymmetry of CH_2 found in PMMA, FTIR identified major discrepancies at other wavenumbers for the solution solids. Apparently, the morphology of the blend or the pellet surface is required to synthesize network structures of PMMA.

FTIR analysis was conducted for the first time in this research on micron size PMMA powder particles produced by autogeneous cryo-grinding of bulk pellets. Prior work in the AMIPP laboratories has shown that the interaction of immiscible domains across the domain surface can lead to subtle changes in the bonding backbone and pendant groups that are FTIR active [25]. Subtle effects have been observed and reported for the extruded and powder processed blends as described in section 3.3.

FTIR is a valuable characterization tool in polymer science and this method has made substantial contributions to this work with regard to our ability to characterize immiscible polymer blends at the molecular level.

2.9.Solvent extraction and redeposition

When processing immiscible polymer blends, solvent etching is commonly used to discriminate the domains of the resulting composites. This is an effective method to enhance the morphological features of the specimen prior to microscopic assessment. Depending on the ultimate goals of the research, solvents are sometimes used to completely dissolve one phase of a binary composite thus leaving the remaining phase and underlying structure for domain identification. In this research, domains were not completely removed in order to preserve important morphological features, but rather to simply open slightly the interfaces between the materials to enable domain identification from the SEM images.

Solvents were selected based on their solubility parameters in relation to the polymers in the composite. Table 3 lists the solubility parameters of the polymers and the solvents used in this work. Dimethyl formamide (DMF) was chosen in this work due to its intermediate solubility parameter ($24.7 \text{ MPa}^{1/2}$) [26] and its known success in etching PMMA in a PMMA/PLLA system. Therefore DMF was also used to etch the PMMA/HDPE system in the current research.

Solvent (S) or Polymer (P)	Solubility Parameter (MPa ^{1/2})
PMMA (P)	22.7
PTT (P)	35.4
PA6,10 (P)	21.3
DMF (S)	24.7

Table 3. Solubility parameters of materials and solvents.

When imaging the binary polymer system of PMMA/HDPE using SEM, a continuous, nanometer scale, self-assembled network was discovered on the etched surfaces of the immiscible blends (figure 24) [27]. Other unique features of the network was its uniformity and thickness, a high level of surface area, and its continuous and open character. Solution and precipitation of polymers is strongly affected by the type of solvent used and DMF was the solvent among several that was tested and was successful in achieving this structure in what presumably is a solvent extraction and redeposition process. Samples of the network were obtained by scraping the etched blends and further by reproducing the effect on virgin PMMA pellets. A similar but different material was also generated by evaporation to dryness of the solvent after etching (section 3.7). Subsequent characterization of this network by FTIR and DSC revealed that the network was comprised of PMMA and had a glass transition temperature nearly identical to the PMMA pellets used in processing the composites. This solvent extraction/redeposition process can be used to create this network in-situ as an interfacial bonding enhancement agent for polymer/polymer or bio-polymer composites depending on the specific properties of the network and the degree to which it is bonded to the substrate.

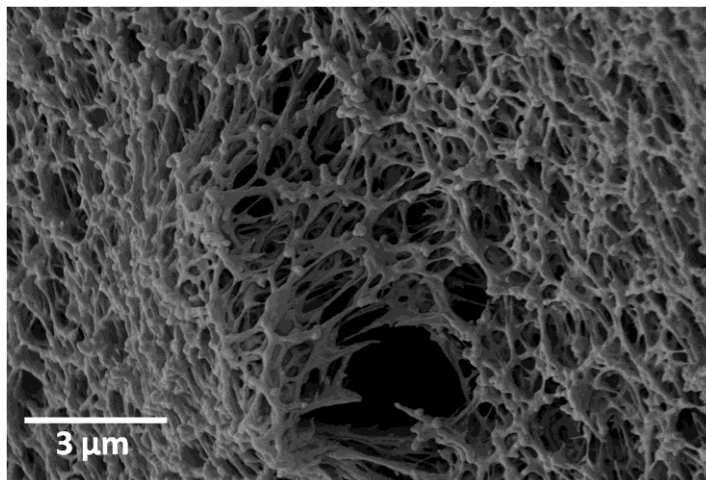


Figure 24. SEM image of nano-network generated on the surface of the 55PMMA/35HDPE/10SiO₂ immiscible polymer blend when reacted with DMF for a 2 minutes at ambient temperature; 20 kX magnification, working distance 16 mm, accelerating voltage 5 kV.

2.10. Differential Scanning Calorimetry

Differential scanning calorimetry was essential in characterizing the properties of the materials used in this research. Since an abundance of variables exist in polymer research, some of which are uncontrolled, understanding and characterizing the constituents prior to experimentation is essential.

In the infancy of the powder segment of this work [14], the PMMA (BPA-500) and HDPE (CL-2080) polymers were characterized using DSC analysis to identify melting points, crystallization, and glass transition temperatures. The DSC results indicated that the PMMA has high-temperature softening behavior and a glass transition temperature of 94.2 °C, which contrasts the conventional PMMA T_g of 105 °C. The melting point of the HDPE was 104 °C, lower than the traditional HDPE value of 120 – 125 °C, thus indicating that this material was not a true HDPE, a feature that correlated with the low melt viscosity.

In all measurements, a TA Instruments DSC Q1000 (figure 25) was used. The Q1000 is equipped with an auto sampler mechanism.



Figure 25. TA Instruments DSC Q1000 equipment.

The temperature range of this instrument, without using liquid nitrogen, ranges from -90 °C to 725 °C. With liquid nitrogen, the lower end of the range is extended to -170 °C. Samples can be solid monoliths or powder. When studying polymers the powder precursors were used in the as-received state and the pellets were reduced in size using a blade to achieve the 10 mg sample size for the equipment. The material was weighed and crimped into an aluminum base/lid assembly. The sample pan along with a pre weighed reference pan was put into the DSC chamber for analysis. TA universal software was used to both control the test and also for data analysis. Standard heat/cool/ heat tests were used in the DSC segment of this research with lower and upper temperature selected based on the material being evaluated. The first heat curve represents the structure of the materials in an as-formed state rather than the quasi-equilibrium DSC behavior that is reflected by the reheat curves. This first heat serves as a way to erase the thermal history of the sample prior to reheating this sample. This first heat versus second heat

information was critical with regard to characterizing the nano-network, as discussed in section 3.7 and in Appendix VII. DSC was instrumental in determining if the network was amorphous, glassy or crystalline, and to compare the transition points with known values of standard materials. DSC confirmed that the synthetic network grown on the pellets was a glassy material with a T_g of 103 °C, comparing favorably with the T_g of the virgin pellets (104 °C). The surface network film gave a strong endothermic enthalpic signal at T_g with a 14% greater shift in heat flow than observed in the pellets, which further pointed to the strong glassy nature of the pellet surface network. The synthetic materials were characterized as amorphous non-crystalline materials in part due to their contrasting behavior to PMMA pellets using DSC [27]. DSC in conjunction with FTIR was essential in classifying the chemical nature of the network material, particularly differentiating the naturally forming network with the synthetic network formed on the PMMA pellets, and the solution solids material. Although the existence of an IMPB was not necessary for the formation of the network, proximity to the parent material was essential for the network to form as a glass rather than just an amorphous solid.

The material characterization information provided by DSC aided in the selection of materials for successful immiscible polymer blending. The melting points of PTT and PA6,10, as measured by DSC, are within a sufficiently close range such that these materials could be satisfactorily processed together to produce an IMPB. Supplier data provided for these materials were in good agreement with the experimental results. Furthermore, the difference between the heating and cooling curves for PA6,10 was a modest 35 °C whereas for PTT it was quite large with a delta of 59 °C (figure 26) [12].

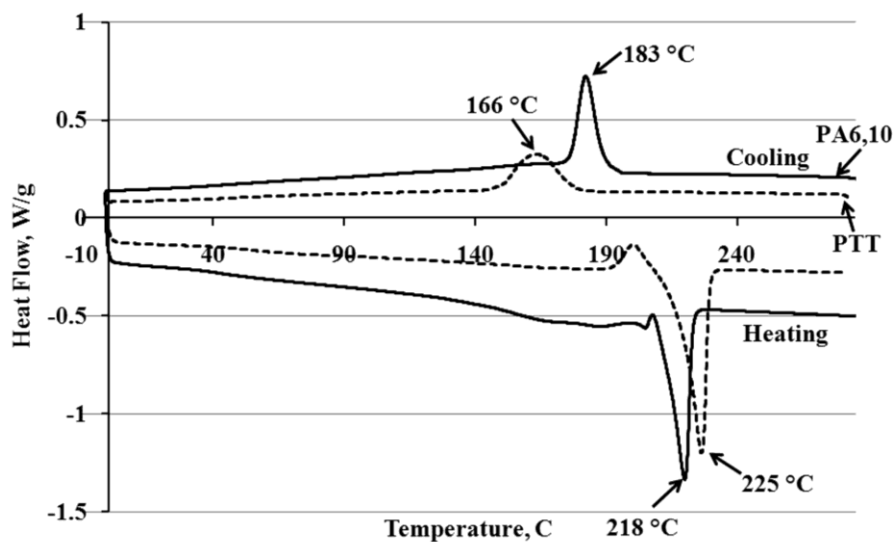


Figure 26. DSC traces of PTT and PA6,10.

The larger value indicates that a substantial amount of undercooling was required to overcome the kinetic barrier to crystallization. The crystallization of PTT was 60% as determined by integrating enthalpy ratios thus resulting in a fluid material. The PA6,10 had contrasting behavior with crystallization of about 27% resulting in a viscous material. Although PTT has a short thermoplastic range, this material has an ideal processing range of PTT (232 – 260 °C) in comparison to a longer worker range of PA6,10 with unfavorable high processing temperature range (230 - 330 °C) of PA6,10. These thermal properties in conjunction with melt rheological data were important in selecting materials which result in improved processing conditions.

3. SUMMARY OF APPENDED PAPERS

This chapter summarizes the papers encompassing all dissertation work. Paper I, II and III address a novel powder processing technology for immiscible polymer blends using a system of PMMA/HDPE/SiO₂. In addition to exploring and characterizing the composites generated from this technology, the powder blends were compared to the conventional extrusion process. Paper IV, V – Parts A & B and VI address a new immiscible polymer blend system, that comprised of the bio-based PTT/PA6,10. These blends were confirmed to make successful IMPBs and an extensive rheological work up was conducted to pin point the location of co-continuity. These experimental data were compared to the empirical model of the Jordhamo relationship to either confirm or refute its validity. Paper VII deals with a serendipitous scientific discovery found while working with PMMA. A continuous open structure with high surface area, low solids fraction and nano-scale morphology was found to self-assemble on the surface of cold fractured surfaces of PMMA/HDPE when reacted with dimethyl formamide. This paper

characterizes the network and documents my efforts to reproduce and characterize the material.

Additional details for the papers addressed in this chapter can be found in Appendix I-VII.

3.1. Paper I: A Powder Processing Route to Polymer Composites

Extensive research has been conducted at the AMIPP Advanced Polymer Center regarding various immiscible polymer blends including PMMA/PLLA and PS/HDPE. Considerable success has been achieved in generating an IMPB comprised of one high modulus glassy polymer and one low modulus semi-crystalline polymer at predetermined volume fractions based on the rheological behavior of the constituents. These composites are most typically fabricated using pellet precursors for melt processing via extrusion or injection molding.

Paper I explores a new blend comprised of a binary system of PMMA (BPA-500) and HDPE (CL-2080). Furthermore the new approach of melt processing powder polymer precursors was assessed in this initial work at a single composition of 30 vol% PMMA- 60 vol% HDPE. A high level of mixedness in the powder blends melt processed by compression molding was essential to produce a composite comparable to that of an extruded composite. In order to monitor the level of homogeneity, an inorganic powder material, SiO₂ (MSS-500/3N), was introduced at 10 vol% to the binary powder system to aid in the subsequent image analysis of the material produced by this new method.

Since processing powder blends was a completely new area of investigation, preliminary experiments focused on understanding the blending and mixing

characteristics of the components. Hence, a powder blend of PMMA/HDPE/SiO₂ was dispersed in an aqueous vehicle containing propanol and a dilute ammonia solution (listed in descending order of presence) at a solids fraction just slightly greater than 50%. Mechanical agitation was applied to fully homogenize the blend prior to double extrusion melt processing. To assess the success of the blending process, the neat component powders were dyed for differentiation and the blend was examined prior to processing under optical microscopy to confirm that a sufficient level of homogeneity was achieved without excessive agglomeration. Higher resolution SEM images were analyzed and the micrographs showed an interesting particle packing behavior in which the finer particles were observed to surround the coarser particles.

SEM investigation into the three phase system of the extruded blend shows a matrix of HDPE with PMMA and SiO₂ dispersed within that matrix (figure 27), an interesting outcome since it was expected to yield a PMMA/HDPE system with dispersed SiO₂ particles. This phenomenon was most likely attributed to the inability of PMMA to fuse as discussed in Section 2.10.

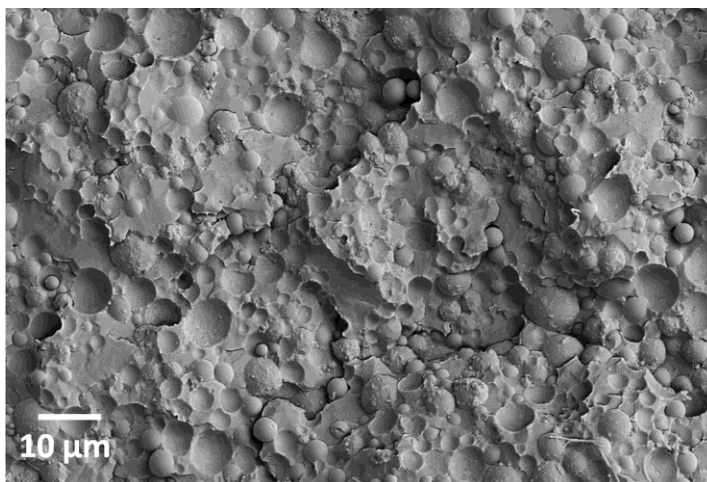


Figure 27. SEM image of HDPE matrix with dispersed PMMA and silica in an extruded composite of 30PMMA/60HDPE/10SiO₂; 2.5 kX magnification, working distance 8.5 mm, accelerating voltage 5 kV.

This paper clearly shows the feasibility of powder processing thermoplastic polymer composites and was the corresponding image analysis was essential to confirm that this method was an effective means to achieve homogeneity prior to melt processing.

3.2. Paper II: Micro/Nano Structure and Morphology of Multi-Phase Polymer/Oxide Composites Prepared by Polymer Melt Processing

Although Paper I was essential to establish the successful method of powder processing an immiscible composite comprised of PMMA and HDPE, it did not address the limitations of extrusion melt processing. Extrusion is a conventional method to melt process polymers and is effective in promoting homogeneity of blend composites by subjecting them to high residence times at elevated temperature and high shear rates. A major drawback, however, is that long residence times are needed that tend to degrade the polymer during the process, thus making it non-ideal for thermally sensitive polymer powder precursors.

The goal of Paper II was to compare pre-blended polymer powder precursors melt processed by compression molding to that of the traditional extrusion method using pelletized precursors. Similarly to the previous work, inorganic silica was added to all blends in this study to monitor their dispersion thus representing the level of homogeneity present in the resulting composites. Most interestingly observed by SEM was that both processes have the ability to yield fine micro-scale morphology, which in both cases were nearly co-continuous (figure 28a&b).

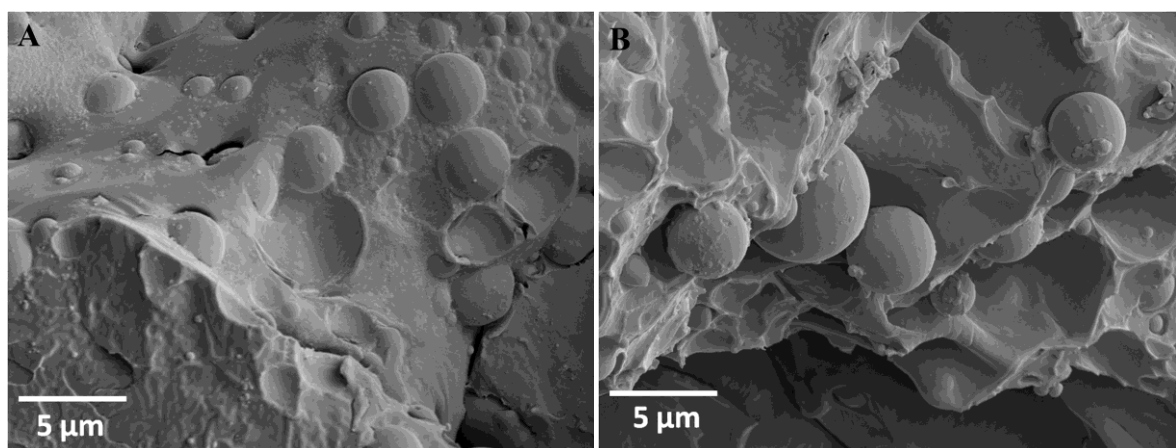


Figure 28a&b. SEM images showing (a) compression molded (40PMMA/50HDPE/10SiO₂) and (b) extruded (55PMMA/35HDPE/10SiO₂) morphologies respectively; 10 kX magnification, working distance 14 mm, accelerating voltage 5 kV.

Visually assessing the SiO₂ spheres revealed that the particulates were well dispersed, strongly suggesting that these opposing methods have the ability to achieve similar levels of mixedness.

EDS was employed to conduct elemental analysis on the blend specimens. Not only is this useful in analyzing the location of the silica and determining their dispersion, EDS was also used to differentiate between PMMA and HDPE domains. PMMA is oxygen rich whereas HDPE is a hydrocarbon – rendering oxygen and carbon

concentrations an excellent way to discriminate between the two materials. EDS gave a vivid representation of the domains and further revealed the SiO₂ spheres, even including some spheres situated below the surface. This EDS study that enabled polymer domain differentiation by chemical composition was a major finding of this work. EDS revealed a comparable level of distribution and dispersive mixing within both processes. The domain sizes of the compression molded specimens seemed to be similar though may be slightly larger than that of the extruded blends.

This work was successful in processing delicate powder polymer precursors which yield similar composites to those of traditional pellet extrusion. EDS was initially employed to assess silica sphere distribution within the blends however it was also highly successful in distinguishing the domains of the polymers present. Although EDS is a technique widely used in the science community there has been no published work prior to this paper that uses EDS to differentiate polymers in an immiscible blend.

3.3 Paper III: Melt processing and domain morphology of PMMA/HDPE polymer blends prepared from powder precursors

Paper III continues on the idea of powder polymer processing an IMPB of PMMA and HDPE from micron sphere polymer powder precursors. A two stage mixing approach comprised of initially mixing the dry powders and subsequent mixing during compression molding melt processing was employed. Minimization of time, temperature and shear during processing is essential with delicate thermoplastic polymers. FTIR spectroscopy of the neat materials, extruded blends and compression molded blends was conducted. Image analysis of EDS maps were used to assess the compression molded blends. This work was aimed at characterizing the morphology of the powder processed

blend in terms of its fineness and compared it to the known domain sizes of pellet processed composites. Subtle changes were sought in the FTIR spectra as an indication of conformational or bonding variations in the blends due to the nature of the interfacial region.

The immiscible morphology of a compression molded specimen (by vol. 30HDPE/ 60PMMA/ 10silica) featured a combination of dispersed and co-continuous phases and was subjected to a quantitative assessment. Area fraction of the traced domains (figure 29) revealed a 31.2% portion of the image area was attributed to HDPE which was in excellent agreement with the formulated composition.

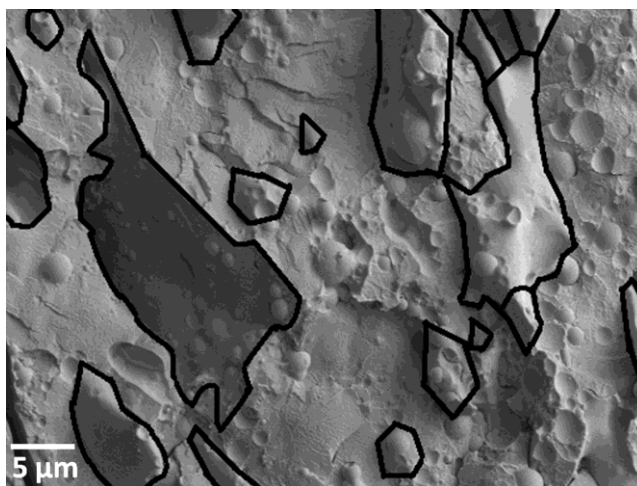


Figure 29. Traced domains of the immiscible polymer blend composite.

In co-continuous blends, the width of the traced domain is an important parameter since domain strands commonly extend throughout the entire composite. In this specific case, the domain width range was between 3-27 μm. The geometric mean domain size of the compression molded specimen was 14 μm, considerably larger to the 3-6 μm range seen in pellet composites. However, numeric average size of the compression molded specimen was 5.2 μm which in turn was much closer to the pellet range mentioned.

Furthermore, taking into consideration the two regions of coalescence that are part of the analysis and removing their numerical values (17 and 27 μm), then the domain sizes fell into a range of 3-11 μm , an effective domain size range for immiscible polymer composites.

Immiscible blend domain interaction across the domain interface can lead to subtle changes in the bonding of a backbone and pendant groups that are FTIR active. FTIR spectra were acquired for a compression molded blend specimen (by volume 30HDPE/ 60PMMA/ 10silica), an extruded blend specimen (by volume 35HDPE/ 55PMMA/ 10silica) and neat constituents of the blends. Most of the spectral features of the blends that differ from those of the neat materials occurred at high wavenumbers (2700-3100 cm^{-1}). Minimal variation of the additive behavior was seen in the spectra for the extruded composite. On the other hand, the powder processed composite spectrum showed more of a variation from the additive behavior which seemed to be caused from the powder processing route.

This paper and the previous papers dealing with this novel powder processing route were essential in establishing that these powder precursors have the ability to be successfully melt processed and exhibit similar if not superior properties to those composites generated using extrusion. Powder processing will be useful for molding delicate thermoplastic polymers found in certain bio-material, pharmaceutical and cosmetic applications.

3.4 Paper IV: Sustainable Polymer Composites: Immiscible Blends Prepared by Extrusion of Poly(trimethylene terephthalate) and Polyamide6,10 with High Bio-Based Content

Paper IV deals with a binary immiscible polymer blend of PTT and PA6,10. This blend is unique in that it possesses sustainable content which limits the use of petroleum based feedstocks. This initial work regarding bio-based materials was aimed at matching suitable polymer constituents and co-processing them by extrusion into a successful IMPB with domains at the micrometer level. The empirical Jordhamo relationship is used as a general guiding principle of co-continuity for processing these immiscible blends based on supplier data and DSC analyses of the melting points.

PTT was initially chosen as one of the neat materials for this binary system. PTT is similar to polyethylene terephthalate (PET), a polyester used previously in our labs and which has been made commercially for decades in fabrics, carpeting, apparel and packaging [28]. PTT possesses superior qualities to PET in that it has superior elastic recovery and has lower elastic modulus. However, the most prominent feature of PTT is its renewable fractional content of nearly 36%. A goal of this work was to find a suitable polymer to match with PTT for blending. A material was sought that would have bulk engineering properties to enhance PTT, functional pendant groups that are partially compatible with PTT, high bio-based content, and viscosity/temperature characteristics to allow the two polymers to be processed together. Many of these qualities were found in PA6,10, particularly good engineering properties and a high bio-based content of nearly 60%. Furthermore, the solubility parameters measured for PTT and PA6,10 (table 3) show that these polymers have sufficient cohesive energy differences to generate an IMPB but also have enough similarity in the cohesive energy and dipole character to

enable compatibility in the interfacial region of the blend. The backbones of these PTT and PA6,10 structures are similar. PTT has 11 carbon atoms in the repeat unit and PA6,10 has 16 carbon atoms. Both molecules have four high electronegativity atoms (nitrogen or oxygen). Two of these atoms are located in the backbone and two are as pendant carbonyl oxygen. The combination of different backbone repeat units but similar distribution of high electronegativity atoms contributes to a level of dipole-dipole interaction and compatibility of these polymers resulting in enhanced interfacial secondary bonding blends.

Ultimately three blend compositions were formulated, 20, 50, and 80 volume percent PTT, and processed by extrusion. All processed well and showed promising immiscible behavior as determined by SEM image analysis. Although none of these blends exhibited well defined definitive co-continuous structures, an oriented structure with columnar, fibrous, fine domains of PA6,10 in a PTT matrix was observed in the blend of 50PTT (figure 30). This type of structure is typical within 10 percentage points of co-continuity.

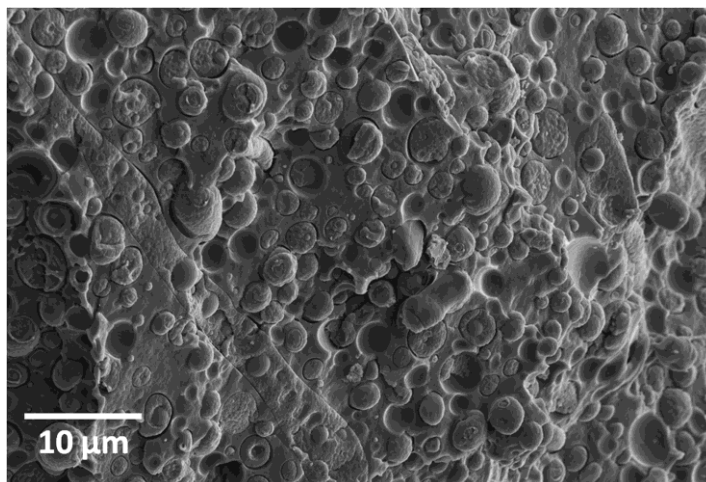


Figure 30. SEM image of the extruded 50PTT blend; 5 kX magnification, working distance 15 mm, accelerating voltage 5 kV.

The research discussed in this paper was essential not only in the selection of suitable bio-based polymers for single extrusion processing but also in the initial pinpointing of the co-continuity region in this unique blend of PTT/PA6,10. Both experimental and quantitative methods (Jordhamo relationship) were employed.

3.5 Paper V – Parts A & B: Phase Inversion Composition and Domain Identification by Energy Dispersive Spectroscopy in Immiscible Blends of Poly(trimethylene terephthalate) and Polyamide 6,10

Previous work demonstrated that PTT and PA6,10 are suitable for melt co-processing. The goal of producing a binary IMPB of these materials was to generate a system with good engineering properties combined with high bio-based fraction. The work in Paper V deals with identifying the phase inversion composition and domain morphology of the extruded composites. Producing a composite that possesses co-continuous morphology is advantageous for structural performance, permeability and thermal conductivity. Finding the phase inversion region is often a difficult process.

Mathematical models are often used to predict this region. Two models commonly used for this purpose are the Jordhamo relationship and the Metelkin and Blekht filament instability concept, both of which seek to determine the critical volume fraction where phase inversion occurs [29]. Experimentally, a common approach to resolving phase structure in an IMPB is to use solvent extraction. Often times, suitable etching solvents are difficult to find and also etching is likely to interfere with subtle features that are present in a new blend system.

In this work SEM imaging on cold-fractured, unetched surfaces was employed to analyze the morphology of the resultant blend. Initially, the similarity in the density and chemical composition of the polymers caused difficulty in discriminating the domains. However, as first introduced in Paper II, EDS was successful in differentiating domains using very subtle chemical differences. The small amount of nitrogen (10.2 wt%) in the PA6,10 offered a promising approach since PTT is essentially free of nitrogen thus allowing a greatly improved signal to noise ratio.

Based on previous work on this binary system, the phase inversion point was estimated to be within 5 percentage point of 50% by volume PTT. Since blends near the end members are highly dispersed (droplet-in-matrix morphology) these blends were not further characterized. Dimethyl formamide (DMF) etching was performed at the 50% composition with the goal of improving SEM imaging at the planar surface with no attempt made to selectively remove an entire phase for the assessment of co-continuity. PTT was identified by the textured etching surfaces whereas PA6,10 remained unaffected by the DMF. Furthermore, the morphology had primary domain sized averaging 2-3 microns. Remnants of dispersed phase morphology existed at the 50% composition but

the blend was predominantly characterized by oriented columnar domains that have more elongated cross sections than in neighboring compositions. However, the most indicative evidence of co-continuity from the image was the occurrence of the phase within phase structure (A-B-A) (figure 31).

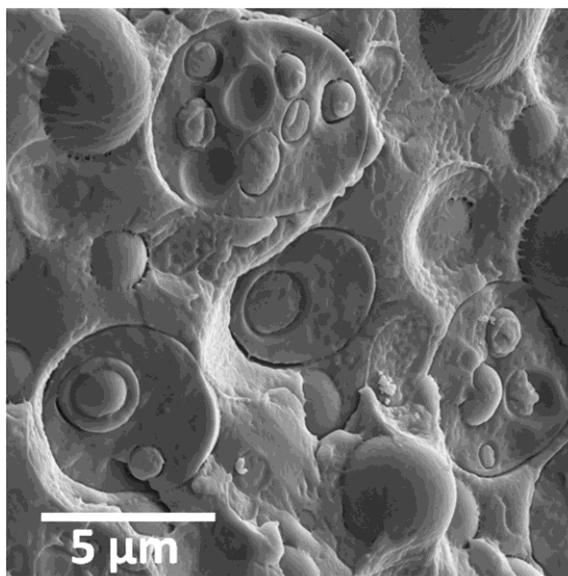


Figure 31. Phase occurring within a phase (A-B-A) morphology; indicative of co-continuity 50PTT blend; 10 kX magnification, working distance 15 mm, accelerating voltage 5 kV.

The application of high resolution EDS to differentiate chemically similar polymers is a new approach in the characterization of IMPB domains and was applied in this work on unetched specimens. The EDS spectra clearly showed that phase inversion exists when PTT is increased from 40%-60%. This finding is somewhat unexpected since the Jordhamo relationship (based on known viscosities and melt processing ranges) suggests phase inversion at higher levels of PA6,10 (appendix V).

3.6 Paper VI: Viscosity and domain morphology in binary immiscible blends of poly(trimethylene terephthalate) and polyamide6,10

Knowledge of the melt viscosity of thermoplastic polymer systems is critical when processing blends. A complete rheological work-up allows for polymer blends to be designed with optimum morphologies. IMPBs typically perform most favorably in the region of co-continuity. This region is characterized by an interconnected morphology, a high degree of interfacial surface tension, and strong interconnectivity and domain/domain clamping – a phenomenon known as mechanical grafting. Improved mechanical properties and enhancement of load transfer are attributed to this phenomenon and is therefore why formulations in this region are typically sought. An interesting feature of IMPBs is that they lack formal chemical bonding since the components of the blends are not cross linked and occur in separate domains. Thus, in the region of co-continuity the properties of the blends are usually additive functions if the mechanical linkage between the domains is sufficient, and some instances of synergistic properties have been observed based on molecular orientation and other special phenomena within domains. This additive behavior was the motivation to blend and extrude the two polymers identified in this study such that the development of favorable properties was expected. The work described in this paper sought to study blends of PTT and PA6,10 and to address the phase inversion point and the region of co-continuity. In Paper V, the viscosity of the end members and blends across the compositional range were measured at various shear rates and at a processing temperature of 250 °C. The morphology was assessed through SEM image analysis. The ultimate goal of this work was to describe the way in which viscosity varies over the binary composition range and the applicability of the power law viscosity relationship to these

two-phase materials. Furthermore it was sought to assess the empirical Jordhamo relationship, a mathematical tool utilized for identifying the phase inversion composition in immiscible blends.

Rheological data were collected for the molten polymers and blends using two contrasting methods, parallel plate and capillary rheometry. These two methods function on different principals and geometry (as described in 2.4 and 2.5), but provide useful checks on each other as well as providing an extended range of shear rates. Furthermore, in order to accurately calculate viscosity values using the Jordhamo relationship, capillary rheometry was essential in collecting viscosity data under the same processing temperatures and shear rates used in extrusion. However, an outstanding problem still exists since polymers are typically shear thinning as shown by the power law model and therefore the viscosities vary within the extruder (since a range of shear rates exist), resulting in a distribution of Jordhamo phase inversion compositions. The Jordhamo relationship relies on viscosity data of the end members collected at the temperature and shear rate used for processing in order to predict the co-continuous region of a blend. In reality the variability of viscosity over the blend compositions and the variation of shear rates in the extruder or injection molder raises the possibility of engineering the phase inversion point by manipulating these processing variables. In this work the Jordhamo predicted phase inversion to occur at about 21PTT at low shear rates (400 s^{-1}) and 44PTT at high shear rates (5000 s^{-1}).

PA6,10 was found to have highly shear thinning behavior and the ratio of the component viscosities varied substantially with shear rate. Viscosities of the blends were determined to be lower than the proportional rule of mixtures and were attributed to slip

between the domain boundaries. Near the phase inversion composition, there were modest increases in viscosity indicating a change in the structure of the domains. This modest increase in viscosity along with a shift in the power law index pointed to occurrence of the phase inversion composition around 55PTT. SEM image analysis showed droplet-in-matrix morphology at 50PTT and 60PTT. Although there was some indication in the image analysis that co-continuity was present at 55PTT, the lack of a classical co-continuous structure suggested that the co-continuous compositional range for the PTT/PA6,10 binary system does not span 55PTT and is in fact considerably narrower.

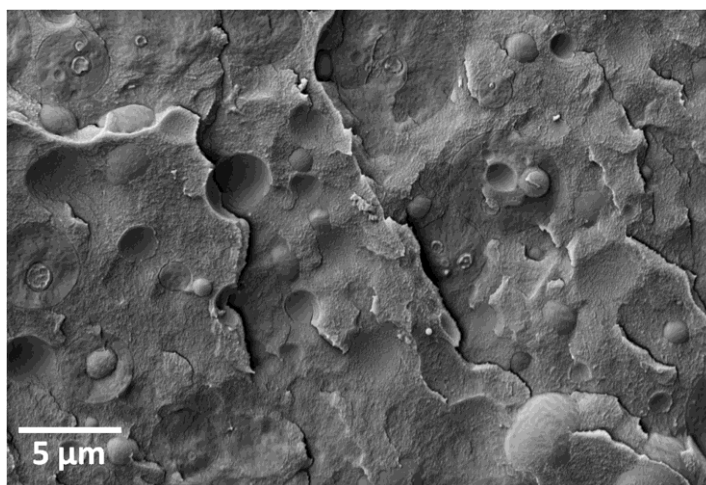


Figure 32. SEM image of 55PTT; 8 kX magnification, working distance 8 mm, accelerating voltage 5 kV.

A principal conclusion of this work is that a discrepancy exists between the experimental behavior and the predicted behavior using the Jordhamo relationship, which calls into question the validity of the Jordhamo relationship for the PTT/PA6,10 system [31]. Furthermore, the power law index (n) is unpredictable based on the end members due to nonlinear effects at the intermediate compositions, and proportioning the end members to estimate the value of the power law index results in large errors.

Nonetheless, the index is a useful tool to characterize the nature of the blend with regard to shear flow related considerations such as the degree of domain-domain bonding and associated slip.

3.7 Paper VII: In-situ formation of nano-scale PMMA network structures on the surface of immiscible polymer blends by solvent extraction and redeposition

This paper explored a continuous open-structured network with high surface area, low solids fraction and nano scale domain morphology that was observed to grow from dissolved blend components on cold fractured surfaces of immiscible polymer blends (figure 33) when reacted with DMF.

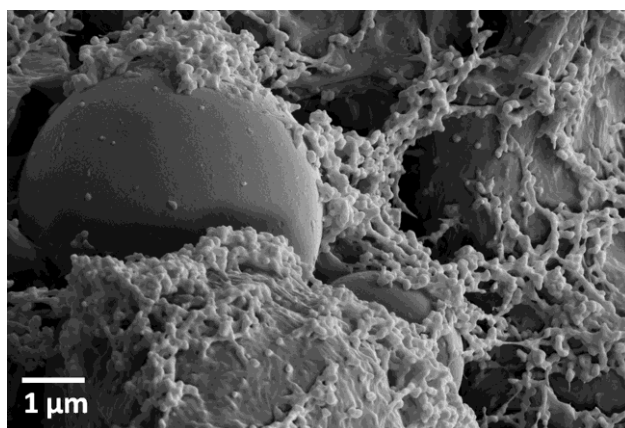


Figure 33. The nano-network observed growing on the surface of the cold fractured surface of the extruded 45PMMA/45HDPE/10 silica surface when reacted with DMF for 30 s; 30 kX magnification, working distance 15 mm, accelerating voltage 5 kV.

Solvent etching of composites is effective in enhancing morphological features and is typically used in binary IMPB systems prior to SEM imaging. DMF was used in this work to etch fractured surfaces of the blend composite of PMMA/HDPE produced by the two-step powder processing route and also to etch the PMMA/HDPE composite melt

processed by extrusion. In both processing cases, the inorganic silica spheres were present at the 10% by volume level. DMF was chosen based on its intermediate solubility parameter ($24.7 \text{ MPA}^{1/2}$) for etching the PMMA that has a solubility parameter of $22.7 \text{ MPA}^{1/2}$. The initial goal of the experiment was to solvent etch the composites to discriminate between the domains. However, during these experiments a new, fine scale ($\sim 50\text{-}150 \text{ nm}$), self-assembled network was discovered serendipitously on the etched surface of the compression molded and extruded blends, presumably by a dissolution and redeposition of one or more of the polymer phases. The focus of the work then shifted to characterizing this new nano-scale phase synthesized during the etching experiment. The nano-network was characterized using SEM, DSC and FTIR. In addition to characterization another goal of this work was to reproduce the nano-network on virgin PMMA pellets.

The nano-network appeared on all PMMA/HDPE blend regardless of the processing technique and was assumed to be PMMA. The network appeared as a web-like structure extending over the surface of the composite in a multi-layer system forming a uniform open network with a volume fraction of solids of about 25%. The extruded blends generally formed a uniform thick layer of the network whereas the network on the compression molded specimens was considerably less. This variability in the quantity of network formed on various blends is an interesting result in that the DMF etch times were halved for compression molding specimens in comparison to extrusion, and additionally the volume percent of PMMA in the compression molded specimen was greater than that of the extruded specimen (70% and 50% respectively). Considering that prior work confirmed that the two melt processing techniques yield similar morphologies and levels

of homogeneity, the reduced generation of this network on compression molded specimens was attributed to the powder precursors. The character of the nano-network on both composites appeared similar, just in varying quantities.

This PMMA network was systematically synthesized directly from PMMA virgin pellets used in extrusion. The appearance of the network as it self-assembled on the surface, and the general morphology of the network, was confirmed by SEM. The pellets were feature free prior to the synthesis experiment (viz, surface network). Furthermore, another type of synthetic material was generated by evaporating the etch solution to dryness in a glass dish (viz, solution solids). DSC showed that the two synthetic materials were amorphous non-crystalline materials. The synthetic network grown on the pellets was glassy and exhibited a glass transition temperature nearly identical to the PMMA virgin pellets used in processing the composites (103 °C and 104 °C respectively), whereas the solution solids did not show a glass transition and were deemed to be simply amorphous, non-glassy solids. FTIR confirmed that the nano-network on the composite blends and the synthetic pellet surface network are comprised of PMMA. The solution solids had the same major absorption peak as PMMA but showed major discrepancies at other wavenumbers, a scenario typical of oligomers where the main features of the compound are present but the full polymer fingerprint is absent.

This work suggests that the morphology of the blend or pellets was necessary for the synthesizing of this in-situ network. The high surface area and semi-ordered structure of this network suggests applications in the fields of catalysis, biomaterials and energy applications.

4. DISCUSSION AND CONCLUSIONS

The core findings of this dissertation are discussed in this chapter in the context of their impact and significance on the scientific and engineering polymer community.

Immiscible polymer blending has become known, just in recent decades, for its unique ability to process known immiscible polymers into novel materials with either rule of mixtures or synergistic engineering properties of the end members. The principal value of this technology is that the vast majority of polymers are immiscible relative to each other and therefore have previously been impractical for blending since poor quality incompatible blends have resulted. The ability to blend these polymers using immiscible blending technology has greatly expanded the number of polymer materials available for a wide range of applications. Selection of blend candidates is governed by the properties desired and on the degree of immiscibility between the components. Binary polymer

systems have produced the most successful blends to date via the use of the standard industrial processing techniques of extrusion and injection molding.

A major innovative development emerging from this dissertation is the concept of using finely divided polymer powders as precursors for polymer blends in order to minimize the amount of mixing required in the molten state. Furthermore, the known method of compression molding has been applied to the formation of blends from such mixed powders in order to consolidate the powders with minimum shear and thermal exposure. Polymer powders, which have only recently become commercially available at high purity and small particle size, are often delicate materials typically found applicable in the cosmetic and pharmaceutical industries, although their presence have transcended a range of other application areas. Such polymer powders are sensitive to high shear, elevated temperatures and extended dwell times which are unfortunately the conditions found in extrusion and injection molding. To resolve this issue, a two-part processing scheme was designed. Polymer powder immiscible blends were mixed in their cold state to a high level of homogeneity and subsequently subjected to compression molding melt processing. Furthermore the addition of (10% by volume) inorganic silica spheres was added to all blends for the purpose of assessing homogeneity of the composites. Optical, SEM imaging and EDS showed that the powder processing method was not only feasible to produce successful IMPBs but this method produced a similar morphology and dispersion of the inorganic particulates to that of extrusion. This new method limits the amount of polymer degradation due to the short processing time in comparison with traditional methods. High levels of shear and elongational stress typically associated with mixing were essentially eliminated. Furthermore, this powder blending approach

enables the processing of constituents that would otherwise be inhibited by unfavorable rheological or solubility parameter conditions. The intimacy of the powder blends and the nature of the polymer/polymer interactions were assessed and a comparative analysis to extruded blends was made via image analysis and FTIR.

An additional key finding of this work is the ability to differentiate polymer domains using EDS. This new approach allows for the abandonment of common phase structure resolving techniques such as solvent extraction which can prove difficult since suitable solvents are often hard to find and also this technique is potentially damaging to surface features of a composite. Most notably, EDS analysis was successful in differentiating component polymers based on subtle chemical differences as small as ten weight percent.

Yet another novel feature of this work is the use and characterization of fine ($\sim 10\ \mu\text{m}$) PMMA particles produced by the autogenous cryo-grinding of bulk pellets. PMMA is an amorphous polymer produced in bulk and supplied commercially as pellets. Cryo-grinding is a means to generate small micrometer sized particles from bulk PMMA, as compared to the emulsion polymerization process generally used to produce similar small particles for the cosmetics industry. The presence of a high degree of surface area relative to the bulk, in combination with the energy imparted during comminution, may be accountable for subtle changes in the molecular conformation noted in FTIR bands. The spectra showed differences between the mechanical mixtures of the neat precursors and melt processed composites in both the powder compression molded blends and the extruded pellet blends. The changes in the spectra were primarily at high wavenumbers

($>2800\text{ cm}^{-1}$) and were attributed to subtle conformational differences in the polymers at the domain interfaces.

Still yet a further significant result is the serendipitous discovery of an in-situ formation of nano-scale PMMA network structures on the surface of immiscible polymer blends by DMF solvent extraction and redeposition. This network is most notable for its high surface area, low solids fraction and nano-scaled domain morphology ($\sim 50\text{-}150\text{ nm}$). This dissertation work was successful in characterizing the network on the surface of the immiscible polymer blends through SEM, image analysis, DSC and FTIR, and was successful in reproducing the network on virgin PMMA pellets. As an in-situ formed surface phase with high surface area and co-continuous access to the surface of the substrate, this network has the potential in a range of applications as discussed in the next section.

Other aspects of this work focus on immiscible polymer processing of bio-based materials with the goal of producing sustainable engineering polymers. Both PTT and PA6,10 are materials new to the AMIPP Advanced Polymer Center and there was little experience processing them. Initially, the goal of the work was to process this binary system in an attempt to raise the bio-based content of PTT (36%) by adding PA6,10, a material with a higher bio-based content (60%). The co-processing of these materials was successful and the result was a desirable micrometer scaled morphology. The ability to co-process these polymers is a significant finding and was based on our multi-faceted approach of combining calculations from the empirical Jordhamo relationship, solubility parameters data, and information regarding the electronegativity of backbone and pendant groups, specifically the nitrogen and oxygen atoms of each polymer. Not only

does this blend improve the renewable fraction of the composite over the principal constituent but also serves as a way to improve the engineering properties of both components since IMPBs in the co-continuous range typically follow the rule of mixtures and result in additive properties of the neat polymers. Also employed were the earlier EDS domain identification findings for the analysis of microstructures in the bio-based segment of this work. This technique, quite impressively, was used to differentiate polymers based solely on the 10.2 weight percent nitrogen found in PA6,10 but absent in PTT. Furthermore, EDS was used as a means to narrow down the location of the phase inversion point and as a way to target the co-continuous region. The EDS maps indicated a window of co-continuity as PTT increased from 40%-60% with the phase inversion appearing to occur near 50% PTT based on the appearance of phase within a phase morphology.

In the next phase of the bio-based study the viscosity of the blends was measured over a broad shear rate range with the goal of finding the phase inversion composition and comparing the Jordhamo relationship prediction with experimental data. Never before in the AMIPP labs has the variation of viscosity over the binary composition range been assessed. Using the power law viscosity model as the base concept, two rheological methods (parallel plate and capillary) were used to obtain viscosity data for the binary blends over a wide range of shear rates. The viscosity/composition curves showed interesting non-linear behavior, apparently due to slip between the immiscible domain boundaries. Viscosity increased to a relative maximum near the phase inversion composition, indicating a change in domain structure at that composition. The power law index (n) varied with compositional changes and typically followed the behavior of the

continuous phase polymer. The shift in the power law index in conjunction with the spike in the viscosity curve, and SEM imaging data, pointed to phase inversion occurring around 55PTT. Although at 55PTT, the blend image did not display all the characteristics of a co-continuous structure, this work was important in determining that the co-continuous composition range for PTT/PA6,10 does not span the 55PTT composition and is in fact quite narrow. Furthermore, a major finding of this work is the discrepancy between the phase inversion composition predicted experimentally and that predicted through calculations of the Jordhamo relationship. This discrepancy calls into question the validity of the Jordhamo relationship with regard to the PTT/PA6,10 system.

The findings of this research are critical contributions to the growing body of applied polymer science used by engineers and scientists to develop novel materials with good engineering properties through immiscible polymer processing. These materials have the advantage of being developed from known polymers rather than reverting to the laborious and expensive process of new polymer synthesis. This research has demonstrated that high quality immiscible polymer blends can be prepared by various routes beginning with precursors that range from fine powders to traditional pellets. Furthermore, blend systems have been demonstrated that range from traditional known immiscible blend systems to novel bio-based systems that have the potential to provide high levels of sustainability to the engineering resin field. In all cases, the characterization of the neat polymers prior to blending is an important step in understanding the behavior of the blend system, although various relationships that are popular for predicting blend behavior are not always accurate. Furthermore, the resulting

blended materials must be accessed through various techniques to ensure a feasible material is the outcome.

The outcome of the immiscible blending of polymers is obscure unless there is proper measurement and characterization of the blend properties using the broad range of techniques addressed in this thesis. The conclusions that are drawn from these analyses serve as guidance for the numerous applications where these blended materials are useful.

5. APPLICATIONS

In this research, the primary goals were to develop novel compositions and processes of immiscible polymer blends. The two segments of this work are unique in that the first portion dealt with delicate polymer powder precursors and a novel avenue of processing to develop blends that are comparable to traditional pellet extrusion. The bio-based portion of this work sought to develop a novel material which superseded the properties of the bio-based constituents resulting in a material with an increased bio-based fraction of the components with good engineering properties.

As with all materials, there are many variables which govern final applications. Not only are the blend components important but also the resulting morphological structure and mechanical properties dictate the area of future use. Furthermore, the costs associated with the materials and ease of processing at a larger scale can also inhibit potential fields of application. The materials explored in this work have the potential for

use in practical applications at a later point in development since there is a need for further development of these concepts using experimentation, theory and literature from the scientific community.

In the polymer powder precursor segment of this work, compression molding was used as the melt processing method to produce immiscible polymer blends of PMMA/HDPE. This avenue of processing was shown to be an effective and useful method in producing high quality polymer blends from delicate thermoplastic polymers typically seen in biomedical, pharmaceutical and cosmetic applications. Although most traditional thermoplastic polymers, such as the linear alpha-olefins, can adequately withstand commercial processing conditions, newer, more fragile polymers used in the pharmaceutical, biomaterial and cosmetic industries are sensitive to and cannot tolerate temperature and shear rate conditions of conventional melt processing. Furthermore, processing times must be reduced. Thus, these identified industries, and the products used in these industries, are principal areas of application for the powder processing route to immiscible polymer blends.

Product development goals over a range of commercial sectors focuses polymer systems comprised of multiple components as a means for producing new materials with micro or nanometer scale domains. Such fine domain structures provide the ability to tailor the material with desired mechanical, electrical and optical properties. Polymer composites of this type have found uses in electro-optic/luminescent devices, conducting materials, hybrid inorganic–organic polymer alloys, polymer-supported heterogeneous catalysis and telecommunications [31]. When looking towards microphotonic application, problems arise since polymeric materials are strongly absorbing at near

infrared frequencies and therefore it is difficult to find polymer blend systems that are transmissive in this frequency range. Furthermore, when tailoring an optical/electronic interface to the polymeric structure it is hard to achieve specific frequency input-output conditions [31]. Some immiscible polymer blends are prepared from solution methods. Such methods can promote phase separation and homogeneity is only achieved through the use of compatibilizers to reduce interfacial tension of the materials or through rapid evaporation of the solvent [31]. Through this research, immiscible polymer blends, when properly processed, are suggested as a productive route to preparing multi-phase materials of the types described here at high volumes and low costs.

Polymer powders are found in cosmetic formulations for the purpose of improved product performance and skin feel [32]. Particle concentration and size greatly affect the lubricating properties of powder suspensions [32]. Studies of spherical particle powders in suspension show that solid particles in aqueous suspensions have frictional behaviors that are highly dependent on the dynamics of the particles and the way that they become distributed on surfaces, thus indicating that the design of effective powder-containing cosmetics will be dependent on these parameters [32]. The technology of combining and processing powders developed in this dissertation may be useful in the cosmetics industry to produce higher solids loading and enhanced particle packing in a variety of products.

Blends prepared from FDA-approved polymers and with engineered domain sizes that are particularly suited to biological cell-growth requirements are of high value in biomedical applications such as tissue scaffolds and implant components. Specialized coatings are also envisioned from this work in which a desired engineering morphology is developed via the precursor powders and flash fusion of the powders on a substrate

preserves this morphology for functional advantage. Powder coatings of various types have properties that are valuable in numerous applications. Small amount of polymer are used in very cost-effective manners to develop thin films on substrates to provide enhanced surface performance and characteristics. Examples of such high value-added coatings occur in the environmental, electrostatic, and various diverse industrial applications [33]. The main tribocharging process for polymer powders is corona discharge, a method used due to its control of the charging level of the particles. This method also promotes good adhesion between particles and the substrate, and is characterized by good process repeatability and unipolar charging [33]. When two different materials are put into contact with one another and subsequently separated, the result is electrostatic charging due to an electron transfer between them. Because of this transfer, the two materials in contact will charge oppositely in cases such as metal/metal, insulator/insulator, and metalinsulator contact. Also, it has been reported in the literature that sirolimus-loaded non-erodible polymeric microparticles of poly(ethylene-co-vinyl acetate) (PEVA)/ poly(n-butyl methacrylate) (PBMA) have been used in a new technology of electrostatic dry powder deposition followed by fusion to effectively coat intravascular stents [34]. Blended powders or the development of immiscible polymer blend powders with pharmaceutical or biocompatible properties will be useful in these industries with regard to processing bulk materials such as scaffoldings or implants, and with regard to functional coatings.

Spontaneous, self-assembling of co-polymer systems is noted in the literature to form micellar, cylindrical and lamellar morphologies. The nature of the resulting morphology is dependent on solvents employed in the system and the nature of the

polymeric system [31]. The nano-network generated on the surface of IMPBs when reacted with DMF shows promise in the applied science field with potential applications as an interfacial modification substance or as a functional material in bio-materials and catalysis. Physical and chemical patterning approaches are used to tailor the morphology of materials. Laser structuring techniques are applicable for uses with a variety of materials such as ceramic, metals and polymers to control the resultant scaffold shape and internal microstructure [35]. In this dissertation work, the ability of nano-scale PMMA domains to self-assemble in-situ with co-continuous access to the surface of the binary PMMA/HDPE composites was found to be unique in that it occurs spontaneously under the parameters discussed in Section 3.7. These nano-scale domains may be used in bio-mimetic applications similar to those generated from depth laser structuring techniques. Furthermore, the fineness, co-continuity and openness of this network structure in conjunction with the structure's high level of surface area and morphology may prove useful in a range of applications such as catalytic substrates, biomaterials or as a bonding layer for structural materials. If the network layer is bonded to the domains or can be made to bond to the domains via thermal treatment above T_g , it can provide an interfacial bonding enhancement agent for polymer/polymer or bio-polymer composites. Naturally, the degree of adhesion to the originating base structure and the integrity of the network itself are critical for this application. Furthermore, this nano-scale network, comprised of a relatively high elastic modulus polymer, will be an effective reinforcement phase when impregnated with low viscosity precursors of a matrix polymer that can be polymerized in-situ, thus generating a strong wear resistant coating on the surface of these blends. The high surface area and semi-ordered structure of this network also suggest

applications in the fields of catalysis, biomaterials, and energy applications such as fuel cells and batteries. Such a network can work as an interfacial bonding enhancement agent for polymer/polymer or bio-polymer composites provided the network layer is or can be made to bond to the domains.

Bio-based materials are a new and forthcoming area of research which have the potential to generate structures used in tissue engineering, scaffold, transportation, electrical conductivity/electronic, drug delivery systems and industry. Structural characteristics, biocompatibility and potential biodegradability make these materials ideal for biomedical application such as shape memory polymer systems introduced to the human body as surgical sutures, bone fixation devices, adhesion prevention, artificial skin and drug delivery systems [36] & [37]. Biomedical synthetic polymers are materials used both in soft and hard tissue regeneration due to their ease of processing and biodegradability. Fabricated bio-composite conduits comprised of bio-degradable synthetic polymer, poly(ϵ -caprolactone) (PCL) and natural material, silk fibroin (SF) powder proves beneficial in the applications as vascular grafts and as a peripheral conduit for the nervous system or blood vessels [36]

The results from the viscosity measurements of PTT and PA6,10 blends are essential in assessing the region of co-continuity and are a critical part of the processing science needed to melt and fabricate commercial products from these blends. Binary immiscible blends of PTT and PA6,10 that are melt processed together to form a blend with highly interconnected domains are characteristic of blends with mechanically superior properties useful for a variety of industrial applications. The food packaging field has looked towards bio-based materials and nano reinforcement of bio-based

materials as a means to increase the competitiveness of renewable materials to other polymers on the market both from an economical and engineering standpoint [38]. A high level of dispersion of the nanoparticles in the bio-plastic matrix is essential in order to fully deliver the expected properties of a polymer system. One avenue of dispersion is through melt blending such as in the case of extrusion which is readily used in industry [38]. These renewable polymers or polymeric blends must exhibit certain properties, particularly resistance to gas permeation (barrier) such as exhibited by various polyesters and poly(lactic acid) (PLA) [40]. Bio-based packaging is often seen as a niche market, but developments have been made and commercial trials have been conducted where starch-based packaging has been used for pasta (Italy) and where PLA-based containers (Germany) have been used for yogurt [40]. Toxicological and environmental impact of these renewable materials has yet to be completely explored particularly when introducing nano-particles to the polymer systems but the outcome seems to hold a promising future. This dissertation work that focuses on generating successful bio-based composites will contribute significantly to the growing base of processing science available to guide the development of new materials for industry, commerce, and the military.

The world community is in increasing need of sustainable materials to support the quality of life of the seven billion of us living here. Much of this dissertation has been devoted to developing an important sustainable polymer blend for engineering plastics and coatings. Polyesters such as PTT are an important part of this effort due to their low molecular weight, reactive end groups and a glass transition temperature well above room temperature [40]. PTT is a relatively new engineering resin with properties similar to

high performance poly(butylene terephthalate), good strength and stiffness, and also has excellent finished appearance, reduced warpage, and good dimensional stability. PA6,10 is a member of the polyamide family renowned for outstanding toughness, work of fracture, and ductility. In this work it has been demonstrated that PTT can be combined with PA6,10 to produce a blend of these two polymers that has the potential to produce new engineering resins with enhanced properties as well as improved processing characteristics compared to the generally difficult to melt-process polyamides. Both polymer components have substantial bio-based content and blends of the two will further advance the broad industry initiative to enhance the sustainability of engineering resins. These findings are a critical contribution to the growing body of applied polymer science used by engineers and scientists to develop new engineering resins via the combination of immiscible polymers. With considerable research aimed at producing low molecular weight polyamides that are entirely bio-based, the blending of polyesters and polyamides seems an even more attractive concept [41].

The ability to combine immiscible polymer blends without compatibilizers opens a broad avenue of opportunity for the applied polymer scientist to formulate new materials with specific properties without resorting to expensive synthesis chemistry thus generating new polymer compositions needed to meet the demands of design engineers in industry, commerce and the military.

6. SUGGESTIONS FOR FUTURE RESEARCH

During this research there are topics raised which could not be fully addressed in the scope of the published papers and merit further exploration.

In the powder segment of this work SiO_2 particulates are added at the 10 vol% level to all immiscible blends comprised of PMMA/HDPE. Even at this level, the silica spheres can have significant effect on morphology and domain size of the blend. This is due to enhanced shear in a system which contains rigid spheres and also due to the interfacial surface chemistry effects. It would be beneficial to explore specimens which are devoid of silica spheres to fully illustrate such an effect under the compression molded and extrusion processing conditions. Furthermore, the silica particulates used in this study are of micron size. There has been research conducted where nano-sized silica particles with core-shell structures are used as a functional filler to form a nano-composite polymer matrix [42] & [43]. It would be interesting to blend the immiscible

system of PMMA/HDPE with nanoparticles. These fine, reinforced phases will naturally distribute themselves quasi-uniformly as they occupy interstitial voids between larger particles which will be more effective in distributing themselves during extrusion or injection molding.

As mentioned before, powder precursors are fairly new to the commercial scene. In Paper I PMMA (BPA -500) is used as a constituent to the IMPB system. In that work, there was an unusual outcome in that the PMMA failed to fuse and produces a composite of an HDPE matrix with dispersed PMMA and silica particles. There was an investigation into this matter by using FTIR and DSC analysis of the material and comparing it back to a known sample of traditional PMMA. Although some discrepancies in the results showed that the PMMA (BPA-500) material differed, the investigation was abandoned at that point since studying this phenomenon was beyond the scope of the research. It would be useful to take virgin powder forms of PMMA from either the same or different suppliers to determine whether the material is altered when “powderization” occurs. This concept could be extended into formulating and blending composites using various PMMA powdered material. Extensive analysis using FTIR and Raman could determine where the conformational effects occur and subsequent assignment of the vibrational modes to these features can be made.

In the bio-based segment of this work, rheological characterization was performed to fully elucidate the polymer viscosity behaviors and determine quantitative applicability of the Jordhamo relationship in the PTT/PA6,10 system. As a comparative method SEM image analysis was performed to visually identify if co-continuity occurred at the same blend composition as determined by the Jordhamo relationship. The image analysis for

locating the phase inversion composition is on planar, unetched, cold-fractured surfaces. However, the two dimensional surface offers only hints of co-continuity through the appearance of intertwined channels, filamentary segments and branch points. Although solvent extraction is performed to better define the boundaries, the selective removal of complete phases by suitable solvents to leave the remaining structure would be extremely beneficial. These three dimensional image analyses would further assist in determining the underlying morphology of blend. Ultimately, it was determined that co-continuity of the binary PTT/PA6,10 system does not span (by volume) 55PTT and may be quite narrow. Future work can be directed in formulating blend compositions which differ in small intervals around the 55PTT to pinpoint an exact composition of co-continuity.

Furthermore, the vision for blending PTT/PA6,10 is to generate high levels of bio-based components while maintaining or improving the engineering properties. As such, mechanical testing is necessary to conclude if this new blend fulfills expectations with regard to structural performance.

In the nano-scale PMMA network portion of this work it was found that an in-situ, continuous, open structured, high surface area, low solids fraction, self-assembled network was grown from dissolved blend components on cold fractured surfaces of IMPBs when reacted with DMF. Planar image analysis was conducted and suggested that the pore size present range between 150-900 nm with an average pore size of 500 nm. Mercury intrusion porosimetry and or nitrogen desorption isotherms would be beneficial tools in confirming these data. Furthermore, since DMF was the solvent reported in this work, it would be interesting to explore a broader series of etch times to assess the role of solvent reaction times on the structure and density of the grown

network. An alternate approach would be to focus on the type of solvent used governed by the solubility parameter in relation to the PMMA. Though various solvents are used in this study, none seemed to produce the effects on network formation on PMMA as well as, or even comparable to, DMF.

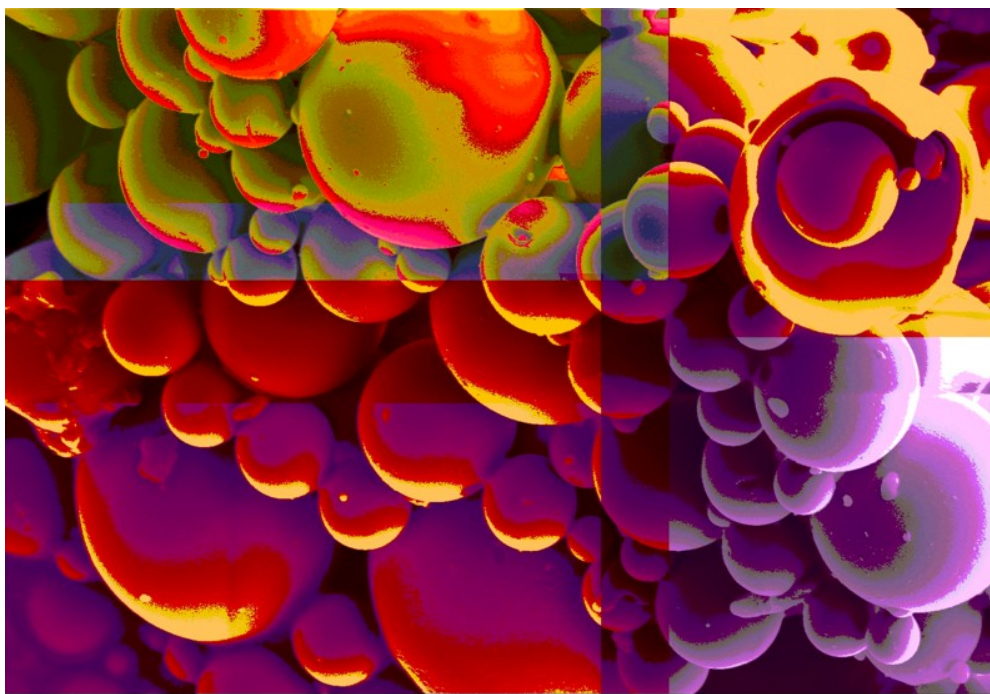


Figure 34. Nominated finalist in the “Science as Art” competition, Materials Research Society, Boston Massachusetts 2011. SiO₂ microspheres with false color. Image and design by Giorgia Giancola.

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APPENDIX

Appendix I: **"A powder processing route to polymer composites."** G. Giancola, and R.L Lehman. *Materials Research Society*. Boston, Massachusetts, 2009. YY07-01.

Appendix II: **"Micro/nano structure and morphology of multi-phase polymer/oxide composites prepared by polymer melt processing."** G.Giancola, and R.L Lehman.. *Materials Research Society Conference Proceedings*. Boston, Massachusetts, 2010. 10-24.

Appendix III: **"Melt processing and domain morphology of PMMA/HDPE polymer blends prepared from powder precursors."** G. Giancola, R. L Lehman and J.D. Idol. *Powder Technology* 218 (2012): 18-22.

Appendix IV: **"Sustainable polymer composites: Immiscible polymer blends prepared by extrusion of poly(trimethylene terephthalate) and polyamide6,10 with high bio-based content."** G. Giancola, R.L Lehman and J.D Idol. *International Journal of Sustainable Engineering*, 2012: in press.

Appendix V – Part A: **"Phase inversion composition and domain identification by energy dispersive spectroscopy in immiscible blends of poly(trimethylene terephthalate and polyamide6,10."** G. Giancola, R.L Lehman and S. Miller. *Polymer Engineering and Science* in press (2012).

Appendix V – Part B: **" Uniquely identifying polymer composite domains using energy-dispersive spectroscopy."** G. Giancola and R.L Lehman. *Invited article by SPE plastics research online* in press (2012).

Appendix VI: **"Viscosity and domain morphology in binary immiscible blends of poly(trimethylene terephthalate) and polyamide 6,10."** G. Giancola, and R.L Lehman. *Journal of Polymer Engineering* accepted (2012).

Appendix VII: **"In-situ formation of nano-scale PMMA network structures on the surface of immiscible polymer blends by solvent extraction and redeposition."** G. Giancola, and R.L Lehman. *Journal of Polymer Engineering and Science* in press (2012).

Appendix I

"A powder processing route to polymer composites."

G. Giancola, and R.L. Lehman

Materials Research Society. Boston, Massachusetts, 2009. YY07-01.



A Powder Processing Route to Polymer Composites

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ABSTRACT

Powder processing of thermoplastic polymer composites offers multiple advantages for both micro- and nano-scale systems. A high degree of component homogenization is achieved prior to melt forming of the composite, thus minimizing degradation associated with extended thermal processing at high shear. Polymer blends can be prepared that would otherwise not be possible due to thermodynamic incompatibility. Initial evaluation of this concept was conducted by processing PMMA and HDPE micron size powder prepared by emulsion polymerization. Spherical silica particles of comparable size (mean size = 5 μm) were added to a 30/60 PMMA/HDPE blend at the 10 volume percent concentration and mixed in an aqueous medium prior to drying and extrusion. Analysis of optical and electron microscope images of the raw mixture shows good homogeneity and distribution of the small inorganic particles around the larger matrix phase particles by the process of interstitial filling. The melt-processed composite was observed by SEM and consisted of a three-phase system of dispersed silica and PMMA particles in a HDPE matrix.

INTRODUCTION

Polymer/inorganic composites are multi-phase systems comprised of materials with varied chemical and physical properties. The combining of dissimilar materials for structural applications is aimed at achieving improved properties over any single material by generating ductility, specialized load transfer, and improved fracture behavior.^[1-2]

The morphological scale of composites is critical and the optimum size depends on the applications. Copolymer blends and interpenetrating polymer networks are examples of molecular level compositing. Particulate nanocomposites and certain fine-domain immiscible polymer blends are examples of coarser meso-scale composites. Commercial immiscible polymer blends and fiber composites are macro-scale composites with domain sizes greater than one micrometer.

Immiscible polymer blends comprise a widely researched subject that focuses on novel materials with synergistic properties.^[3] Mechanical properties can be enhanced by engineering the blend composition as well as the processing parameters.^[3] The development of such materials is of special interest because this approach reduces the need to begin at the synthesis stage to develop new materials with specific properties.^[4] Thus, blends prepared from FDA-approved polymers and with engineered domain sizes that are particularly suited to biological cell-growth requirements are of high value in biomedical applications such as tissue scaffolds and implant components.

The addition of inorganic particulates is an attractive approach to producing polymer composites with a blend of organic and inorganic behaviors. A substantial body of work exists devoted to generating hybrid systems and also identifying effective methods for grafting PMMA onto silica surfaces. Nano sized silica particles with core-shell structures used as a functional filler to form a nanocomposite in a polymer matrix have been studied.^[5-6]

Ideal polymer blends and/or composites are homogeneous with well dispersed multiple phases, if present.^[4] Powdered polymers of varying fineness, typically prepared by cryogenic methods, have been used as binders for mixed powder products.^[7] In the

present work we are studying a new approach to processing thermoplastic composites, one that uses powder precursors to improve mixing and distribution of the components prior to melt processing. Such an approach has multiple advantages. Homogeneity of fine micron or nanometer size particulates can be mixed thoroughly with the polymer, thus minimizing the high levels of shear and elongational stress that would otherwise be necessary for mixing. Reduced processing at elevated temperatures reduces polymer degradation^[8] and permits a wider range of polymer blends to be processed. Powder blending also enables polymer blends that are not possible to produce by melt methods, such as when rheology and solubility parameters are not favorable. Specialized coatings are envisioned in which a desired engineered morphology is developed via the precursor powders and flash fusion of the powders on a substrate preserves this morphology for functional advantage. As an initial system, we have studied the processing of a HDPE/PMMA/SiO₂ composite prepared exclusively from micron size powders. The present paper describes the availability, characterization, and processing of suitable powders, and the mixing and extrusion of these powders to form three-phase composites.

EXPERIMENT

Materials selection

The concept of preparing polymer composites by powder methods has only recently become practical at commercial scale due to the emergence of several bulk forms of high purity polymer powder. Traditional methods of disk milling or hammer milling polymers to fine sizes are not feasible due to contamination and process inefficiencies. A new cryogenic process of autogenously milling^[i] produces micron size particles of equi-axed but irregular shape, and emulsion polymerization^[iii] produces spherical commercial

polymer powders. Both materials are part of our study, but only the emulsion polymerized materials are reported in this paper. Specific materials used in this work are given in Table I.

The polymethylmethacrylate (PMMA) chosen for this work is a non-crosslinked PMMA with mean particle size of 10 μm and a range of 70% within 5 – 16 μm . The high density polyethylene (HDPE) is a low melting (105 $^{\circ}\text{C}$) material with an average particle size of 11 μm and a range specification of 85% < 25 μm . The similar particle size of these materials assures good mixing with a minimum of particle segregation. For the inorganic additive, a 5 μm spherical SiO_2 particle was chosen.

Table I – Materials

Material	Supplier	Product	Density, g/cm³
PMMA	Kobo Products	BPA-500	1.17
HDPE	Kobo Products	CL-2080	0.92
SiO_2	Kobo Products	MSS-500-3N	2.4

Materials characterization

Although the polymer materials used in this study are commercial products and approximate properties are available from the supplier, we desired our own data for confirmation. FTIR spectra were collected for the PMMA since early trials showed that the material had unusual high-temperature melting behavior and appeared to be at least partially cross-linked. The FT-IR spectra of the BPA-500 PMMA product did not show major differences when compared to conventional bulk polymerized PMMA. However, some slightly greater absorbance was observed in the 2800-3000 range, attributed to C-H stretching^[9], and also some reduced absorbance in the 1166 – 1291 range, assigned to C-

O stretching, may be indicative of some cross-linking or other structural effects. This issue has not currently been resolved.

The glass transition of the PMMA (94.2 °C) as measured by DSC and compared to conventional PMMA (105.5 °C) is shown in Figures 1 and 2. The melting point (104 °C) of the HDPE by DSC is given in Figure 3. The HDPE exhibited low viscosity, only 53.6 Pa's at 220 °C and 100 s⁻¹, as expected from the low melting point (Figure 4).

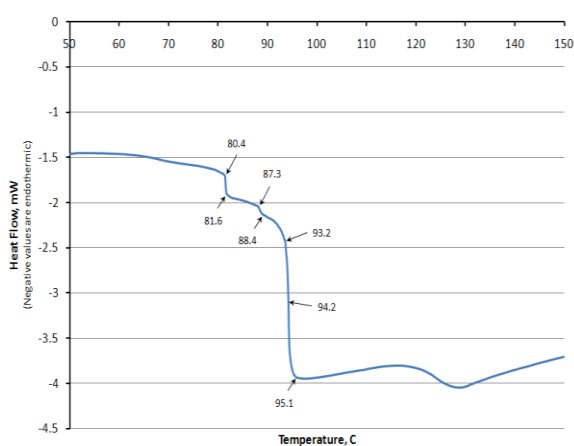


Figure 1. DSC trace of Kobo BPA-500 PMMA showing T_g at 94 °C.

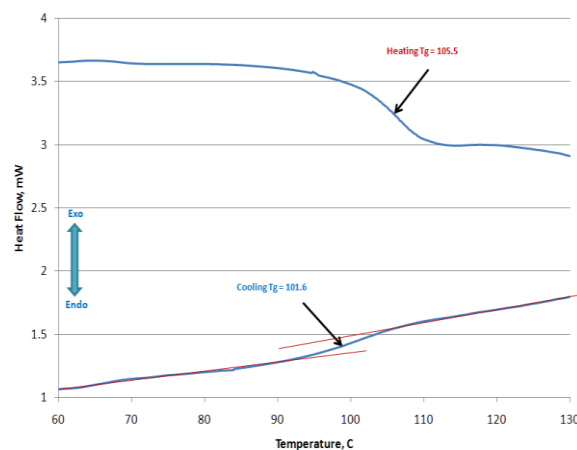


Figure 2. Glass transition by DSC of conventional bulk polymerized PMMA

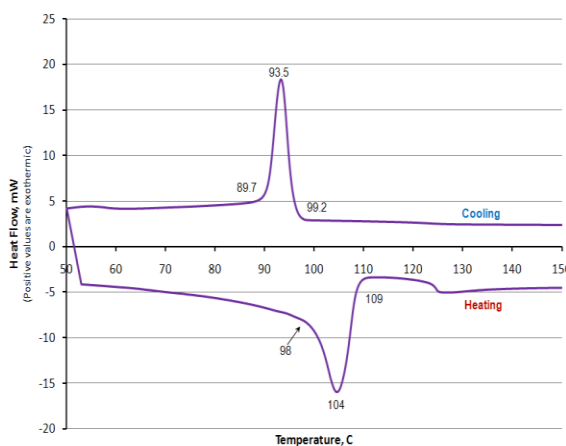


Figure 3. DSC trace of Kobo CL-2080 showing melting point on heating and cooling.

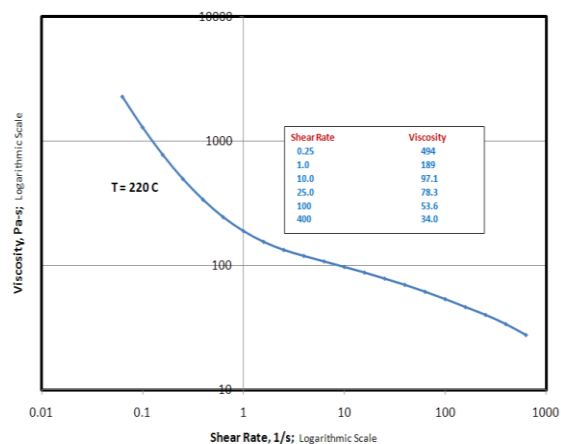


Figure 4. Viscosity/shear rate behavior of Kobo CL-2080 at 220 °C.

Formulation and blending

A composition of 60% HDPE, 30% PMMA, and 10% SiO₂ (by volume) was chosen for this initial study. The most successful immiscible polymer blends to date are comprised of one high modulus glassy polymer and one low modulus semicrystalline polymer with the volume fraction of each determined from rheological behavior. However, in this work, the PMMA exhibited unusual non-melting behavior and we sought to make a blend of PMMA and SiO₂ particles uniformly dispersed in a HDPE matrix. Thus, the low melting nature of the HDPE was an advantage and the resulting composite was of two particulate species in a HDPE matrix.

Table II – Blend Formulation

	Vol %	Vol, ml	Mass, g	Weight %	Batch
		100			1000
HDPE	55%	55	50.6	41.6%	416
PMMA	30%	30	35.1	28.8%	288
SiO ₂	15%	15	36	29.6%	296
	100%	100	121.7	100.0%	1000

The dry powders were dispersed in an aqueous vehicle containing 68% water, 24% 2-propanol, and 6% dilute ammonia solution. The solids fraction in the dispersion was 53%. High shear mixing was provided by a mechanical agitator for five minutes. No sonication was applied. The resulting mixture was well dispersed and stable for more than 24 h, after which some settling was observed. The sol was dried at 160 °C until the free water was gone and the blend began to form a partially densified cake. This cake was ground to 9 mm pellets and further dried for 24 h at 110 °C in a vacuum oven.

Extrusion

The pelletized mixture was double-extruded in a Brabender Intellitorque 0.75” extruder. The initial extrudate was prepared at 160 °C with the vent port open to allow any remaining moisture to escape and chopped into pellets, which were returned to the extruder for a second processing at final temperatures of 160°, 190°, and 220 °C. Resulting specimens from each of the three temperature runs were cryo-fractured for electron microscopy.

RESULTS AND DISCUSSION

Specimens of the blended powder and the extruded composite were examined to assess the homogeneity of the blend and the morphology of the resulting composite. To assess the mixedness of the blend, both optical and electron microscopy were used. Optical microscopy enabled differentiation of the three components by dyeing two of them (Figure 5, red=PMMA, blue=SiO₂, white=HDPE) to enable image analysis by color. Generally, good homogeneity is observed, although some agglomerates are seen as well. Quantitative image analysis of this system is the topic of a future paper. An SEM image of the blended powder (Figure 6) shows the range of particle sizes present and the tendency for the fine particles to surround the coarser ones as expected from particle packing dynamics. In the present system, the SiO₂ particles are the finest particles in the blend, and it is the goal of this work to distribute them uniformly in the powder mixing stage rather than to rely on melt processing. Although the silica particles are of micron size, i.e. coarser than the nanometer size particles ultimately envisioned for this work, the principal of this interstitial distribution concept is demonstrated.

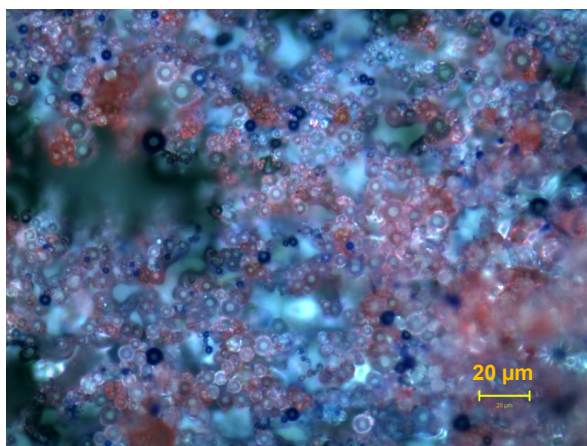


Figure 5. Optical image of powder blend with PMMA dyed red and SiO₂ dyed blue.

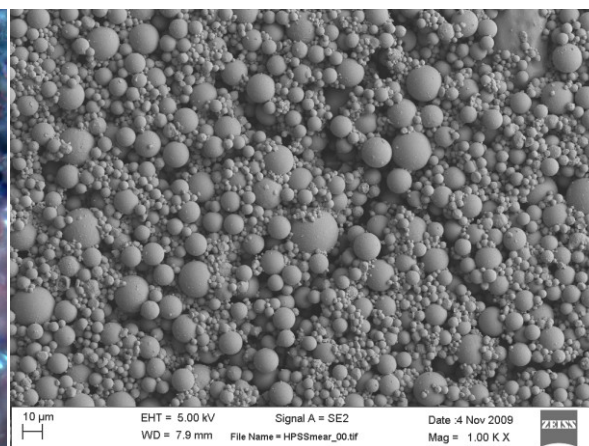


Figure 6. SEM image of powder blend. Largest particles are HDPE, smallest are SiO₂.

In the extruded composites (Figures 7 and 8) the fused matrix (HDPE) is seen surrounding the silica and PMMA particles. Separately, we determined by EDS analysis that the particles showing partially adhering matrix on their surfaces are PMMA particles and the smooth ones are the SiO₂ particles. Thus, this composite extruded at 220 °C is a composite of two particles, PMMA and SiO₂, dispersed in HDPE, rather than an immiscible blend of PMMA/HDPE with dispersed SiO₂ particles. The failure of the PMMA to fuse is under investigation.

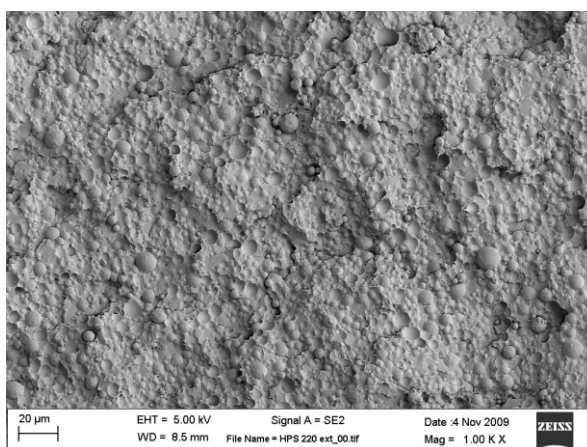


Figure 7. SEM image of extruded blend.

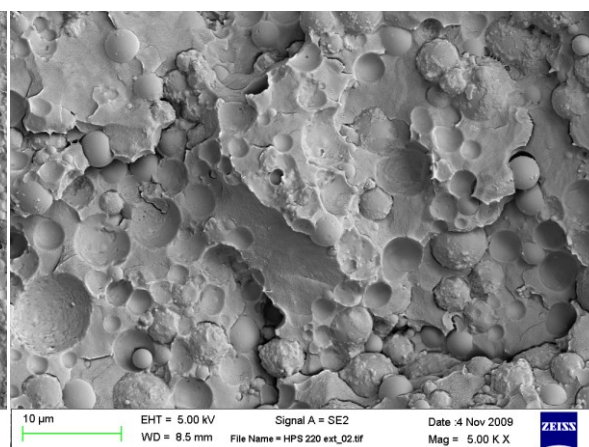


Figure 8. SEM image of extruded blend illustrating fused matrix surrounding particles.

CONCLUSIONS

Powder processing of thermoplastic polymer composites is an effective way to achieve a high level of mixedness in the raw blend prior to melt processing, thus reducing the thermal and shear stress on the components. Fine reinforcement phases, such as nanoparticles, will naturally distribute themselves quasi-uniformly as they occupy the interstitial voids between larger particles. These particles are then more effectively distributed during extrusion or injection molding as compared bulk blending.

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^[i] LiquaJet LLC, Moorestown, NJ

^[iii] Kobo Products, Piscataway, NJ

Appendix II

"Micro/nano structure and morphology of multi-phase polymer/oxide composites prepared by polymer melt processing."

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Micro/Nano Structure and Morphology of Multi-Phase Polymer/Oxide Composites Prepared by Polymer Melt Processing

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ABSTRACT

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Powder polymer processing techniques were evaluated as a means to generate homogeneous immiscible polymer blends without the high residence times at elevated temperature and high shear rates required by extrusion. Using emulsion polymerized and cryogenically jet pulverized PMMA and HDPE powder precursors, blends were prepared with morphologies comparable to extruded blends. Advanced EDS imaging methods combined with SiO₂ marker spheres enhanced electron imaging and analysis of all blend phases. These processing methods will be useful in producing polymer blends from fragile polymers, such as those used in biomedical applications, that cannot tolerate the temperature or shear rates of conventional melt processing.

INTRODUCTION

Blending immiscible polymers is a useful way of producing novel materials with enhanced properties that exceed the rule of mixtures of the constituents. Typically, polymer blends are not thermodynamically compatible due to entropy constraints resulting from high molecular weight of the polymers,^[2] and immiscible structures result. Three general types of blends are observed when polymers “A” and “B” are combined: phase “A” dispersed in a continuous matrix of “B”, “B” dispersed in “A”, and a co-continuous blend in which both polymers are intertwined in a complex morphology.^[1,3] Fine micro-to-nano morphologies are preferred in such blends to produce optimum

mechanical properties via efficient load transfer mechanisms. From a polymer physics perspective, these fine structures have a strong affect on the glass transition and crystallization behavior of the components even though no chemical interactions exist. [2,4]

Extrusion is an ideal method for processing thermoplastic immiscible polymer blends, although temperatures and shear rates must be controlled to avoid degradation of the polymers.^[5] Compression molding minimizes such degradation since dwell time and shear are low, although little mixing occurs since the flow path is short.^[6] For preblended micron sized polymer powder precursors, compression molding offers the ability to preserve the integrity of the materials while achieving a homogeneous morphology.

In this paper, we compare the morphology of PMMA/HDPE blends prepared by extrusion and compression molding using electron microscopy and EDS elemental analysis. Our principal goal is to determine whether homogeneous fine-scale immiscible polymer composites can be made via preliminary mixing of micrometer-size polymers followed by fast, low shear melt processing. Ultimately, these methods will enable processing of blends that are too fragile to survive the conditions of conventional extrusion.

EXPERIMENTAL

Materials

The polymethylmethacrylate/polyethylene immiscible blend system was selected for this study based on the strong immiscibility between these two polymers and their common use in many systems. To achieve fine micro-size powders for powder processing, we sought to avoid conventionally milled powders since they are often

contaminated during milling. Instead, we selected emulsion polymerized polyethylene spheres with average particle size of 11 μm but with a broad size range, e.g. 85% < 25 μm .^[1] The polymethyl methacrylate (PMMA) powder was produced by cryogenic jet-milling of Altuglas V045I pellets. The jet milling process is highly autogeneous and effectively avoids contamination of the polymer. The resulting particles are micron sized (~ 10 μm) with a blocky equiaxed shape. For the conventional extrusion processing segment of this work, pelletized materials were used. Specifically, the HDPE pellets were Exxon HD7960 and the PMMA pellets were Altuglas V045I. Spherical inorganic particles of silicon dioxide (SiO_2) of approximately 5 μm size were added at the 10 volume percent level to all blends. These particles provided a means to monitor the homogenization of the blends by assessing their degree of dispersion.

Table I. Materials used in Powder and Extrusion Processing

Material/Product	Form	Supplier	Density (g/cm^3)
HDPE/ CL-2080	Powder	Kobo Products	0.92
PMMA/Altuglas V045I	Powder	Jet Pulverizer	1.15
SiO_2 / MSS-500/3N	Powder	Kobo Products	2.4
HDPE/ Virgin Exxon HD7960	Pellets	Sabic	0.95
PMMA/Altuglas V045I	Pellets	Sabic	1.15

Characterization

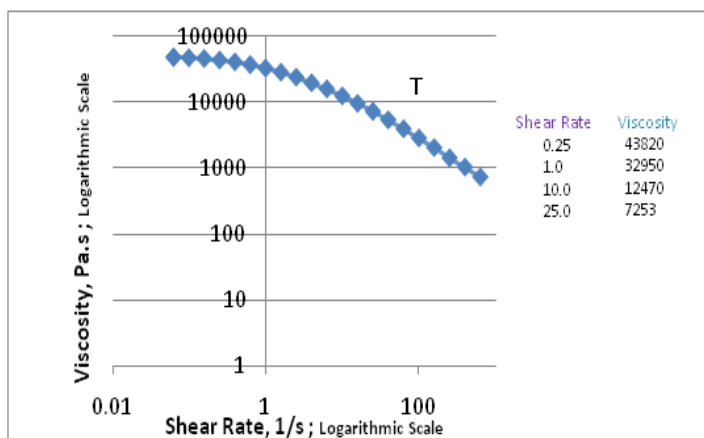


Figure 1. Viscosity/shear rate behavior of PMMA/Altuglas V045I at 200°C.

Viscosity relationships are important in immiscible polymer blends, particularly with respect to locating the phase inversion composition. The viscosity of the PMMA was measured to verify the supplier values at our processing temperature, 200° C. A TA Instruments AR 2000 rheometer equipped with parallel plate geometry was used. PMMA test specimens were compression molded as 25 mm diameter disks, and were subsequently dried overnight under vacuum at 80°C. The data are graphed in Figure 1 as viscosity versus shear rate using a logarithmic scale. These values were obtained via the Cox Merz transformation of the TTS data collected from the rheometer. The viscosity values of the other materials have been previously reported.^[1]

Formulation

Guided by the viscosity data,^[1] line series formulations were developed and blends were formulated from the polymer powder precursors as well as a separate series of formulations for the pelletized powders. Blends were made from the powders using compression molding and similar blends were made from the pellets by extrusion.

Table 2. Pellet Blend Formulations

Blend	Vol. % Composition			Weight % Composition			1000g Batch Formula		
	HDPE	PMMA	SiO ₂	HDPE	PMMA	SiO ₂	HDPE	PMMA	SiO ₂
1L	55%	35%	10%	43.8%	35.4%	20.8%	438	354	208
2L	45%	45%	10%	35.1%	44.6%	20.3%	351	446	203
3L	35%	55%	10%	26.7%	53.4%	19.9%	267	534	199

Table 3. Powder Blend Formulations

Blend	Vol. % Composition			Weight % Composition			1000g Batch Formula		
	HDPE	PMMA	SiO ₂	HDPE	PMMA	SiO ₂	HDPE	PMMA	SiO ₂
1W	30.0%	60.0%	10.0%	22.7%	57.6%	19.7%	22.66	57.64	19.70
2W	50.0%	40.0%	10.0%	39.4%	40.1%	20.5%	39.38	40.07	20.55
3W	20.0%	70.0%	10.0%	14.80%	65.9%	19.3%	14.80	65.89	19.31

Melt Processing**Extrusion**

PMMA and HDPE pellets were combined with the SiO₂ spheres and manually blended until a visually uniform mix was obtained. The PMMA was dried under vacuum at 80°C before blending. Each composition was double extruded using a Brabender Intellitorque 0.75" extruder with a 30:1 auger with various pressure zones and mixing elements. The initial extrudate was processed with all heating zones set at 200°C. The extrudate was cooled and pelletized off-line and then returned to the extruder for a second processing under the same conditions. The resulting specimens were cryo-fractured for electron microscopy.

Compression Molding

The PMMA, HDPE and SiO₂ powder precursors for each composition were blended in a jar mixer with a small quantity of 3 mm spherical alumina media to provide agitation and promote mixing. Each composition was dried overnight under vacuum at 60°C to eliminate moisture. The various blends were then compression molded with a Carver[®] press with parallel heated platens maintained at 200°C. Approximately 5 g of blended polymer powder was placed between two Teflon[®]-coated steel plates and pressed

for 150 s with a force of 40 kN. Although a precise value of the pressure is hard to determine since the polymer is flowing to form a film, the final area of the film was nominally 200 cm², which corresponds to a pressure of 2 MPa. The Teflon[®] plates were removed, with the specimen between them, and quenched. After separation of the film from the plates, cold-fractured surfaces were prepared for electron imaging.

Electron Microscopy/EDS

The cold-fractured specimens from both processes were analyzed using the Zeiss Sigma FESEM with Oxford INCA PentaFETx3 EDS system. The SEM images were essential in evaluating the morphology and mixedness of the blend. EDS uses elemental analysis to fingerprint the image by overlaying elemental maps of the constituents onto the original SEM image for chemical conformation.

RESULTS AND DISCUSSION

Electron Microscopy and Image Analysis

The morphology generated by the extrusion and compression molding processes is shown in the two SEM images of Figures 2 and 3. In both instances a fine micro-scale morphology is observed that is nearly co-continuous, but in many instances appears to consist of HDPE strands dispersed in a PMMA matrix, particularly for the extruded blend. More importantly, the marker spheres of SiO₂ are relatively well dispersed in both cases, suggesting that similar levels of mixing were generated by both processes. These images show well dispersed spheres, although the image field in both cases is too small to assess a large number of particles. Even at just ten volume percent, the silica sphere can have a significant effect on the morphology and domain size of the blend, both due to enhanced shear in a system partially filled with rigid spheres and due to interfacial

surface chemistry effects. Hence, control specimens containing no silica spheres are needed to explicitly illustrate this effect. Unfortunately no such specimens were ready in time for this manuscript and the current data reveal only the differences in two filled systems.

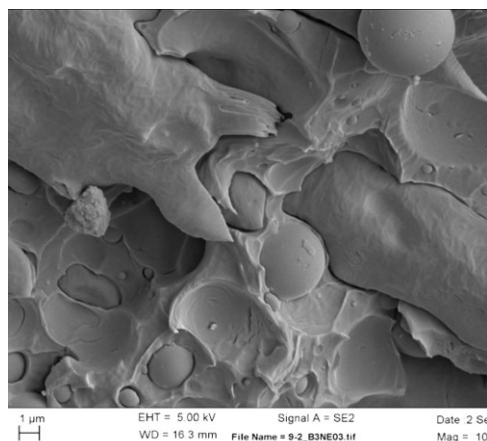


Figure 2. Image of
55PMMA/35HDPE/10SiO₂ Extruded
Blend [No.3L]

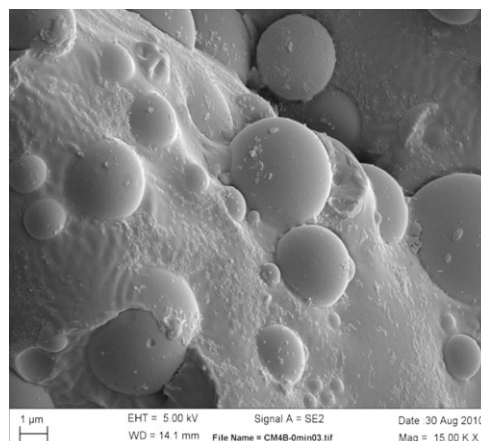


Figure 3. Image of
40PMMA/50HDPE/10SiO₂ Compression
Molded Blend [No. 2W]

Elemental Analysis

Energy Dispersive Spectroscopy [EDS] was used to conduct elemental analysis on blend specimens. This analysis was designed as a means to identify the SiO_2 spheres in the blend and assess their level of dispersion, but we also sought to differentiate the oxygen-rich PMMA from the HDPE hydrocarbon. The morphology of the 55PMMA/35HDPE/10 SiO_2 is displayed in Figure 4a for reference with Figure 4b, which is an overlay of EDS chemical data. The green area represents silicon and thus identifies the silica particles in the blend. The distribution of the green areas are a measure of the mixedness of the blend and the hence the level of homogenization generated by the process. Red areas represents oxygen which occurs in the carbonyl and acrylic ester groups found in PMMA. The blue area represents carbon which occurs in both polymers used in this study. The area where only blue occurs corresponds to HDPE, a pure hydrocarbon.

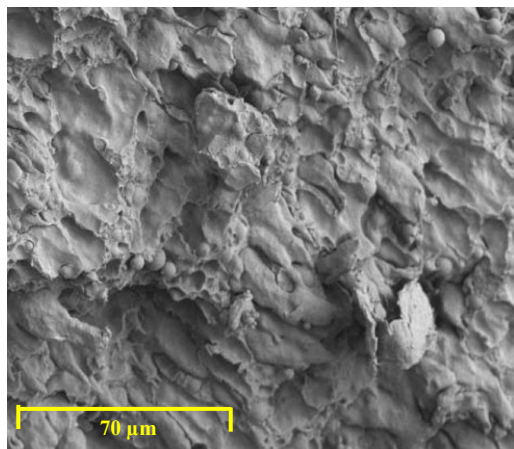


Figure 4a. Extruded 55PMMA/35HDPE/10 SiO_2 Blend [No.3L]

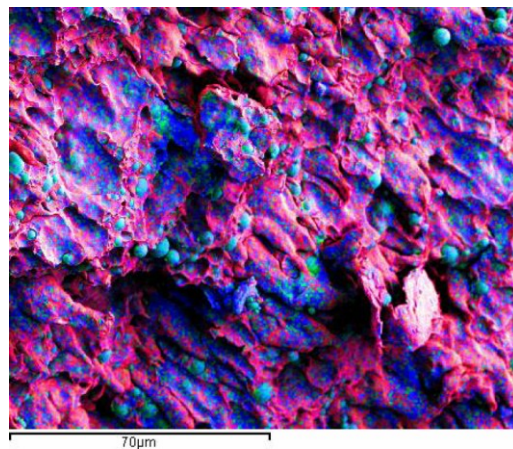


Figure 4b. Elemental analysis overlaid on Fig 4a. Red=O, green=Si, blue=C.

A similar analysis was conducted for the compression molded blends and the morphology image and map are shown in Figure 5. Color/element associations are the same as in Figure 4.

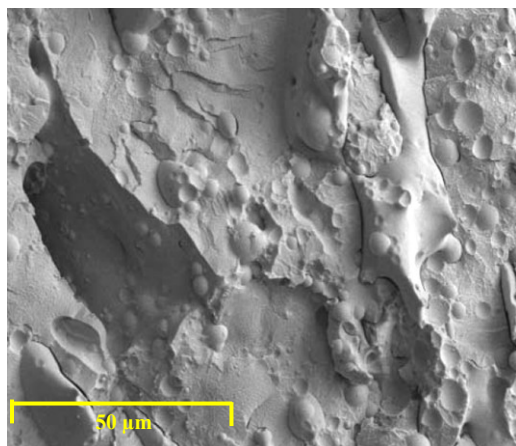


Figure 5a. Compression Molded 60PMMA/30HDPE/10SiO₂ Blend [No.1W]

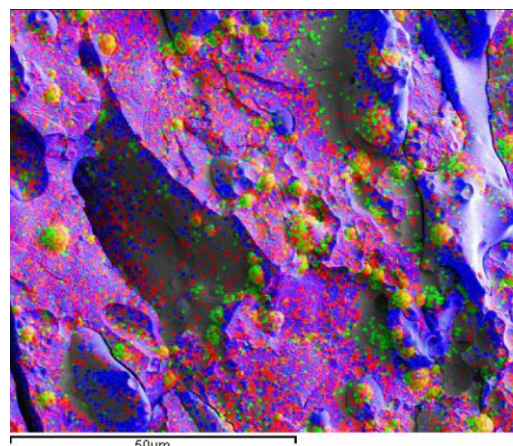


Figure 5b. Elemental analysis overlaid on Fig 5a. Red=O, green=Si, blue=C.

The EDS results provide valuable additional information about the phase distribution and homogeneity of the blends prepared by these processing methods. In both cases, the silica marker spheres are shown more vividly by EDS as compared to the secondary electron image, even revealing subsurface spheres. A casual analysis of the distribution of these spheres suggests a comparable level of distributive and dispersive mixing in both processes. A major finding of this work is the ability to differentiate polymer domains using EDS. The carbonyl and ester oxygen in the PMMA produce strong signals that enable PMMA to be effectively identified in the blend. This result is particularly notable in Figure 5b in which the red-blue phase is PMMA and the blue-only phase is HDPE. Lastly, we sought to make blends of comparable domain size by compression molding. These images suggest that the domain sizes for the two processes are similar, although the compression molding domain size may be slightly larger. Future effort will be devoted to a more formalized image analysis approach and a comparison of the current images and data with those from control specimens without silica spheres. Such results will provide a measure of the effect of rigid spheres on domain morphology under these processing conditions.

SUMMARY AND CONCLUSIONS

Powder polymer processing techniques were evaluated as a means to generate homogeneous immiscible polymer blends without the high residence times at elevated temperatures and high shear rates required by extrusion. Results show that high-quality fine-domain size blends can be made by the compression molding process. Silica marker spheres were used to qualitatively assess the level of distributive and dispersive mixing. EDS chemical analysis was particularly effective in providing image contrast between PMMA and HDPE based on the carbonyl and ester oxygen. EDS image maps, combined with secondary electron images show that compression molding of blended powder precursors produces composites of comparable homogeneity and domain size as extrusion processing. This work has shown that powder processing of polymers is an effective means by which fragile polymers such as those used in biomedical applications, can be melt processed to high quality blends.

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Appendix III

"Melt processing and domain morphology of PMMA/HDPE polymer blends prepared from powder precursors."

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Powder Technology 218 (2012): 18-22.



Melt processing and domain morphology of PMMA/HDPE polymer blends prepared from powder precursors

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ABSTRACT

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Powder polymer processing was used to prepare immiscible PMMA/HDPE blends from micrometer sized polymers spheres that were physically mixed prior to compression molding to a fused blended film. This two-stage mixing approach, initially as dry powders and subsequently during compression molding, seeks to minimize the time/temperature/shear to which delicate thermoplastic polymers would otherwise be exposed by conventional extrusion processing. The powder processing route effectively generates fine domain blends (3-10 μm) similar to extruded blends, although some coalescence was present. Conformational effects were observed by FTIR at high wavenumbers, indicating intimate interfacial proximity. The spectral effects are similar to those observed in extruded pellet blends. This powder processing route will be useful for molding delicate thermoplastic polymers found in certain biomaterial, pharmaceutical, and cosmetic applications.

INTRODUCTION

The blending of immiscible polymers has gained credibility as an approach to create novel materials without the cost associated with synthesis of completely new polymers. The goal of such blending is to achieve a material with at linear, and possibly synergistic, properties of the components.[1] A co continuous morphology is usually sought since this compositional region presents a morphology of maximum interconnectivity and interaction between the two phases. Such structures are essential in

engineering tissue scaffolds and other applications.[2] The exact nature of the co-continuous morphology is highly dependent on the processing temperature, shear rates and dwell time during processing as well as the initial mixedness of the constituents.

Although most traditional thermoplastic polymers, such as the linear alpha-olefins, withstand commercial processing conditions quite well, newer polymers used in the pharmaceutical, biomaterial, and cosmetic industries are sensitive to temperature and shear rate conditions and processing times must be reduced. Compression molding is an alternative processing approach that aids in preserving these delicate thermoplastics since dwell time is short and the shear rate is low. On the other hand mixing can be less due to reduced flow path and the absence of high shear mechanical mixing.[3] In related work in our laboratory, we have achieved good mixedness at low residence times and shear rates by dividing the processing into two steps. Initially fine powders rather than pellets are the raw materials and these powders are actively mixed prior to melting. The mixed powder blend is then fused to an immiscible polymer blend in a compression molding press.

The type of processing strongly influences the resulting morphology of the blends and will subsequently govern the final properties produced.[4] The domain size of well-prepared immiscible polymer blends can be quite small, ranging from several micrometers down to below 100 nm.[5] Such fine morphologies possess high levels of interfacial boundaries and the juxtapositioning of these phases can slightly alter the conformation of the molecules.

In this work, we sought to prepare PMMA/HDPE blends by the novel method of powder blending followed by compression molding. To assess the intimacy of the blends

and the nature of the polymer/polymer interactions, we characterized blends with FTIR spectroscopy and conducted image analysis on the powder processed blend. Comparisons are made with blends prepared by the conventional means of pellet extrusion.

EXPERIMENTAL

Materials & Formulation

The polymethylmethacrylate/polyethylene immiscible blend system was selected for study due to the strong immiscibility of PMMA and HDPE and prior success in the processing of this system.^[3] Although pellets of these polymers are readily available, high purity powders in commercial quantities have been hard to obtain since all such powders have been produced by conventional milling processes that are prone to contamination. More recently a commercial scale cryogenic autogeneous milling process has been commercialized^[6] that produces uniform particles in the micrometer range. PMMA pellets were cryogenically jet-milling to produce a micron size ($\sim 10\mu\text{m}$) powder of equi-axed, irregularly shaped particles.^[7] HDPE powder produced through emulsion polymerization and comprised of spherical particles of $\sim 11\mu\text{m}$ and with range size $85\% < 25\mu\text{m}$ was obtained from Kobo Products². Spherical silica particles, $\sim 5\mu\text{m}$, were added to all blends at 10% by volume. This inorganic additive serves as a tool to monitor the mixedness of the blends, and as a morphological scale marker. Specific material and supplier information is given in Table 1.

¹ Liqua Jet LLC; Jet Pulverizer, Moorestown NJ

² Kobo Products Inc, South Plainfield, NJ

In this work a simple set of formulations was studied around the co-continuous phase inversion composition near 50/50 HDPE/PMMA. This co-continuous region is observed when the volume fraction ratio of the polymers is equal to the viscosity ratio at the shear rate and temperature of processing, i.e. the well known Jordhamo relationship. The viscosity values at the processing temperatures of the polymers have been previously published.^[1&3] In addition to producing blends with superior properties, the co-continuous region also provides the highest amount of interfacial surface area between the polymers, a desirable feature in assessing molecular conformational changes using the spectroscopic methods featured in this work. Formulations prepared for extrusion and compression molding are given in Table 2.

Extrusion and Compression Molding

The PMMA pellets were dried overnight under vacuum at 80 °C. The pellets were manually mixed with the SiO₂ spheres until a uniform blend was achieved. Processing was done on a Brabender Intellitorque 0.75” extruder with a 30:1 auger with all heating zones at 200 °C. All blends were double extruded to provide a high level of mixedness.

The powder blends were weighed out and dried overnight under vacuum at 60 °C. Mixing was achieved by tumbling in a rotating cylinder with approximately 10 volume percent of alumina spheres (~3mm) for 10 h. The alumina spheres were removed by screening after the mixing was complete. A Carver® press with parallel plate heated platens (200 °C) was used to compression mold the blends. A approximately 5g of the blended powders was pressed between Teflon® coated steel plated using a force of 40kN for 150 seconds. The plates were immediately removed and quenched. Resulting specimens were thin (~250 µm) and possessed a final area of approximately 200 cm².

FTIR Spectroscopy

FTIR spectra were acquired using a Perkin Elmer Spectrum RX I FTIR Spectrometer in conjunction with a MTEC photoacoustic model 300 detector. Neat specimens of HDPE CL-2080 and PMMA/Altuglas V045I(cryo milled) were both analyzed in powdered form. The HDPE/Exxon D7960 and PMMA/Altuglas V045I were analyzed in pellet form. The extruded blend 3E and compression molded blend 2C were analyzed in pellet and thin film forms respectively. The spectrometer scan was from 600 cm⁻¹ to 4000 cm⁻¹ with a 64 scan count. Duplicate and sometimes triplicate replication of the spectra were conducted to assure reproducible results. Background corrections were applied and the spectra were normalized.

Image Analysis

Image analysis was conducted by a variety of techniques used in our laboratory for dispersed and co-continuous polymer blends. The methodology consists of perimeter tracing of domains, integration of the area traced for each domain, and comparison of this integrated value with the known volume fraction of the phase in the composite. Area and cumulative area curves versus domains size are calculated from the area data and graphed. To enhance phase identification, energy dispersive spectroscopy [EDS] was used to conduct chemical analysis on compression molded samples to reveal areas elevated oxygen concentration (PMMA) or deficiency (PE), and to identify the location of the silica marker spheres.^[8]

RESULTS AND DISCUSSION

Overall the blends processed well by both methods and produced composites appearing similar in texture. In this sense, the powder processing methods seems to be a

viable approach for the processing of temperature and shear rate sensitive immiscible polymers such as those used in certain biomedical, pharmaceutical, and cosmetic applications. Specifically in this work we characterized the morphology of the powder processed blend in terms of its fineness and compared it to the known domain sizes of pellet processed composites. Furthermore, we looked for subtle changes in the FTIR spectra as an indication of conformational or bonding variations in the blends due the nature of the interfacial region.

Composite Morphology and Image Analysis

Since the overall goal of the powder processing route is to develop a means by which immiscible polymer blends can be processed to fine micrometer-scale morphologies similar to pellet extruded composites but with less time/temperature/shear history, an examination of the resultant morphology is essential. Figure 1^[3] illustrates the immiscible morphology of the powder processed blend as a combination of dispersed and co-continuous elements. The bold lines between domains were added during image analysis to aid in the quantitative assessment. A full description of the three dimension nature of this blend is beyond the scope of this paper, but the key point here is that the domain size is in the micrometer size range and comparable in structure to blends produced by extrusion of pellets.^[3] The area fraction of the traced domains comprises 31.2% of the image area, in remarkably good agreement with the 30 volume percent formulated composition. Simple quantitative image analysis using perimeter traced shows a distribution of domain widths in the 3 – 27 μm range. When tracing domains in co-continuous blends, the average width of a domain is the relevant parameter since

³ Figure 1 adapted with permission from MRS 2010.

domain strands often extend through the entire composite. Areas of the domains are graphed versus the domain width in Figure 2. A range of domain sizes is observed and two very large areas of coalescence (17 and 27 μm) dominate the graph and the overall geometric mean domain size is 14 μm , considerably larger than the 3 – 6 μm size typically seen in pellet produced composites. The numeric average size in Figure 2 is 5.2 μm , much closer to the pellet range. Furthermore, if the two coalesced domains are removed from the analysis, then a rather tight distribution of domain sizes in the 3 – 11 μm range is observed. This is an effective domain size range for immiscible polymer composites and the uniformity of the powder precursors likely contributed to this close distribution.

FTIR Spectroscopy

Fourier transform infrared spectroscopy [FTIR] is useful for fingerprinting polymers according to the various functional groups present.^[9] Prior work in our laboratory has shown that the interaction of immiscible blend domains across the domain interface can lead to subtle changes in the bonding of backbone and pendant groups that are FTIR and/or Raman active.^[10] In this paper we describe the subtle effects observed in the extruded and powder processed blends.

The FTIR spectra for the composite samples prepared by powder process and traditional extrusion processing from pellets are shown in Figures 3 - 5 along with the spectra for the neat raw materials. The silica marker spheres were a significant help in the image analysis part of this work, but the strong absorption of SiO_2 in the infrared served to mask many of the FTIR effects and made interpretation of the spectra at low wave numbers difficult. Fortunately, most of the spectral features of the blends that

differed from those of the neat materials occurred at high wavenumbers, approximately in the range $2700 - 3100\text{ cm}^{-1}$, a region in which the absorbance of SiO_2 is quite low and did not affect the qualitative interpretation of absorbance effects between the polymers. Refer to Figures 3a,b.

The spectra for the extruded composite (Figure 4) show only minimal variation from additive behavior as would be expected from a mechanical blend of the components. At the lower energy end of the $2700 - 3100\text{ cm}^{-1}$ window, the composite is dominated by the PE behavior (observed 2849 band) and the PMMA band at 2835 is mostly absent. The absorption bands at higher energy, i.e. at 2918 and 2951 (PE asymmetric CH_2 stretching and PMMA C-H stretching), and at 2990 (PMMA asymmetric stretching of $\text{CH}_3\text{-O}$ and CH_2), are consistent with additive intensities from the components.

Figure 5 compares the absorbance spectra of the powder processed composites. The powder processed composite spectrum shows more significant variation from the additive behavior and these differences appear to result from the powder processing route. Beginning on the lower energy side of the figure, the well known PMMA and PE asymmetrical CH_2 stretching bands are observed at 2841 and 2849 cm^{-1} respectively. Although the composite contains 60 volume percent PMMA, the spectrum reveals principally the PE absorption band with only a trivial shoulder of the PMMA band, suggesting that the assigned stretching mode is inhibited considerably in the composite. As the spectrum proceeds towards the strong 2918 (2922 in the figure) CH_2 asymmetrical stretching band for PE, several artifacts are seen in the sample spectrum (2874, 2889, 2907) that are weak but reproducible. Conformational effects in the powder processed

composite are likely responsible for these features, although the present work simply observes their presence and does not seek to assign vibrational modes. At higher wavenumbers the strong 2951 C-H stretching bands for PMMA, and to a lesser extent PE are reproduced in the composite. The PMMA C-H stretching doublet at 2988 and 2997 appears in the blend spectrum with a slight shift towards higher energies.

Overall, the blending of these immiscible polymers, whether by conventional pellet extrusion or by compression molding of powder precursors, produces structures that give FTIR spectra that vary in certain instances compared to a linear combination of the components. Notably, for the powder processed materials one well-known PMMA band (2841) does not appear in the sample spectrum, indicating an alteration of the polymer conformation. The extruded composite also shows some variation from component additive behavior with the repression of the 2841 band and a shift in the intensity ratio of the 2988/2997 doublet intensities.

An interesting feature of this work is the FTIR analysis conducted for the first time on small PMMA particles ($\sim 10\ \mu\text{m}$) produced by the autogenous cryo-grinding of bulk pellets. Although PMMA is an amorphous polymer, the milled powders have finer domain size, which combined with the energy imparted during comminution, may be responsible for subtle changes in molecular conformation and hence FTIR absorption bands. The milled PMMA spectrum shows a more symmetric 2835 peak, fewer minor bands in the 2835 – 2951 range, and a decided difference in the 2991 band. The 2991 absorption band, well formed and symmetric in the bulk PMMA, splits into two bands at 2988 and 2999. Naturally, these features are emulated in the blends prepared from these materials.

SUMMARY AND CONCLUSIONS

Immiscible PMMA/HDPE composites prepared from compression molding of powder precursors form composites with similar domain size as those prepared from conventional extrusion of pellet mixtures although coalescence of the micrometer size polymer sphere generates large domains among an otherwise fine distribution centered in the 3 – 10 micron range. FTIR spectra show differences between mechanical mixtures of the neat precursors and the melt formed composites for both powder processed blends and extruded pellet blends. The differences, which occur principally at high wavenumber, appear to result from subtle conformation differences in the polymers at the domain interfaces.

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VITAE

Giorgiana Giancola is a Research Associate at Rutgers University Department of Materials Science and Engineering, where she conducts research on the processing and characterization of immiscible polymer blends. Her current interests and expertise are in

the processing of polymer blends and the application of electron microscopy imaging to characterize the resulting morphologies. Most recently, she has developed an interest in the application of spectroscopic methods (FTIR and Raman) to identify perturbations at the domain interfaces. She received her MS in Materials Science in October 2010 and is presently working towards a PhD.

Richard Lehman is Professor and Department Chair of the Materials Science and Engineering Department at Rutgers University. His research interests center on organic and inorganic glasses, relaxation and glass transition behaviors in these materials, and the processing of commercial immiscible polymer blends and glasses. Most recently Professor Lehman's interest has evolved towards recycling and renewable materials, and he is an organizer of the sustainability center at Rutgers that seeks to develop and promote new sustainable polymer materials over a broad range of disciplines and applications.

James D. Idol is Professor emeritus and Director of Polymer Science at the Rutgers University Polymer Center. He is known for his pioneering work in the development of acrylonitrile synthesis and process technology. His current research interests are in synthesis and structure-property relationships of polymers and composites, permeability of films, monomer manufacturing technology, catalysis and support structures.

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Material/Product	Form	Process	Supplier	Density (g/cm ³)
HDPE/ CL-2080	Powder	Compression Mold	Kobo Products	0.92
SiO ₂ / MSS-500/3N	Powder	Compression Mold	Kobo Products	2.1
PMMA/Altuglas V045I, cryo milled	Powder	Compression Mold	Jet Pulverizer	1.15
HDPE/ Virgin Exxon D7960	Pellets	Extrusion	Sabic	0.95
PMMA/Altuglas V045I	Pellets	Extrusion	Sabic	1.15

Table 1. Materials Selection

Percent by Volume (<i>Weight</i>)							
Extruded Blends				Compression Molded Blends			
Blend	HDPE	PMMA	SiO ₂	Blend	HDPE	PMMA	SiO ₂
1E	55(43.8)	35(35.4)	10(20.8)	1C	50(39.4)	40(40.1)	10(20.5)
2E	45(35.1)	45(44.6)	10(20.3)	2C	30(22.7)	60(57.6)	10(19.7)
3E	35(26.7)	55(53.4)	10(19.9)	3C	20(14.8)	70(65.9)	10(19.3)

Table 2. Formulations used in extrusion and compression molding.

Wavenumber, observed	Wavenumber reference	Polymer	Assignment
2841	2849	PMMA	Sym. CH ₂ Stretch
2848	2849	PE	Sym. CH ₂ Stretch
2922	2927-2986	PMMA	stretching of CH ₃ -O
2922	2918	PE	CH ₂ asym. stretch
2951	2927-2986	PMMA	C-H stretch range
2951	2927-2986	PE	C-H stretch range.
2988	2927-2986	PMMA	CH stretch range
2997	2927-2986	PMMA	CH stretch range

Table 3. FTIR Absorption Bands and Molecular Assignments for Powder Processed Composite.

Wavenumber, observed	Wavenumber reference	Polymer	Assignment
2835	2835	PMMA	stretching of CH ₃ -O
2849	2848, 2851	PE	CH ₂ Sym Stretch
2918	2918	PE	Asym CH ₂ stretch
2951	2927-2986	PMMA	CH stretching
2990, 2992	2995	PMMA	Asymmetric stretching of CH ₃ -O and CH ₂

Table 4. FTIR Absorption Bands and Molecular Assignments for Pellet Processed Composite.

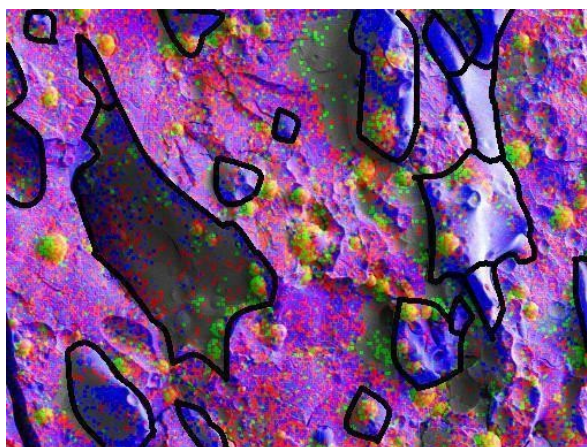


Figure 1. SEM image of powder processed composite (2C) illustrating phase constitution by EDS mapping overlaid on a secondary electron image. Blue is PE, red is PMMA and green is SiO₂. Demarcation of phases with black line was done by image analysis.

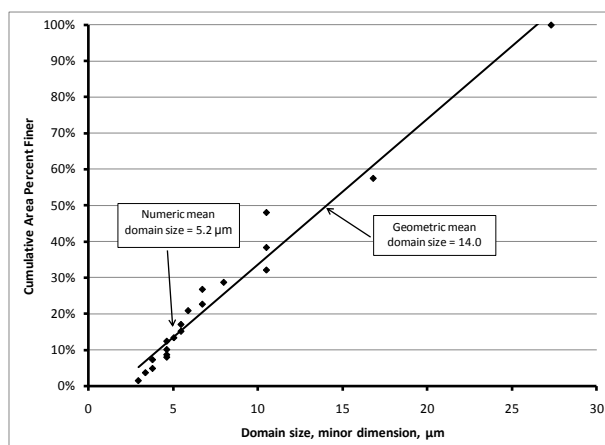


Figure 2. Cumulative percent finer area plot of minor domain sizes in powder processed composite (2C).

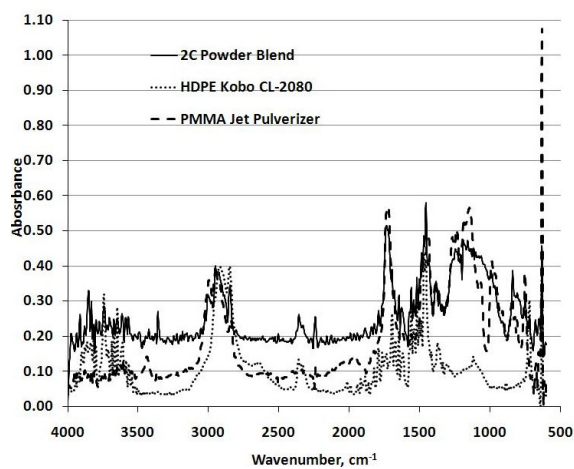


Figure 3a. FTIR spectra of the 2C powder blend and the neat polymer constituents of the blend over a range of wavenumbers from 500 – 4000 cm⁻¹.

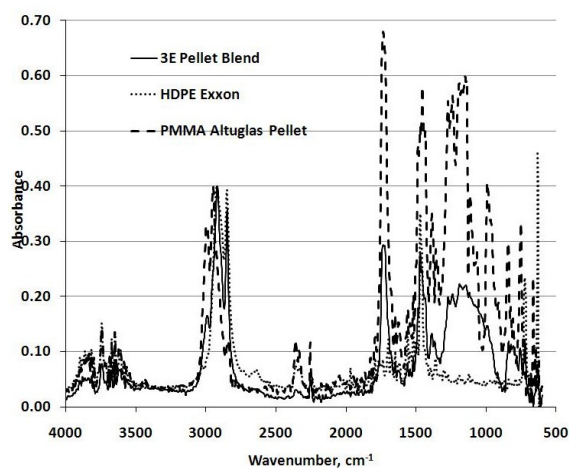


Figure 3b. FTIR spectra of the 3E powder blend and the neat polymer constituents of the blend over a range of wavenumbers from 500 – 4000 cm⁻¹.

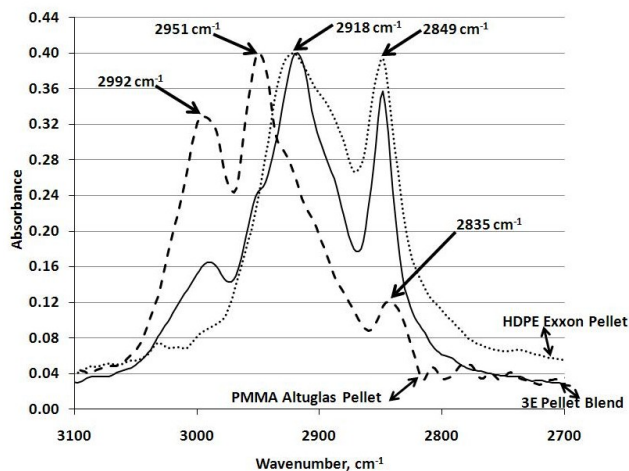


Figure 4. FTIR spectra of the 3E powder blend and the neat polymer constituents of the blend at higher wavenumbers ranging from 2700 – 3100 cm^{-1} .

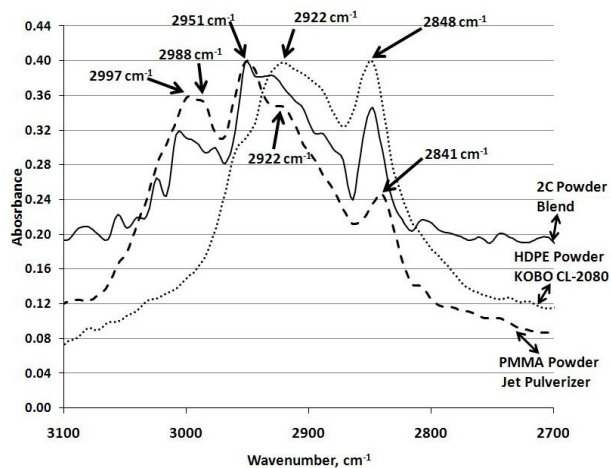


Figure 5. FTIR spectra of the 2C powder blend and the neat polymer constituents of the blend at higher wavenumbers ranging from 2700 – 3100 cm^{-1} .

Appendix IV

"Sustainable polymer composites: Immiscible polymer blends prepared by extrusion of poly(trimethylene terephthalate) and polyamide6,10 with high bio-based content."

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International Journal of Sustainable Engineering



Sustainable polymer composites: Immiscible blends prepared by extrusion of poly[trimethylene terephthalate] and polyamide6,10 with high bio-based content

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ABSTRACT

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green engineering.

Components for binary polymer blends were sought to produce an immiscible blend of improved renewable character and with good structural properties. The poly[trimethylene terephthalate] and polyamide6,10 system was selected based on the molecular structure of the molecules and the bio-based origin of the feedstocks. A preliminary study of three compositions in this system demonstrated the similar thermal properties of the two polymers as measured by DSC and the ability of these polymers to be processed together in conventional extrusion equipment to produce blends with micrometer scale domains. Dispersed phases were observed by electron microscopy near the end-members. Available viscosity data and the appearance of columnar blends at the 50/50 composition suggest the possibility of co-continuous blends above 50% PA6,10.

INTRODUCTION

Polymers based on renewable feedstocks are of increasing interest due to the sustainable nature of these raw materials and the need to reduce our ever increasing reliance on petroleum.

The blending of immiscible polymers via specialized melt processing either with or without compatibilizers is an important and productive approach to the development of composites with targeted properties from existing polymer components. This approach reduces the need to engineer new polymers from the synthesis stage^[1], a long and costly development effort usually limited to well-funded research efforts at large corporations. Successful immiscible polymer blending has produced composites with either rule of mixture properties or synergistic properties in excess of the linear relationship.^[2]

The goal of the present work was to make a preliminary investigation into the use of immiscible polymer blending to improve the bio-based content of a relatively new polymer, poly[trimethylene terephthalate], while maintaining or increasing the engineering and processing properties. Empirical viscosity/volume fraction relationships were used to determine the co-continuous region of the blended polymers in order to develop interconnected morphologies where mechanical grafting^[3] provides good load transfer even in the absence of chemical bonding.^[2] Examples of applications where such structures can be used are tissue engineering scaffolds, electrical conductivity and drug delivery devices.^[4]

METHODOLOGY

The thermoplastic polyester, poly[trimethylene terephthalate] (PTT) is a comparatively new polymer with excellent properties similar to the well-known polyethylene terephthalate (PET), a polyester used commercially for decades in fabrics, carpeting, apparel and packaging. PTT is used in similar applications but contrasts in that PTT exhibits superior elastic recovery and possesses lower elastic modulus than PET.^[5] One of the most prominent features of PTT is that it possesses partial renewable content,

arising from the fact that it is derived by reacting terephthalic acid with 1,3 propanediol (trimethylene glycol). The diol part of 1,3 propanediol is derived from corn sugar and is the contributing factor to making PTT a bio-based polymer with a renewable fraction of approximately 36%.^[6]

A good matching polymer for blending with PTT will have bulk engineering properties that enhance PTT, functional pendant groups that are just partially compatible with PTT, a high bio-based content, and viscosity/temperature characteristics that allow the two polymers to be processed together. After reviewing numerous polymers, the polyamide family was selected and polyamide_{6,10} in particular was picked as a good candidate for blending with PTT. The polyamide polymers exhibit good engineering properties such as superior toughness, strength and abrasion resistance,^[7] properties that will complement PTT.

Polyamide_{6,10} currently finds uses in monofilament form in applications such as bristles and brushes.^[2] The molecular configuration of polyamide_{6,10} provides an ideal level of compatibility with the PTT molecule. The goal for a good immiscible blend is to have sufficient cohesive energy density differences, as measured by solubility parameter, to make the polymers immiscible, but with sufficient similarity in cohesive energy density and dipole character to enable some level of compatibility in the interfacial region of the blend. The molecular structures of PTT and PA_{6,10} (Figures 1a&b) illustrate the similarities and differences. PTT is a thermoplastic aromatic polyester with 11 carbon atoms in the repeat unit, whereas PA_{6,10} has 16 carbon atoms in a longer linear backbone. However, both molecules have four high-electronegativity atoms (nitrogen or oxygen), two in the backbone and two as pendant carbonyl oxygen. This combination of

different backbone repeating units but with a similar distribution of high electronegativity atoms in the backbone and pendant groups provides a level of dipole-dipole interaction and compatibility that enhances interfacial secondary bonding in the blends. From a more macroscopic perspective, the solubility parameter of PTT and PA_{6,10} calculated from the Hoy group contribution method^[8] are 35.4 MPa^{1/2} and 21.3 MPa^{1/2} respectively. The polymers are suited for immiscible blending since their solubility parameters differ by 14.1 MPa^{1/2}, greater than the generally accepted $\Delta\delta > 10\text{MPa}^{1/2}$ ^[8,9&10] needed to create immiscibility, but not so great as to preclude secondary bonding in the interfacial regions.

With regard to producing an immiscible blend with PTT that has increased bio-based content, the companion polymer must have greater bio-based content. Polyamide_{6,10} is a good choice in this regard since approximately 60% of PA_{6,10} can originate from renewable sources. The polymer is synthesized by reacting hexamethylenediamine with sebacic acid (dicarboxylic acid). The renewable portion of this polymer is attributed to sebacic acid which is a derivative of castor oil. Castor oil is a byproduct of the castor seed, extracted from the seed of *Ricinus communis*.^[11] Castor plants grow prolifically in tropical and sub-tropical climates and their toxicity as a food substance makes the plants readily available for non-food uses.^[11]

Melt processing of thermoplastic polymers to produce a two-component immiscible polymer blend requires specific viscosity temperature characteristics. Although this work sought to simply demonstrate that the two selected polymers can be co-processed by extrusion to produce an immiscible polymer blend with domains at the micrometer level, the general guiding principles of co-continuous immiscible blend processing were followed. Such principles include empirical relationships that relate the

viscosity (η) of each polymer at the processing temperature to the necessary volume fraction (Φ).^[6] The Jordhamo relation (equation 1) is one such relationship and was used in this work.

$$\frac{\eta_A}{\eta_B} \cong \frac{\Phi_A}{\Phi_B} \quad [1]$$

This relationship indicates that co-continuity occurs when the volume fraction ratio of the blend is approximately equal to the viscosity ratio at the shear rate and temperature of the extrusion processing. In a comprehensive assessment of any immiscible blend system, a full rheology work-up is needed spanning all shear rates and temperatures. In this preliminary study, we approximated values based on supplier data and DSC analyses of melting points described in the materials characterization section.

EXPERIMENTAL

Materials Selection and Characterization

The poly[trimethylene terephthalate] and polyamide_{6,10} used in the work were obtained in pellet form from commercial suppliers as indicated in (Table 1). PTT is a semicrystalline polymer and the pellets are opaque with a density of 1.33 g/cm³. Polyamide_{6,10} is also semicrystalline and the pellets are translucent with a density of 1.08 g/cm³.

Although some thermal data are available from the suppliers for these commercial products, we sought to confirm the properties via DSC. Approximately 10 mg specimens of each polymer were run on a TA Instruments DSC Q1000 from ambient to 275 °C at a heating rate of 10 °C/min. After a brief hold at 275 °C, additional enthalpy data were

collected on cooling at 5 °C/min. The analyses were replicated three times and averaged, although only miniscule variability was observed between runs. Results are shown in (Figures 2a and b). The PTT polymer melted on heating at 225 °C and on cooling at 166 °C, a difference of 59 °C, a comparatively large value indicating that a substantial amount of undercooling is required to overcome the kinetic barrier to crystallization. The comparatively low amount of crystallization that occurs during cooling, approximately 27% of the crystallinity revealed during melting as measured by integrated enthalpy ratios, again suggests a relatively viscous material at this temperature. The polyamide_{6,10} melting point, as measured during heating is 218 °C and upon cooling is 183 °C, a somewhat smaller difference of 35 °C. From enthalpy ratios, 47% of the pellet crystallinity is recovered during cooling. The lesser difference in temperatures and the greater crystallization of the polyamide suggests a lesser kinetic barrier to crystallization compared to the PTT and possibly a lower viscosity at the melting point. Regardless of the exact behavior, this simple DSC analysis suggests that both polymers have similar melting points (PTT heat/cool mean = 196 °C; PA_{6,10} heat/cool mean=201 °C) and can likely be processed satisfactorily together as an immiscible polymer blend at temperatures nominally above the melting point of both polymers. Melting temperatures (heating) from supplier data for PTT and PA_{6,10} are 228 °C and 218 °C, respectively, in good agreement with the 225 °C and 218 °C values measured in this study.

Formulation and Blending

Several simple blend compositions were formulated to determine if these polymers could be melt processed together and to demonstrate the degree of immiscibility in this system. Furthermore, we sought to identify the degree of dispersion

and domain size near the end members and at the 50/50 composition. Batch formulations are given in (Table 2) both in volume and weight percentages. Both the PTT and PA6,10 pellets were dried under vacuum at 120 °C and 80 °C respectively for 12 h. The batch formulations were weighed and mixed to a homogeneous state and either immediately melt processed or stored in a hermetically sealed glass jar held at 80 °C until just before the composition was extruded.

Extrusion

The pelletized blends were processed using a Brabender Intellitorque 0.75” 30:1 single screw extruder with four controlled heating zones over all processing zones; the conveying zone, the transition zone, the metering zone, and the die. Temperatures for these zones varied considerably and were adjusted empirically to enable good extrusion. Most critical was adjustment of the solids conveying zone temperature to enable good wetting of the extruder wall to provide sufficient shear stress for extrusion. Exit temperatures at the die were controlled to give good extrudate surface texture without melt fracture or excess fluidity. After processing, specimens were cryo-fractured in preparation for SEM analysis.

Image Analysis

Cold-fractured specimens from the various formulations were analyzed using the Zeiss Sigma FESEM. All specimens were coated with 5nm of iridium to prevent charging. Images were collected at a working distance of 14mm and an accelerating voltage of 5kV. SEM analysis was important in observing the microstructure present to determine the immiscible morphology generated by the extrusion process.

DISCUSSION

Poly[trimethylene terephthalate] and polyamide_{6,10} are well suited as immiscible blend components. The polymers have complimentary properties that together provide a superior engineering polymer property profile. Furthermore, the polymers have similar melting points (PTT heat = 225 °C; PA_{6,10} heat = 218 °C) and their molecular structures and solubility parameters suggest that the immiscible polymer interfaces will be partially bonded by secondary chemical bonds.

In this preliminary study of this novel system, three compositions were processed and the extruder operation was adjusted empirically to produce good extrudates. In future work, rigorous rheological characterization will guide composition and processing parameters as a region of co-continuity is sought. Nonetheless, the three compositions prepared in this study processed well and the morphology of the three blends shows promising immiscible behavior as illustrated in the electron micrographs. The 20/80 and 80/20 blend compositions (Figures 3 & 4) illustrated strong dispersed domain behavior, as expected since the thermal properties of the components are not extremely different. The domain size of the dispersed phase is approximately one micrometer, indicating a good level of dispersion under the processing conditions used. The cold fracture image reveals hemispherical depressions and full dispersed spheres on the surface, showing that the interphase boundary is only weakly bonded. The 50/50 blend (Figure 5) shows a somewhat oriented structure with columnar, fibrous, fine domains of PA_{6,10} in a PTT matrix. The size of these columnar elements varies in the range of approximately 2 – 5 microns, consistent with typical processing morphologies of immiscible polymer blends. Although this is not a co-continuous structure, our experience with systems of this type

suggests that columnar structures such as that shown in (Figure 4) are often close, typically within 10 percentage points, of the co-continuous composition.

In examination of the 50/50 blend cold fracture surface, the columnar fibers show some evidence of ductility and are clearly the polyamide phase, whereas the matrix is universally a brittle fracture surface. Since the appearance of a columnar semi-dispersed phase precedes the appearance of the co-continuous regions, the PA6,10 volume fraction is below that needed to form co-continuity. Thus, according to this reasoning, the co-continuous region will be found at compositions greater than 50% PA6,10. More quantitatively, application of the Jordhamo relationship (equation 1) to available viscosity data ($T=260\text{ }^{\circ}\text{C}$, $\gamma(\text{s}^{-1})=100$; $\eta=565\text{ Pa}\cdot\text{s}$ for PTT and $900\text{ Pa}\cdot\text{s}$ for PA6,10)^[5] suggests the co-continuous region will be near 60% PA6,10. Both PTT and PA6,10 are thought to have viscosities that sharply decrease with temperature under these processing conditions and future efforts in rheological characterization will more fully elucidate this behavior and determine the quantitative applicability of the Jordhamo relationship to this system.

SUMMARY AND CONCLUSIONS

Poly[trimethylene terephthalate] and polyamide6,10 were thermally co-processed in a single screw extruder to form micrometer scale immiscible blends. Dispersed blends were observed near each endpoint in this binary system and a columnar-type blend was observed at the 50/50 volume fraction composition, suggesting that co-continuous blend structures of $2 - 5\text{ }\mu\text{m}$ domain size are achievable near this composition. The ability to process these polymers together is significant since blends of these polymers appear compatible based on solubility parameter and the electronegativity of nitrogen and oxygen atoms in the backbone and pendant groups of each polymer. Most importantly,

blends in this system offer the opportunity for highly renewable materials via bio-based fractions approaching 50% and the potential for maintaining or improving the mechanical properties of the blend over that of the component polymers.

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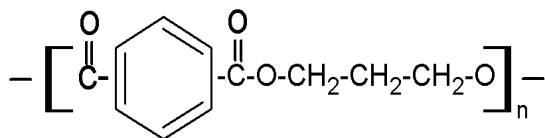
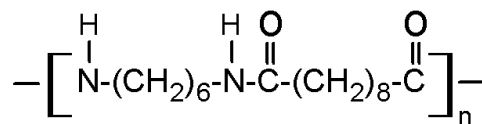
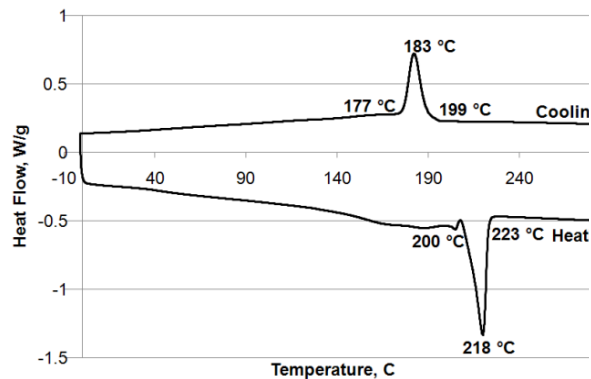
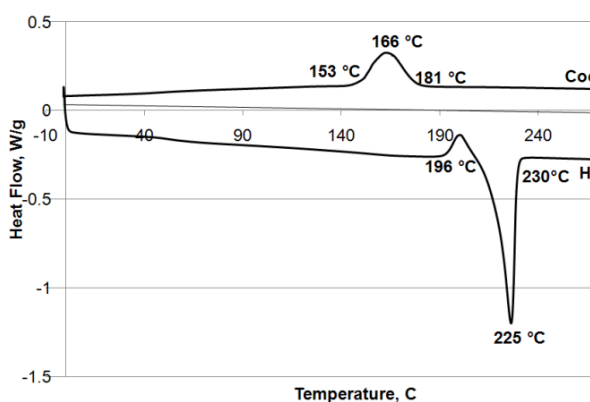
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Table 1. Materials selection

Material	Product	Supplier	Density (g/cm ³)
Poly[trimethylene terephthalate]	Sorona® 3001	DuPont	1.33
Polyamide6,10	ZYTRSLC3090	DuPont	1.08

Table 2. Formulations used in extrusion.

Extruded Blends			
Percent by Volume (<i>Weight</i>)			Extruded Thermal Profile (°C)
Blend	PTT	Polyamide6,10	Solids/Trans/Metering/Die
1	20(23.5)	80(76.6)	215/230/250/245
2	50(55.2)	50(44.8)	230/250/255/235
3	80(83.1)	20(16.9)	200/230/250/245

**Figure 1a.** The structure of PTT**Figure 1b.** The structure of polyamide6,10.**Figure 2a and 2b.** DSC traces of PTT and polyamide6,10 respectively.

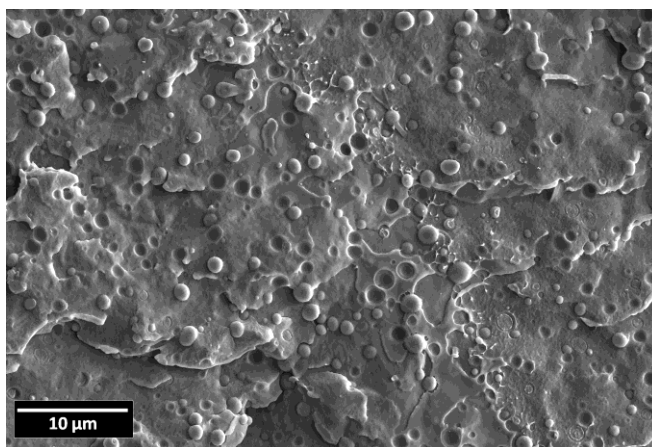


Figure 3. FESEM image of single extruded 80% polyamide6,10 and 20% poly[trimethylene terephthalate] blend (by volume).

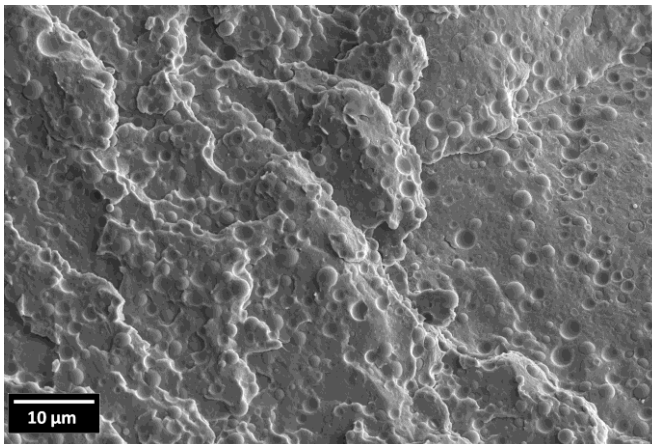


Figure 4. FESEM image of single extruded 20% polyamide6,10 and 80% poly[trimethylene terephthalate] blend (by volume).

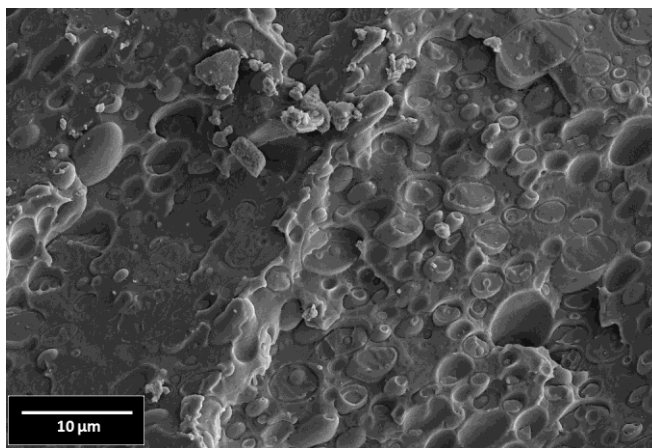


Figure 5. FESEM image of single extruded 50% polyamide6,10 and 50% poly[trimethylene terephthalate] blend (by volume).

Appendix V – Part A

"Phase inversion composition and domain identification by energy dispersive spectroscopy in immiscible blends of poly(trimethylene terephthalate and polyamide6,10)."

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Phase Inversion Composition and Domain Identification by Energy Dispersive Spectroscopy in Immiscible Blends of Poly(trimethylene terephthalate) and Polyamide6,10

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ABSTRACT

Immiscible blends were prepared from polyamide6,10 and poly(trimethylene terephthalate) by extrusion with the goal of identifying the phase inversion composition and domain morphology. Broadly, we studied this system to develop new polymer blends with good engineering properties combined with a high bio-based fraction. Earlier work has demonstrated that the polymers are suitable for melt co-processing. In this work, we sought to bracket the phase inversion composition, to identify any elements of co-continuity, and to characterize the domain morphology by a traditional and a novel means. After extrusion of a full range of compositions, the morphologies in the 40 – 60 volume percent range appeared to coarsely bracket the phase inversion point and composition in this range were selected for detailed microscopic examination. High resolution energy dispersive spectroscopy (EDS) was used to differentiate these chemically similar polymers based on the nitrogen content of the polyamide. Results show elements of co-continuity appearing at the 50 volume percent composition. The EDS mapping techniques employed in this work were successful in sharply differentiating the domains of the two polymers.

INTRODUCTION

Immiscible polymer blends are an approach to producing novel materials without the time-consuming and costly process of synthesis [1]. Although the domains in these blends are not formally bonded to each other, some similarity in cohesive energy density is essential to promote a modest level of phase compatibility and to assist in load transfer

across the interfacial region [2]. While immiscible polymer blends lack ligands or other formal bonding between the phases, the most effectively processed blends with co-continuity possess a tightly interconnected structure known as mechanical grafting[3] that affords efficient load transfer as well as optimum mechanical properties. An immiscible blend processed under optimum extrusion conditions displays a predominantly co-continuous network of the constituents with only limited regions of dispersed phases [4]. Binary blends of immiscible polymers exhibit a range of morphologies, such as fibrillar, lamellar, droplet in matrix and co-continuous, depending on the viscosity and interfacial surface tension of the neat polymers. Additionally, the temperature and the shear rate of the processing environment and the volume fraction of the polymers are important extrinsic variables. Although various empirical models exist to predict regions of various morphologies, experimental testing is required to conclusively determine the types of morphologies and the compositions at which they are formed[5]. Conventional extrusion is a common way to process immiscible blends of thermoplastic polymers [6]. In either single or double screw extrusion machinery, pelletized precursors are melted and blended to produce a homogeneous two-phase morphology near the phase inversion composition with major phase domains on the micrometer scale. Excessive temperature and shear conditions must be avoided to minimize thermal degradation, particularly in sensitive polymers such as those commonly used in biomedical, pharmaceutical, and cosmetic applications [2].

Bio-based materials are a new and promising area of research. Sustainable materials provide the ability to use renewable feedstocks in lieu of petroleum [7]. In our laboratory, we have previously shown that the bio-based content of poly(trimethylene

terephthalate) (PTT) can be increased by introducing various quantities of polyamide6,10 (PA6,10) to form immiscible blends [8]. Although that initial work was simply aimed at showing that the two polymers have thermal and cohesive energy density properties that enable them to be co-processed, our broader vision is to develop blends of these two polymers that generate high levels of bio-based components while simultaneously maintaining or improving the engineering properties and processing parameters [8].

In this work, we have formulated binary blends of PA6,10 and PTT over the full compositional range with the goal of locating the approximate phase inversion point, assessing the degree of co-continuity in this region, and differentiating the domains of the component polymers by EDS.

METHODOLOGY

PTT is a comparatively new member of the thermoplastic polyester family and is closely related to polyethylene terephthalate (PET). Properties and applications of PTT and PET are similar, although PTT has several defining properties that set it apart from other polyesters and make it useful in a wide range of applications. PTT has complete elastic recover even after applied strains of up to 20% [7] and the polymer has excellent weathering and stain resistance, ideal traits for applications in fabric and apparel. The ease of processing PTT and its recyclability differentiate this polymer from many of its thermoplastic polyester predecessors [7]. From a green engineering perspective the most impressive attribute of PTT is its partial renewable content derived from the corn sugar sourced diol used in its synthesis [9]. The renewable fraction of this polymer is 36% [8]. The family of polyamide polymers is known for their good engineering properties such as superior toughness, strength and abrasion resistance [10]. One member of this family,

PA6,10, is an attractive material to blend with PTT to generate a highly bio-based blend since the bio-based fraction of PA6,10 is approximately 60% by weight [8]. In the bio-based synthesis of PA6,10, sebacic acid derived from the castor seed is reacted with other petroleum-based components to generate the polyamide PA6,10 [11]. The chemical structures for PTT and PA6,10 are shown in Figure 1(a) and (b) respectively.

To form a two-phase immiscible blend rather than a single phase alloy by melt extrusion, the components must have a certain cohesive energy density difference so that a two phase system develops and the melt temperatures must be within a suitable range. Solubility parameter calculations using the Hoy contribution method [12] and the known melt temperatures of each suggested that PTT and PA6,10 will produce a binary blend during melt processing. In earlier work aimed at establishing the feasibility of melt processing these two materials, the phase inversion point appeared to be near the 50% composition, although only a limited number of compositions were examined [8].

Various phase morphologies occur in immiscible systems depending on the composition of the blend and the processing conditions. Although the advantages of the co-continuous morphology have been demonstrated for structural performance, permeability, and thermal conductivity, several instance of improved properties, such as impact resistance and improved tensile properties of fibrillar morphologies, in the dispersed (droplet in matrix) regime have been confirmed [5]. Finding the phase inversion composition, which identifies the region of co-continuity, can be a difficult process and there are on-going efforts aimed at developing new techniques to ascertain where this phenomena occurs [5]. One useful mathematical tool for identifying the phase inversion point that is based on rheology data and does not require preparation of the

actual blends is the Jordhamo relationship. This relationship states that co-continuity exists where the ratio of the volume fraction of the two polymers is equal to the ratio of the viscosities of the polymers at a predetermined temperature and shear rate [4]. As with most non-experimental methods, the Jordhamo equation is only approximate and it depends on the validity and accuracy of the rheology data. Besides the Jordhamo relationship, other methods for predicting the region of co-continuity have been proposed such as one by Metelkin and Blekht which is based on a filament instability concept to determine the critical volume fraction where phase inversion occurs.[13]

Experimentally, the most common approach to resolving phase structure in immiscible blends is to use solvent extraction to etch or even fully dissolve one phase such that the structure is easily imaged by scanning electron microscopy (SEM). Two problems with this approach are that suitable solvents are difficult to find, particularly for advanced engineering blend systems such as the one studied in this work, and the etching process changes the structure so that subtle features may be lost. Furthermore, without the proper preparation, polymers can be difficult to image due to their low density, low atomic number, and dielectric character. Coatings of various metals or carbon can alleviate this problem.

Our preferred method for precise phase identification was to use SEM on cold-fractured, unetched specimens that were only thinly coated (7 nm Au) to assure good imaging without obscuring important features. SEM is advantageous for analyzing the morphology of the blend and in identifying features of co-continuity, but the similarity in the density and chemical composition of the polymers causes difficulty in determining the identity of specific domains. Earlier work in our laboratory demonstrated the

feasibility of differentiating domains based on very subtle chemical differences employing energy dispersive spectroscopy (EDS). Poly(methyl methacrylate) (PMMA) and high density polyethylene (HDPE) have been differentiated based on the ester and carbonyl oxygen present in PMMA compared to HDPE [2]. In the PA6,10/PTT system, the two polymers have differing oxygen concentrations and this presents an option for a similar EDS analysis. However, the relatively minor oxygen concentration difference ($\Delta=19.7$ wt.%) meant that signal to noise ratios would not be good and sharp differentiation of domains would be impractical. The small amount of nitrogen (10.2 wt.%) in PA6,10 nevertheless offered a more promising approach. Although the intensity of the nitrogen signal is low, as shown in Figure 2, the absence of nitrogen in PTT allows for greatly improved signal/noise and was the basis for this segment of the experimental approach.

Once a quality planar SEM image of blend has been obtained, the volume fraction of the phases is readily achieved from the area fraction calculated by image analysis. Indeed, the phase inversion point can be determined with reasonable accuracy from these two-dimensional images. However, the question of co-continuity is a more difficult issue and the two-dimensional surface offers only hints, such as the appearance of intertwined channels, filamentary segments, and branch points. Ultimately, to conclusively identify co-continuity, the selective remove of each phase by suitable solvents followed by image analysis of the remaining structure is needed. Such studies were beyond the scope of the present work.

EXPERIMENTAL

Materials Selection

Materials were selected based on their potential to produce an immiscible blend with good engineering properties and high bio-based content. Both PTT and PA6,10 are semicrystalline polymers with good properties and densities of 1.33g/cm³ and 1.08g/cm³ respectively. The neat materials used were in pellet form. Physical appearance of the pellets contrast in that the PTT pellets are opaque and the PA6,10 pellets are translucent. Table 1 contains a list of the materials and suppliers. The melting points of PTT and PA6,10 from the DSC heating curve are similar, 228 °C and 218 °C respectively, suggesting that these polymers can be successfully melt processed together at reasonable temperatures [8]. Polyamides are unique in that they have a high power law viscosity index, i.e. are less shear thinning, than many polymers while at the same time their consistencies (power law coefficient) are highly temperature dependent. PTT suffers from a short thermoplastic range but possesses a more ideal melt processing range of (232 – 260 °C) than PA6,10 (230-330 °C). A mix of these two opposing behaviors may result in a blend with improved melt rheology and processing conditions.

Formulation and Blending

In preliminary work, immiscible blends of PTT and PA6,10 were formulated and extruded at critical bounding and intermediate compositions to determine that this system of materials can be successfully processed [8]. In this work, a complete line series of compositions were formulated. In all blends, we examined the morphology present, degree of dispersion and the size of the domains, but our principal interest was on finding the phase inversion composition and characterizing the morphology of the blends near this composition. Table 2 lists the batch formulations of all the blends.

PTT and PA6,10 were dried under vacuum at 120 °C and 80 °C respectively for 12 hours. The blends were weighed and mixed manually until a visually uniform mixture was obtained. Blends were stored in air tight glass jars at a temperature of 80 °C prior to extrusion.

Extrusion

Blend compositions were melt processed via extrusion using a Brabender Intellitorque single screw extruder with an L:D of 30:1 operated at 100 RPM with a rod extrusion die and a 1/8 inch orifice insert. The temperature of each extruder processing zone was controlled according to a present program summarized in Table 2. These temperature profiles had considerable differences depending on the composition of the blend and the profile was adjusted empirically online to ensure successful processing. Two critical features of the extruder operation was the maintenance of low temperatures where the pellets were fed and relatively low temperatures in the transition zone to maintain a sufficient level of wall friction. Lastly, the die exit temperature was closely controlled to ensure specimens of good quality as indicated by surface finish and the avoidance of melt-fracture.

Image Analysis

Solvent etching was used as the traditional approach for discriminating phases in this binary system. Cryo-fractured specimens were etched with dimethyl formamide (DMF) in combination with ultrasonic agitation. Etch times were 5 and 10 minutes with ultrasonic agitation applied for only 20 seconds of each minute. After removal from the DMF, specimens were washed in ethanol and dried, then mounted and coated with 7 nm Au to minimize charging effects. All compositions were analyzed using a Zeiss Sigma

FESEM. Images were collected at an accelerating voltage of 5 kV and an approximate working distance of 10 mm.

SEM was the first crucial step in narrowing the range of compositions where phase inversion exists by evaluating morphologies and domain sizes. EDS was then used to definitively discriminate between phases through the mapping of nitrogen. The EDS system used was the Oxford INCA PentaFET x3. Maps were acquired with an accelerating voltage of 3kV, high current and an increased aperture size to the standard 30 μ m.

EDS of polymers such as PTT and PA_{6,10} is particularly difficult, especially when evaluating phase separation in the submicron regime. The high dielectric constants of polymers make them prone to charging. The high beam currents required to obtain reasonable x-ray counts exacerbate the charging problem and may contribute to specimen beam damage. Further, considering the approximately inverse relationship between electron range and atomic number, the low atomic number elements in these polymers (as well as their low density) cause large interaction volumes at the required high beam energies. Through experimentation, we were able to develop unusually good EDS signal and resolution by acquiring x-y element maps at low beam energy (3kV) and high current. This technique produced excellent signal/noise and good resolution such that we were able to sharply discriminate between the PTT and PA_{6,10} phases by mapping the K α line (0.392kV) of nitrogen. The x-ray signal processing times were set to the maximum values permitted by the device software (Oxford INCA) in order to minimize noise and improve the x-ray peak resolution. This approach is particularly important in the present polymer system since strong K α signals were present from neighboring elements, carbon

and oxygen. Additionally, extended scan times and drift correction were employed to positively identify the nitrogen at submicron resolution.

DISCUSSION

All compositions processed (Table 2.), except the neat end members, have homogeneous two-phase morphologies of various types with micrometer scale domains. Based on a limited prior study of this PTT/PA6,10 system, the phase inversion composition was estimated to occur near the 50% composition or greater. Blends processed in this study show that compositions near the end members are highly dispersed droplet-in-matrix type morphologies, as expected, and were not further characterized.

At the 50% composition an interesting morphology is formed as shown in Figure 3. The morphology is shown at two magnifications and with the aid of two DMF etching levels. The view is parallel to the extrusion axis. In this work the etching was conducted to improve SEM imaging of the planar surface and no attempt was made to selectively remove entire phases for the assessment of co-continuity. A fine well mixed morphology is evident with primary domain sizes averaging 2-3 micrometers. The PTT can be identified by the textured etching of the surfaces, whereas PA6,10 is unaffected by DMF. The domain interfaces are in excellent contact as is evident even after five minutes of etching, suggesting the potential for moderately good load transfer in these blends through interfacial shear strength alone. After a 10 minute etch some of the domain interfaces are partially opened, better revealing the domain boundaries and the overall morphology. Although some remnants of dispersed phase morphology were observed, i.e. isolated spherical domains in a matrix, this blend is more characterized by oriented

columnar primary domains (parallel to the extrusion axis) that have more elongated cross sections than in neighboring compositions and which exhibit some evidence of branching. Most interestingly and most indicative of possible approaching co-continuity is the appearance of secondary domains (upper left and lower right of Fig. 3 (b)) in which phases occur within phases (A within B within A, etc.). In future work directed exclusively at assessing the co-continuity of these blends, we will seek solvents that enable complete removal of individual phases such that the detailed structure of the remaining phase can be characterized.

Although SEM analysis of etched specimens is a powerful tool in imaging these composites, we sought a different approach to differentiating the domain compositions in the intricate blends that surround the phase inversion composition. EDS is not new, of course, but its application at high resolution to chemically similar polymers is a challenge and a new approach to domain identification in immiscible polymer blends. As described in the method section, we used nitrogen as the differentiating chemical tag between PTT and PA6,10 to collect EDS maps, which were then collected for several blend compositions. The unetched 40% PTT composite (Figure. 4) is shown as-is and with a nitrogen elemental map overlaid. The value of the unetched specimen is clear in that the domain interfaces are revealed in their partially bonded natural state, a feature that can hinder domain identification but which allows better assessment of the physical character of the composite. Relying on the EDS map for phase identification, the polyamide is clearly identified as the surrounding matrix phase. EDS resolution, optimized for this study as described in the experimental section, is still much lower than the SEM resolution and for this system 0.5 to 1.0 μm is the best EDS resolution that could be

achieved. Thus, very small domains are not resolved well, subsurface domains can confuse analysis since signal is generated from a volume and not just the surface, and even though signal/noise ratios are good some false mapping elements will result. Nonetheless, we have shown that EDS mapping is a viable approach to domain identification in immiscible polymer blends, even when the signaling element has a low atomic number and is present in concentrations as low as 10 weight percent.

EDS was also applied to the 60% and 50% PTT compositions (Figures 5 & 6). At 60% PTT the morphology is inverted and much more dispersed than at 40% PTT, as evidenced by the spherical droplets in matrix structure. The value of the unetched approach is apparent here. The interfaces between the phases are not well bonded and in fact the separation of the phases that occurred during cooling from the melt is apparent in gaps between the spheres and the matrix and also by small strands of polymer stretching between the interfacial gaps. Clearly, the spheres contracted more during cooling than the matrix, and good load transfer between these phases will not occur. In Figure 5(b), the EDS mapping shows the phases clearly, the droplets are polyamide and the matrix is PTT. This image is a good example of the EDS resolution accuracy and precision. Very few false signals exist. The bleed-over from the spheres into the matrix is a result of the binning process of the x-ray signal and the resolution of the pixels. The occasional yellow spots on the matrix may be errors or they may reflect subsurface polyamide.

The 50% blend is revisited in Figure 6 with the no-etch SEM image and the EDS mapping. Domain identification is clear and the developing co-continuity features are more evident and in a more natural state than in the etched specimens of Figure 3. Many of the domains on the EDS map were outlined in black to assist the eye, and two domains

in a phase-within-a-phase region are marked with an “X” to clearly distinguish the unusual morphology.

Overall, the unetched specimens and the EDS maps show that phase inversion occurs as PTT is increased from 40% to 60%. Phase inversion with possible co-continuity is most closely linked to the 50% composition although additional study is needed around this composition to more accurately assess the nature of these blends. The commencement of co-continuous blends is identified in the 50% blend from a variety of features such as domain elongation, branching, and the appearance of the “phase-within-a-phase” morphology shown in Figure 6. The presence of the phase inversion composition close to 50% is somewhat unexpected considering the Jordhamo relationship suggests, based on known viscosities and melt processing ranges, phase inversion at higher levels of PA6,10. [7] Future effort will focus on fine-tuning the composition scan and collecting capillary rheometry data to provide correlation between the domain morphologies and the viscosities of the components at the exact processing temperature of the blends.

CONCLUSION

A line series of compositions comprised of PTT and PA6,10 were extrusion processed. SEM imaging confirmed that these materials produce a range of homogeneous morphologies with major phase domains on the 1-6 μm scale. We sought to locate the phase inversion point with an ultimate goal of finding the region of co-continuity. SEM was used to point towards this region through morphological analysis. The polymer identity of individual domains was confirmed by high resolution EDS to map the nitrogen found exclusively in the polyamide. Phase inversion occurs as PTT is

increased from 40% to 60%. Some indications of co-continuity, e.g. an unusual A-B-A domain pattern, were observed in the 50% blends, suggesting from experience that true co-continuity occurs within less than five volume percent of this composition.

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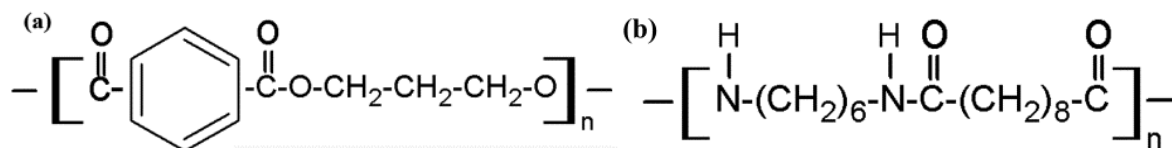


Figure 1. (a) The structure of PTT and (b) of PA_{6,10}.

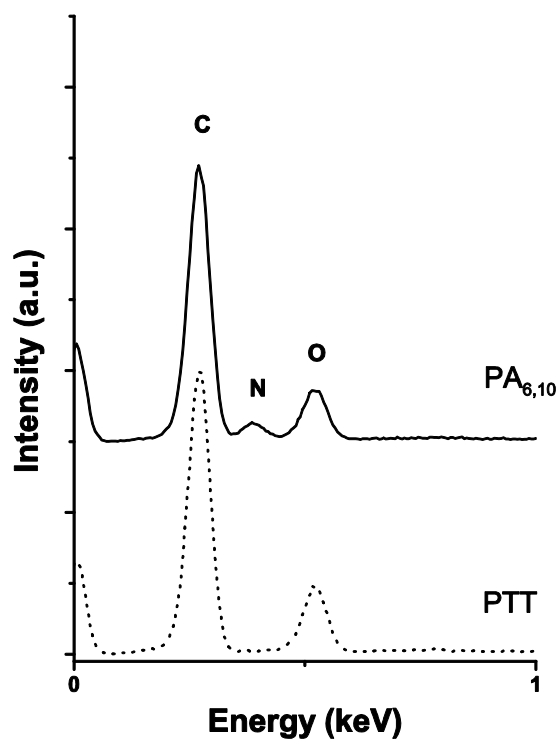


Figure 2. EDS Energy Spectra for PTT and PA_{6,10}.

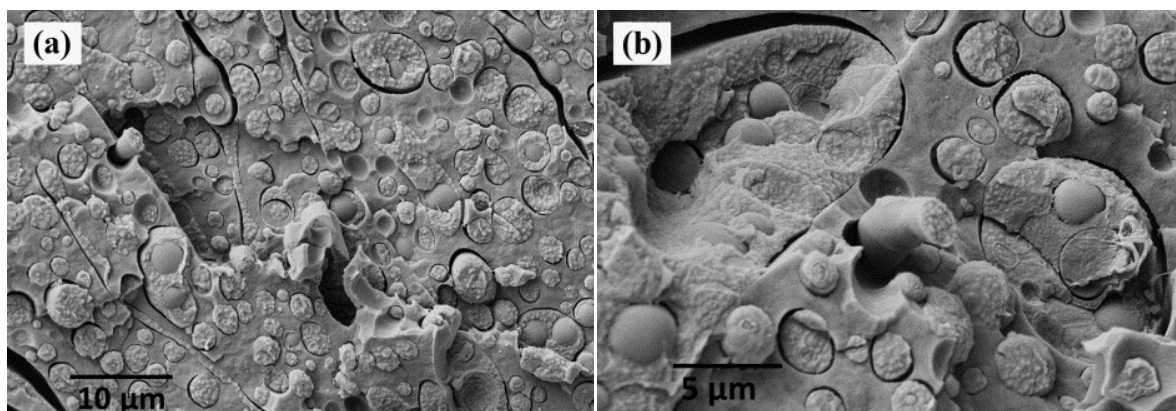


Figure 3. Etched surface of 50% blend illustrating domain interfaces and structure approaching co-continuity. Etched with dimethyl formamide with ultrasonic agitation, (a) 5 min. (b) 10 min.

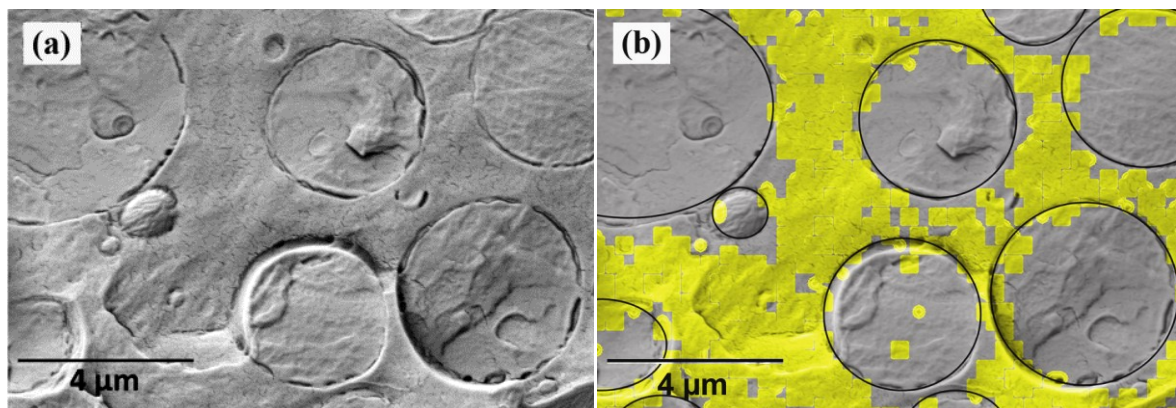


Figure 4. (a) SEM image of 40% PTT Blend and (b) Nitrogen EDS map overlaid on the image.

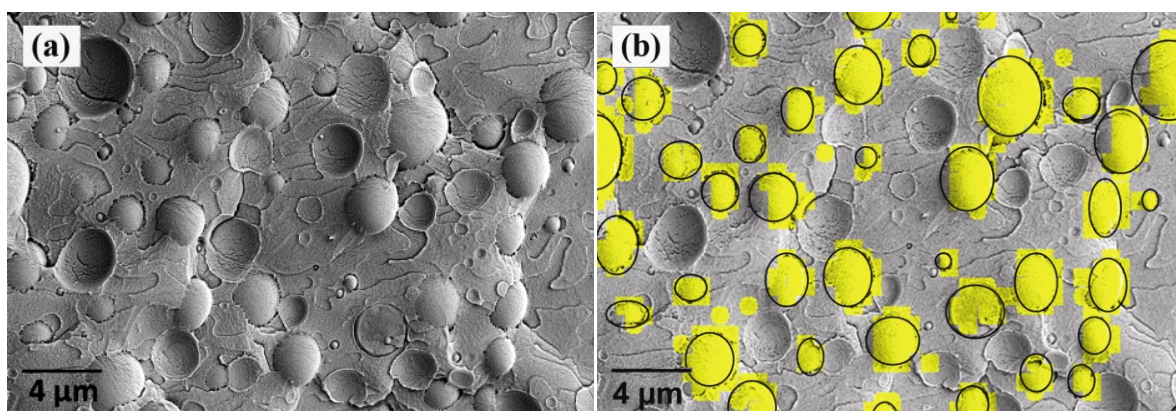


Figure 5. (a) SEM image of the 60% PTT Blend (b) Nitrogen EDS map overlaid on the image

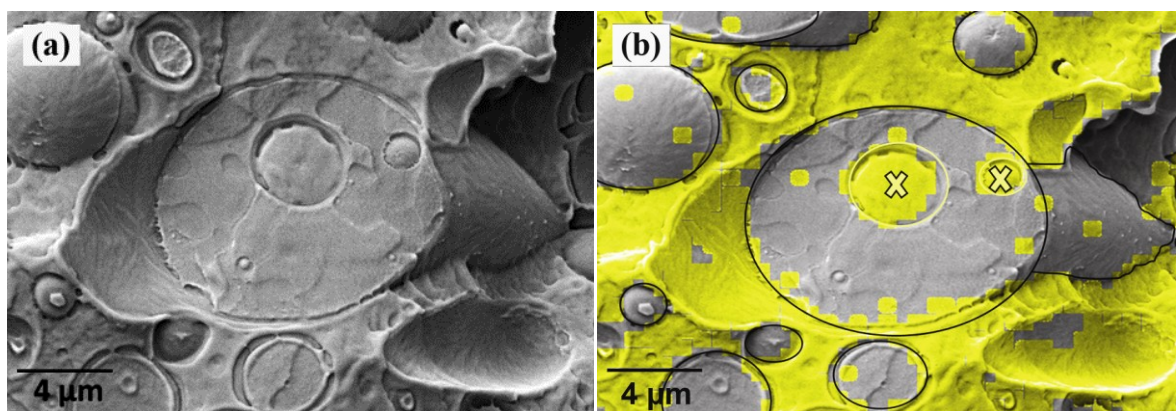


Figure 6. (a) SEM image of the 50% Blend (b) Nitrogen EDS map overlaid on the image.

Appendix V – Part B

"Uniquely identifying polymer composite domains using energy-dispersive spectroscopy "

G. Giancola and R.L. Lehman

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Society of Plastics Engineers Online



Uniquely identifying polymer composite domains using energy-dispersive spectroscopy

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ABSTRACT

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A new approach has been employed to identify the phase inversion composition of a bio-based immiscible polymer blend by discriminating between the domains of the constituents which have chemically similar structures.

Sustainable materials are widely popular due to decreasing reliance on costly petroleum and the desire to focus efforts toward recycling and limiting energy usage. To generate a highly bio-based polymer composite, renewable feedstock [1,2&3] derived poly(trimethylene terephthalate (PTT) and polyamide6,10 (PA6,10) are immiscibly blended. Immiscible polymer blends (IMPBs) are an advantageous approach to generating novel materials while bypassing the synthesis stage [4]. Forming a successful blend includes the difficult process of finding the phase inversion region [5] in order to pinpoint the co-continuous composition. Co-continuity exhibits an interconnected morphology called mechanical grafting [6] although the domains of the blends are not formally bonded. Co-continuity affords the composite efficient load transfer across the interfacial regions [7], optimum mechanical properties and rule of mixture values. The phase structure of an IMPB is commonly resolved using scanning electron microscopy

(SEM) to visually assess the morphology or by using solvent extraction to dissolve phases for analysis.

Efforts are aimed at developing new techniques to identify co-continuity since the existing experimental techniques [5] of SEM analysis and solvent extraction raise issues. SEM is advantageous in analyzing morphological features typical of co-continuity however the similarity in the density and chemical composition of the PTT/PA6,10 system proves difficult to accurately discriminating the domains. Suitable solvents are often hard to find particularly for advanced engineering systems. Also, etching disrupts the naturally occurring structure and inhibits the preservation of subtle features. Furthermore, polymers are often difficult to image due to their low density and dielectric character without the proper preparation. To circumvent these difficulties our preferred method for precise phase identification is energy dispersive spectroscopy (EDS) to differentiate the polymeric domains based on very subtle chemical differences [7].

Formulated blend compositions are melt processed using a Brabender Intellitorque single screw extruder at the critical bounding and intermediate compositions to determine successful process of this system into micron scaled domain IMPBs. Temperature profiles for the melt processing are set according to a pre-determined program and adjusted online to ensure successful composites (table 1). The unetched specimens are cold fractured, mounted and coated with a 7nm layer of gold to minimize charging effects. A Zeiss Sigma Field Emission Scanning Electron Microscope (FESEM) is used to narrow down the range of compositions where phase inversion is most likely to occur based on morphological changes in the structure. Using an Oxford

INCA PentaFET x3 EDS system the domains of the polymers are identified by mapping an element which can be attributed to one of the phases.

In the PTT/PA6,10 system, the polymers have differing oxygen concentrations that are relatively minor ($\Delta = 19.7$ wt%) proving difficult to distinguish the difference in domains based solely on this factor. PA6,10 is unique in that it contains a (10.2 wt%) of nitrogen. The intensity of the nitrogen is notably low however PTT is void of this element affording us with a greatly improved signal/noise ratio for the EDS work (figure 1). EDS analysis of polymers are especially difficult due to high dielectric constant of the polymers making them prone to charging with this problem further exacerbated by the high beam current needed to obtain X-Ray counts. Furthermore, the low atomic number elements contained in these polymers cause large interaction volumes at the required high beam energies. Using low beam energy, high current, extended scan times, drift correction and an increased aperture size we were able to discriminate between the PTT/PA6,10 domains by mapping the $K\alpha$ line (0.392 kV) of nitrogen a particularly remarkable feat considering strong $K\alpha$ signals are present from neighboring elements.

Phase inversion occurs as PTT is increased from 40 to 60% and is closely linked to the 50% composition due to observed morphological features such as domain elongation and branching formed contrasting the droplet-in-matrix morphology present at 40PTT or 60PTT. EDS revealed a phase-within-a-phase structure at the 50PTT composition (figure 2a&b) as well, a strong indicative feature of approaching co-continuity.

These results are important to further elucidate the important co-continuous region in the PTT/PA6,10 system by determining the location to be within 10 percentage

points of the 50PTT composition. Revealing this region is often an arduous task when using time consuming approaches such as solvent extraction.

This research is valuable in generating a successful bio-based IMPB of PTT/PA6,10.. The region of co-continuity has been limited to a span of 10 percentage points of the 50PTT composition paving the way to making a highly functional material by working in this optimum region. Furthermore, a new EDS technique has been employed to discriminate between polymer domains based on subtle chemical difference thus offering an alternate approach to the not always desirable existing techniques such as solvent extraction. It would be beneficial to melt processed specimens with compositions differing in one percentage point across the 40PTT-60PTT region and use EDS to determine and exact co-continuous composition.

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Blend Compositions and Processing Profiles			
Percent by Volume (<i>Weight</i>)			Extruder Thermal Profile (°C)
Blend	PTT Sorona® 3001	Polyamide6,10 ZYTRSLC3090	Solids/Trans/Metering/Die
1	0(0)	100(100)	230/245/260/275
2	10(12.0)	90(88.0)	215/235/245/250
3	20(23.5)	80(76.5)	215/230/250/245
4	30(34.5)	70(65.5)	215/245/250/260
5	40(45.1)	60(54.9)	230/245/250/260
6	50(55.2)	50(44.8)	230/250/255/235
7	60(64.9)	40(35.1)	230/250/250/245
8	70(74.2)	30(25.8)	180/230/250/245
9	80(83.1)	20(16.9)	200/230/250/245
10	90(91.7)	10(8.3)	215/245/250/260
11	100(100)	0(0)	235/250/265/280

Table 1. Blend compositions and processing profiles.

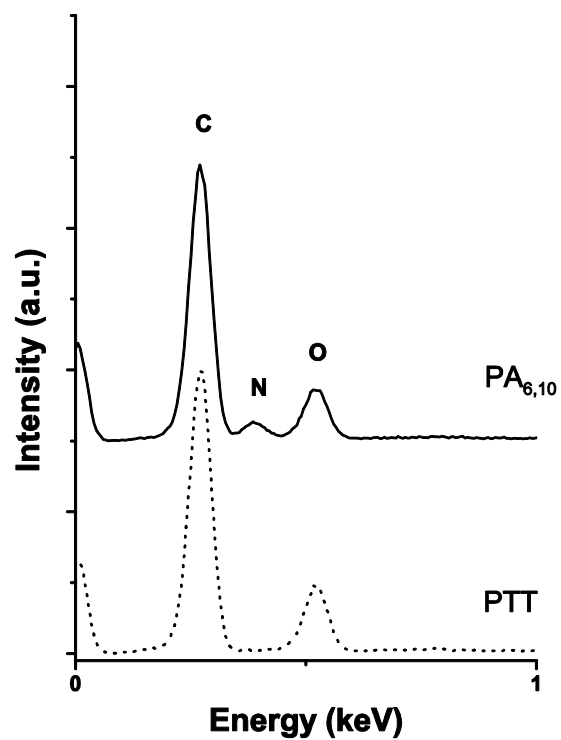


Figure 1. EDS Energy Spectra for PTT and PA_{6,10}.

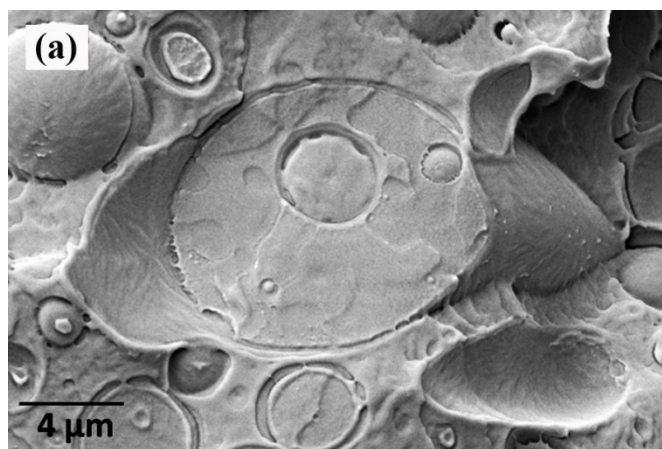


Figure 2. (a) SEM image of the 50% Blend

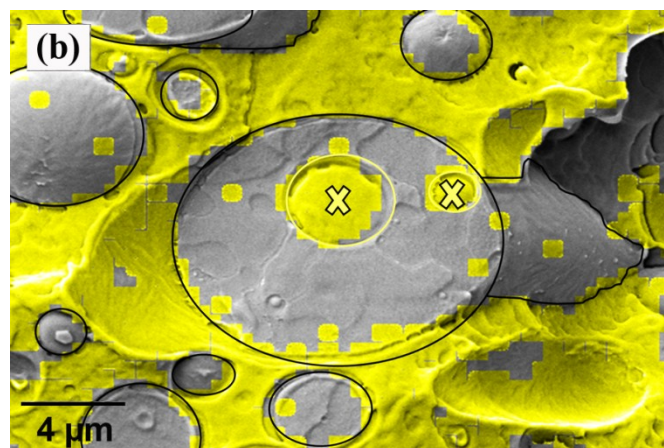


Figure 2. (b) Nitrogen EDS map overlaid on the image.

Appendix VI

**"Viscosity and domain morphology in binary immiscible blends of
poly(trimethylene terephthalate) and polyamide 6,10."**

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Viscosity and domain morphology in binary immiscible blends of poly(trimethylene terephthalate) and polyamide6,10

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ABSTRACT

Poly(trimethylene terephthalate) and polyamide6,10 are polymers with significant bio-based content that form an immiscible blend system of high-value engineering materials with enhanced sustainability for use in an array of applications in transportation, electronics, and industry. Knowledge of the melt viscosity of these thermoplastic materials is critical when processing blends to achieve optimum morphologies. We measured the viscosities of five extruded blends near the phase inversion composition over a range of shear rates using both parallel plate and capillary methods. Based on the viscosities of the end-members, Jordhamo co-continuity should be observed in the 21 – 44 volume percent PTT range, depending on the processing shear rate. Extruded blend viscosities were lower than the linear rule of mixtures, but a modest viscosity peak and a shift in the power law index signaled the phase inversion composition near 55 volume percent PTT. SEM images showed clear indications of phase inversion and co-continuity in the 55% PTT FESEM image. We conclude that the viscosities of immiscible polymer blends in this system do not follow the rule of mixtures due to slip between immiscible domain interfaces, but that the viscosity and the power law index are useful in locating the phase inversion composition. The empirical Jordhamo relationship, although generally useful in immiscible polymer systems, is not as valuable in this system and underestimates the phase inversion point by nearly a factor of two. These results are a critical part of the processing science needed to melt and fabricate commercial products from these blends.

INTRODUCTION

In recent years the polymer industry has sought to develop polymers and blends that reduce the use of non-renewable feedstocks, such as those derived from crude oil, and to use in their place renewable feedstocks, such as those obtained from plant sources [1]. Some initial successes in this direction have been the synthesis of partially bio-based polymers in which significant segments of the molecule are derived from products such as corn and the castor bean [2,3]. In addition to direct synthesis of bio-based polymers, there are several motivations for the blending of bio-based polymers. Not all polymers can be re-engineered to contain significant renewable feedstock content. Therefore materials with increased bio-based fractions may often be obtained by the blending of a second higher bio-based content polymer to the initial polymer of interest.

Most polymer pairs are immiscible, thus precluding alloy blending and directing development towards the growing field of immiscible polymer blending, which has been shown to enable certain polymer pairs to be prepared with excellent mechanical properties [4,5]. Immiscible polymer blending is an attractive and inexpensive alternative to new polymer synthesis for the development of new materials with specific engineered properties. Since the polymer components in immiscible polymer blends occur in separate domains and lack chemical bonding [6], the properties of such blends are normally additive functions of the compositions in the region of co-continuity. This region is characterized by an interconnected morphology, a high degree of interfacial surface area, and strong interconnectivity and domain/domain clamping -- a phenomenon known as mechanical grafting that enhances load transfer and improves mechanical properties [6,7, & 8]. Knowledge of the viscosities of the blend components is essential

in locating the co-continuous composition in a binary blend. Generally, the phase inversion point will occur at compositions dominated by the more viscous component and tend towards 50/50 compositions when the viscosities of both components are equal. Although numerous empirical relationships exist that assist in locating the co-continuous compositions, one of the most commonly used is the Jordhamo relationship [9,10].

We sought to demonstrate that binary immiscible blends of poly(trimethylene terephthalate) (PTT) and polyamide6,10 (PA6,10) could be melt processed together to form a blend with the highly interconnected domains that are characteristic of blends with mechanically superior properties useful for a variety of industrial applications. In this study we focused on measuring the viscosity over a wide shear rate range, and we assessed the morphology of these blends by image analysis of scanning electron microscope (SEM) micrographs. Our goal was to describe how viscosity varies over the binary composition range and to judge the applicability of the power law viscosity relationship to this two-phase blend system. An additional aim was to assess the validity of an empirical rule for identifying the phase inversion composition, the Jordhamo relationship, in this system. Combined, the results of this work should contribute significantly to the growing base of processing science available to guide the development of new materials for industry, commerce, and the military.

METHODOLOGY

PTT is a comparatively new polymer that can be synthesized from bio-based precursors, such as sugar based diols, to possess a renewable fraction of approximately 36% [2]. PTT is a variant of the well-known polymer poly(ethylene terephthalate) (PET), although PTT exhibits superior properties such as stain resistance, ease of

recycling and processing as well as superior elastic recovery [1,2]. In an effort to increase bio-based content while maintaining an immiscible blend, PTT has been processed with PA6,10 to show the feasibility of producing immiscible blends near the phase inversion composition [11]. The bio-based fraction of PA6,10 is nearly 60% since the polymer is synthesized in part by using sebacic acid, a derivative of the castor seed [12]. The strength and abrasion resistance of PA6,10, among other superior engineering properties, make this material ideal as an immiscible blend component with PTT [13].

Binary immiscible blends are characterized by significant differences in the cohesive energy density of the components as measured by the solubility parameter. As a result, the interfacial surface energy is high and a two-phase morphology is maintained. PTT and PA6,10 possess these qualities by virtue of the varied dipole character of the polymer molecules and form immiscible blends throughout the binary composition range. When blending polymers that result in an immiscible system the morphology is of critical interest since it determines the mechanical properties in structural composites and is an enabling element of functional composites, such as in developing low resistance pathways in electrically conductive materials. Since morphology is closely linked to the rheological characteristics of the components, a full rheological work-up is necessary to identify the co-continuous region of the blend [14]. This region is particularly essential for blends that feature heat resistance and electrical or thermal conductivity [9]. Rheology measurements were made to evaluate the morphology of the PTT/PA6,10 compositions to target the region of co-continuity. Measurements were made on both the neat materials and the blend compositions after extrusion. Visually, through SEM analysis, the morphological differences were evaluated and compared to the predicted

behavior in which empirical relationships were used to pin point the phase inversion composition.

Rheological data were collected for the molten polymers and blends using two contrasting methods. Parallel plate rheometry is a common and reliable method for characterizing the viscosity of molten polymers and it has been used extensively in our laboratories. However, it is an off-line measurement and it does not mimic the shear environment of the extrusion process as faithfully as capillary rheometry [15]. Furthermore, the sample size is small (on the milligram scale) and the long residence time between the heated plates can lead to degradation of the polymer during the test and there is some tendency for the sample to flow out of the aperture at high temperatures over long test durations. We also used capillary rheometry, a well-established method for which several standard test methods exist, to measure the viscosity of the blends and to act as a cross-check for the parallel plate data. Two preferred features of the capillary method is that viscous flow in a capillary more closely mimics the nature of flow during extrusion and new material is constantly being measured in the capillary as opposed to the static sample nature of the parallel plate method. Although both methods fail to present a single-valued shear rate, the range of shear rates is low, particularly in capillary rheometry when small capillaries are used, and thus the error attributed to shear rate averaging is low [16,17]. In addition to providing a cross-check with the parallel plate data, the capillary rheometry enables measurements at higher shear rates ($>1000 \text{ s}^{-1}$) such as those found in commercial extrusion and injection molding processes.

In processing immiscible polymer blends, the phase inversion composition is often sought since co-continuous blends are usually found around this composition. Of

numerous empirical relationships that define the volume percent composition of the co-continuous region as a function of the viscosity of the components, the Jordhamo relationship (equation 1) is perhaps the best known [18].

$$\frac{\eta_A}{\eta_B} = \frac{\Phi_A}{\Phi_B} \quad [1]$$

The Jordhamo relationship applies to binary systems and states that the phase inversion composition is reached when the volume fraction ratio of the components equals the viscosity ratio of the components.

If the volume fraction ratio is less than the viscosity ratio, then discrete domains of phased A are dispersed in a matrix of phase B, whereas if the volume fraction ratio is greater than the viscosity ratio then domains of phase B are dispersed in a continuous matrix of phase A. The Jordhamo relationship is less accurate for certain polymer blends, particularly compatibilized blends, and the relationship has been used most successfully when viscosities are measured at low shear rates [14]. When high shear rates are used to measure the viscosity, the phase inversion composition is overestimated. [18]. Furthermore, additional inaccuracies of the Jordhamo relationship have been noted with rotational parallel plate rheometer data since the shear viscosity of the material dominates the values and other parameters of melt processing such as interfacial tension and the viscoelastic nature of the phases are largely ignored [14].

From our perspective is important to use viscosity values in the Jordhamo relationship that have been collected at the same processing temperature and shear rate as encountered in the extrusion or injection molding of the polymer. This is a problem since polymers are typically shear thinning, as represented by the well-known power law

relationship (equation 2), and thus viscosity varies through most melt processing equipment, giving rise to a distribution of phase inversion compositions.

$$\eta = m(T)\gamma^{(n-1)} \quad [2]$$

The power law model gives the viscosity of a melt as a function of the consistency(m), a highly temperature sensitive parameter, and the power law index(n), a measure of the shear thinning behavior of the polymer melt [16]. The explicit appearance of temperature and shear parameters in this relationship make it ideal for modeling the shear stress and viscosity behavior of polymers and polymer blends.

Morphological features of the blends at the micrometer scale were assessed via analysis of scanning electron microscope (SEM) images. In this work we limited our analysis to planar images of unetched, cold-fractured surfaces to define the approximate location of the phase inversion composition [19]. Naturally, we then correlated the blend morphologies to the viscosity data at appropriate temperatures and shear rate to assess the accuracy and applicability of the Jordhamo relationship.

EXPERIMENTAL

Materials Selection

PTT and PA6,10 were selected for the binary system under study based on their ability to produce an immiscible blend with high bio-based content and potentially excellent engineering properties. Pellets of these polymers were obtained from commercial sources and differential scanning calorimetry (DSC) analysis indicated melting points of 228 °C and 218 °C for PTT and PA6,10 respectively [11]. Both polymers are semi-crystalline materials. Physically the PA6,10 pellets are semi-

transparent whereas the PTT pellets are opaque with densities of 1.08g/cm^3 and 1.33g/cm^3 respectively. Although virtually all polymers are shear thinning, the polyamides are known to be exceptionally so. PTT was selected for blending partially under the premise that the blend would be less shear thinning and possess improved processing properties. Table 1 lists the materials used.

Formulation and Blending

In prior work we showed that the polyamide and thermoplastic polyester can be melt processed into an immiscible blend [11] with micrometer scale domains revealed via energy dispersive spectroscopy (EDS) and SEM image analysis [20]. The goal of that work was to locate the approximate phase inversion composition. The present work sought to refine the location of the phase inversion point and to conduct viscosity measurements in the region from 40% to 60% PTT by volume. The earlier work, which scanned the composition range at 10% increments, identified the phase inversion composition around 50% PTT. To improve the resolution of this determination, two intermediate compositions were added to the line series (blend 3 and 5) which reduced the composition increment to 5% by volume. Table 2 lists the selected batch formulas use in this work and the respective extruding temperature profiles.

Extrusion and Image Analysis

PTT and PA6,10 were vacuumed dried at $120\text{ }^{\circ}\text{C}$ and $80\text{ }^{\circ}\text{C}$ respectively in accordance with commercial recommendations for approximately 12 h. The materials were weighed, manually blended, and held in hermetically sealed glass jars at $80\text{ }^{\circ}\text{C}$ prior to melt processing. A Brabender Intellitorque 0.75" single screw extruder with an L:D of 30:1 was used to extrude the blends. The experimentally determined temperature profiles

for the four extruder heating zones are given in table 2. Close attention was paid to the temperatures at the conveying zone as well as at the die to ensure a steady feed of pellets to the die and to avoid problems with excessive fluidity in the die land resulting from the highly shear thinning nature of the polyamide.

Extruded samples were cryo-fractured in preparation for analysis using the Zeiss Sigma field emission scanning electron microscope (FESEM). Specimens were mounted and coated with 10nm of gold to prevent charging effects. Images were obtained using an accelerating voltage of 5kV and an 8.5mm working distance. Morphologies of the blends were assessed via image analysis. Neither etching nor solvent extraction of the phases was conducted in order to preserve the native nature of the interfaces. Clearly incompatible immiscible blends are characterized by domains of one phase pulling away from the domains of the second phase, as is often seen in dispersed droplet in matrix structures. The domains in co-continuous blends, on the other hand, are often held in close proximity due to “mechanical grafting” and appear to be chemically bonded even though they are not. We did not etch the samples so that we could discern this characteristic of the interface. Domain identity was confirmed by energy dispersive spectroscopy according to a previously described procedure [20].

Parallel Plate Rheometry

Parallel plate rheometry was conducted on the neat end members and on the blends in the phase inversion region (Blends 2,3,4,5,6). A TA AR-2000 rheometer was used with a 25 mm diameter aluminum parallel plate geometry in conjunction with Rheology Advantage software. In preparation for testing, all extruded specimens were chopped into three millimeter pellets, and the neat materials were used in their as-

received state. For the measurements, the equipment was heated to desired temperature and the lower plate was fitted with a melt ring to provide containment for the pellets. The parallel plates were closed to a one millimeter gap and a stress sweep was performed to define the linear viscoelastic region (LVR). The LVR strain values were then used in the time temperature superposition (TTS) oscillatory frequency sweep to obtain shear stress versus shear rate data for the materials at a predetermined temperature profile. Logarithmic viscosity versus shear rate curves were generated using the Cox-Merz transformation.

Capillary Rheometry

Capillary rheometry was conducted at 250 °C using a Brabender single screw extruder with the capillary die and various one millimeter diameter capillary inserts installed (L:D = 15 and 30). Prior to each measurement the extrudate flow must reach plastication equilibrium with a steady flow of material. This process, known as line-out, requires about five minutes of flow [17]. Once line-out is achieved, the material exiting the extruder was collected over a one minute period and the specimen's mass was recorded. During the one minute sample collection period, the pressure at the capillary entrance was measured by two pressure transducers and the temperature was monitored over four temperature zones. Multiple specimens were collected under each condition and the values averaged. This process was repeated using two different capillary inserts and at least two extruder drive speeds for the purpose of obtaining shear stress and viscosity values according to ASTM D5422-09.

DISCUSSION

Viscosity

The well-known and reliable rheology measuring methods of parallel plate and capillary rheometry produced good, consistent data over a wide range of shear rates. Although combined, the methods are capable of shear rate ranges from fractional inverse seconds to above 10^4 s^{-1} , we found the best and most reliable data to occur in the range of 200 to 6000 s^{-1} . Table 3 summarizes the viscosity data from both methods from 250 s^{-1} to 5000 s^{-1} . Most notable is the strong shear thinning over this wide shear rate range and the low range of viscosity values among all compositions at 5000 s^{-1} . Clearly, at 250°C and 5000 s^{-1} the contribution of weak chain-chain attractive forces is greatly reduced.

Neat end members

Polyamides have a reputation for being difficult to process by virtue of the strong dependence of their viscosities on temperature and shear rate. Although in this study we cannot comment on the temperature effect, we do confirm the strong shear thinning behavior for PA6,10, with the viscosity falling 89% (1106 to 123 Pa-s) over the shear rate range 250 to 5000 s^{-1} . PTT on the other hand exhibits a much lesser degree of shear thinning wherein the viscosity falls only 63% (268 to 98 Pa-s) over this same shear rate range.

The Jordhamo relationship used to estimate phase inversion and co-continuity behavior in binary immiscible blends relies on the viscosity of the neat end-members, measured at the temperature and shear rates used for processing, to predict the volume fraction composition. From the data in table 2 the necessity of accurately estimating the shear rate of the forming process, or conversely the sensitivity of the morphology to the

shear rate of the process, is apparent. Low shear rate processes operating at, say, 400 s^{-1} will produce phase inversion compositions at 21% PTT according to Jordhamo, whereas high shear rate processes such as injection molding (as high as 5000 s^{-1}) will produce phase inversion compositions at 44% PTT. Thus, not only do these data suggest a way to engineer the phase inversion point, i.e. by modifying the shear rate of the process, but they also point to the necessity of a high shear rate viscosity measuring method, i.e. capillary viscometry, to model Jordhamo effects for high shear processes such as certain extrusion and injection molding processes.

Blends

In addition to the viscosity of the neat components, viscosity data for all the blends are also presented in table 3 and shown in figure 1 as log viscosity versus log shear rate curves in the shear rate range of $10 - 630 \text{ s}^{-1}$. The sharply higher viscosity of the polyamide compared to the polyester is clearly shown by the top and bottom lines, as is the intermediate nature of the blends. The effect of composition on viscosity, at 400 s^{-1} is illustrated in figure 2. At this shear rate, the log viscosity is monotonically decreasing as the composition becomes richer in PTT, except for a region between 50 and 60% PTT. Earlier work suggested that phase inversion in these blends occurs in this region and the viscosity data indicate that a structural change is occurring in the blends that affects the viscosity near 55% PTT. The dotted tangent line is for clarity. The coarse spacing of the line series compositions (5%) and the overlapping of the error bars (\pm standard deviation) make it difficult to make a precise statement of the effect, but the reproducibility is good. Across the composition range the log viscosity is below the linear rule of mixtures line (not shown). This effect most likely results from slip between the immiscible domains

due to their non-bonded interfacial boundaries. At the phase inversion composition, morphology elements of co-continuity appear that function to mechanically bond the structure together, a phenomenon identified as “mechanical grafting.” The slight increase in log viscosity near 55% PTT is an indication of just such an effect in the PTT/PA6,10 blends. The power law index (equation 2) dependence on composition (figure 2) provides additional support for phase inversion and possible co-continuity occurring near 55% PTT. The power law index is comparatively constant at compositions less than 50% PTT where PA6,10 is the matrix phase. A transition to a higher index value occurs near 55% PTT as determined by the inflection point in the transition to high index (n) characteristic of PTT on the right side of (figure 3).

At higher shear rates, as measured by capillary viscometry, similar but slightly different effects are seen. At a 3000 s^{-1} shear rate (figure 4 and table 3) the viscosities of the blends drop well below the linear rule of mixtures line (not shown) and reaches a minimum at 40% PTT (71 Pa-s). At this shear rate, a localized peak in the viscosity curve occurs at 50% PTT, in good agreement with the lower shear rate data. Thus over a wide range of shear rates, and as measured by two different viscosity characterization methods, the immiscible blends of PTT and PA6,10 consistently show two features: a reduced viscosity compared to the linear rule of mixtures and a slight local increase in viscosity around the 50 to 55% PTT compositions. The first effect seems to occur from the slip between the non-bonded immiscible domain interfaces and the second effect occurs from a degree of “mechanical grafting” at the phase inversion composition.

Overall, the use of the power law relationship (equation 2) provides a conundrum in the assessment of immiscible polymer blends in the PTT/PA6,10 system, and perhaps

for all immiscible polymer blends. On one hand the power law index (n) is unpredictable based on the end-members and efforts to estimate a blend index by proportioning the end-members will lead to sizable errors. On the other hand, the index is a useful tool to assist in characterizing the nature of the blend with regard to shear flow related considerations, such as the degree of domain-domain bonding and associated slip.

Morphology

The viscosity data suggest a phase inversion composition with possible co-continuity in the 50 – 55% PTT composition range. Some indications from the viscosity data are that the composition is around 54 to 55%, although the line series step-size and precision of the data do not support defining the phase inversion composition so precisely.

Images from FESEM analysis of samples at 50, 55, and 60% PTT (fig 6a-d) illustrate the evolving morphology over this range. At 50% PTT (figure 6a) the morphology is largely comprised of the droplet(PTT)-in-matrix(PA6,10) structure seen at lower PTT compositions, although some phase-within-phase elements are observed in which droplets of PA6,10 are dispersed within larger droplets, or evolving fibrous cylinders, of PTT. Such elements are early indications of developing co-continuity. Nonetheless, the 50% composition demonstrates a clearly pre-phase inversion morphology. The 55% composition is close to the co-continuous composition although it does not demonstrate the highly branched and intertwined structure classically considered hallmarks of co-continuity, at least as represented by the planar non-etched image of (figure 6b). In this image the PTT can be differentiated from the PA6,10 by its smooth fracture surface compared to the stippled surface generated by small localized ductile

deformations during cold fracturing. As noted in the methodology, the respective phase identification was confirmed by EDS during FESEM analysis. This is an interesting image in that it shows two types of structures: numerous dispersed droplets of PTT that have clear gaps separating them from the PA6,10; and other irregularly shaped PTT domains that are held intimately in contact with PA6,10. Such close contact of domains is an indication of developing co-continuity wherein the mutually intertwined character of domains promotes so-called “mechanical grafting.” (Figure 6b) is reproduced in (figure 6c) with the addition of line traces of the domains to clarify the structure. Proceeding to 60% PTT produces the fully phase inverted structure (figure 6d) in which droplets of PA6,10 are dispersed in a continuous matrix of PTT.

Applications and significance of the technology

New polymer compositions are constantly needed to meet the needs of design engineers in industry, commerce and the military. The ability to combine immiscible polymer blends without compatibilizers opens a broad avenue of opportunity for the applied polymer scientist to formulate new materials with specific properties without resorting to expensive synthesis chemistry. In the present system of PTT and PA6,10 we have demonstrated that PTT, a relatively new engineering resin with properties similar to high performance polybutylene terephthalate, i.e. good strength and stiffness, but also with excellent finished appearance, reduced warpage, and good dimensional stability, can be combined with PA6,10, a member of the polyamide family renowned for outstanding toughness, work of fracture, and ductility. The blend of these two polymers has the potential to produce new engineering resins with enhanced properties as well as improved processing characteristics compared to the generally difficult to melt-process polyamides.

Lastly, both polymer components have substantial bio-based content and blends of the two will further advance the broad industry initiative to enhance the sustainability of engineering resins.

SUMMARY AND CONCLUSIONS

Binary immiscible polymer blends of PTT and PA6,10 were prepared from commercial components and the viscosity behaviors of the neat end-members and five blend compositions in the vicinity of the phase inversion composition were studied at the blend processing temperatures (250 °C) over a range of shear rates by both parallel plate and capillary methods. PA6,10 demonstrated a highly shear thinning character and the ratio of the component viscosities varied substantially with shear rate, producing variable Jordhamo volume fractions for co-continuity depending on shear rate (21 - 44% PTT). The viscosities of the blends did not follow a proportional rule of mixtures behavior but were lower, as may be expected due to slip between the immiscible domain boundaries. However, modest increases in viscosity were observed near the phase inversion composition, indicating a changing domain structure. The power law index (n) varied with composition, principally reflecting the behavior of the continuous phase polymer. The shift in the power law index and the modest spiking of the viscosity curve are useful in pointing to the phase inversion composition at about 55% PTT. SEM images showed droplet-in-matrix structures at 50 and 60% PTT, but clear indications of phase inversion and co-continuity were evident in the 55% PTT FESEM image. The image was not, however, a classical co-continuous structure which leads to the conclusion that the co-continuous composition range for PTT/PA6,10 does not span the 55% composition and in fact may be quite narrow. The discrepancy between the phase inversion composition as

measured experimentally and that predicted by the Jordhamo relationship calls into question the applicability of that relationship for the PTT/PA6,10 system. These findings are a critical contribution to the growing body of applied polymer science used by engineers and scientists to develop new engineering resins via the combination of immiscible polymers, compared to the more lengthy and expensive process of new polymer synthesis.

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VITAE

Giorgiana Giancola is a Research Associate at Rutgers University Department of Materials Science and Engineering, where she conducts research on the processing and characterization of immiscible polymer blends. Her current interests and expertise are in the processing of polymer blends and the application of electron microscopy imaging to characterize the resulting morphologies. Most recently, she has developed an interest in the application of spectroscopic methods (FTIR and Raman) to identify perturbations at the domain interfaces. She received her MS in Materials Science in October 2010 and is presently working toward a PhD.

Richard Lehman is Professor and Department Chair of the Materials Science and Engineering Department at Rutgers University. His research interests center on organic and inorganic glasses, relaxation and glass transition behaviors in these materials, and the

processing of commercial immiscible polymer blends and glasses. Most recently Professor Lehman's interest has evolved toward recycling and renewable materials, and he is an organizer of the sustainability center at Rutgers that seeks to develop and promote new sustainable polymer materials over a broad range of disciplines and applications.

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Material	Abbreviation	DuPont Product Names
Poly(trimethylene terephthalate)	PTT	Sorona® 3001
Polyamide6,10	PA6,10	ZYTRSLC3090

Table 1. Polymer materials used in the blends.

Blends used in Extrusion and Rheological Testing			
Percent by Volume (<i>Weight</i>)		Extruded Thermal Profile (°C)	
Blend	PTT	PA6,10	Solids/Trans/Metering/Die
1	0(0)	100(100)	215/230/250/245
2	40(45.1)	60(54.9)	230/245/250/260
3	45(50.2)	55(49.8)	240/250/240/250
4	50(55.2)	50(44.8)	230/250/255/235
5	55(60.1)	45(39.9)	220/250/240/250
6	60(64.9)	40(35.1)	230/250/250/245
7	100(100)	0(0)	235/250/265/280

Table 2. Extrusion formulations with temperature profiles.

Percent PTT	Viscosity, Pa-s (<i>at indicated shear rates</i>)			
	Parallel Plate		Capillary	
	250 s ⁻¹	400 s ⁻¹	3000 s ⁻¹	5000 s ⁻¹
0	1106	885	128	123
40	472	391	71	60
45	420	349	72	62
50	386	324	98	82
55	370	317	90	66
60	333	285	95	75
100	268	242	112	98

Table 3. Parallel plate and capillary viscosities at varied shear rates in binary blends of PTT and PA6,10 at 250 °C.

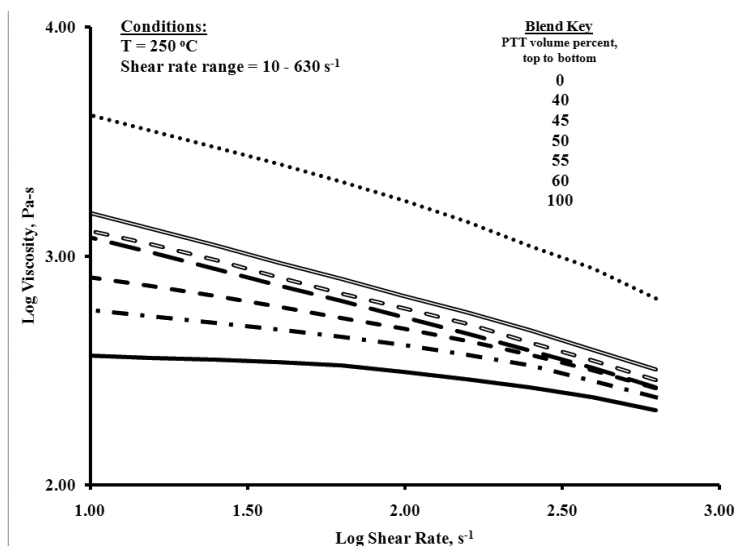


Figure 1. Viscosity shear rate relationships measured by parallel plate rheometry for PTT/PA6,10 blends.

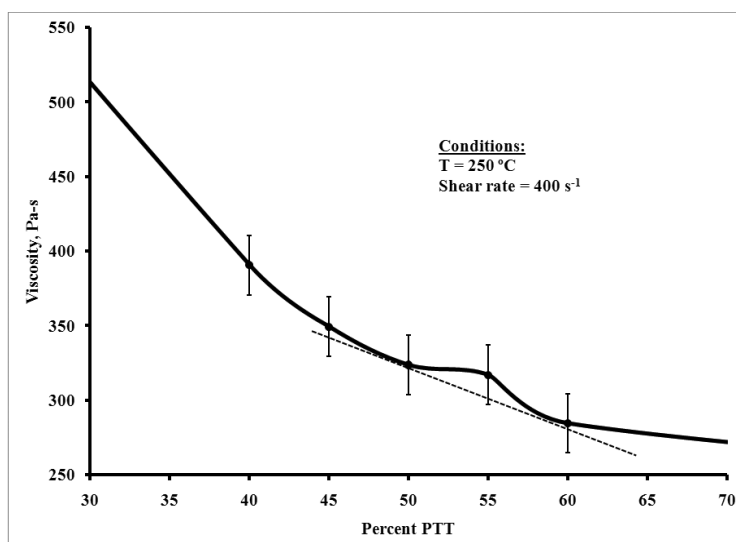


Figure 2. Viscosity composition relationships measured by parallel plate rheometry for PTT/PA6,10 blends.

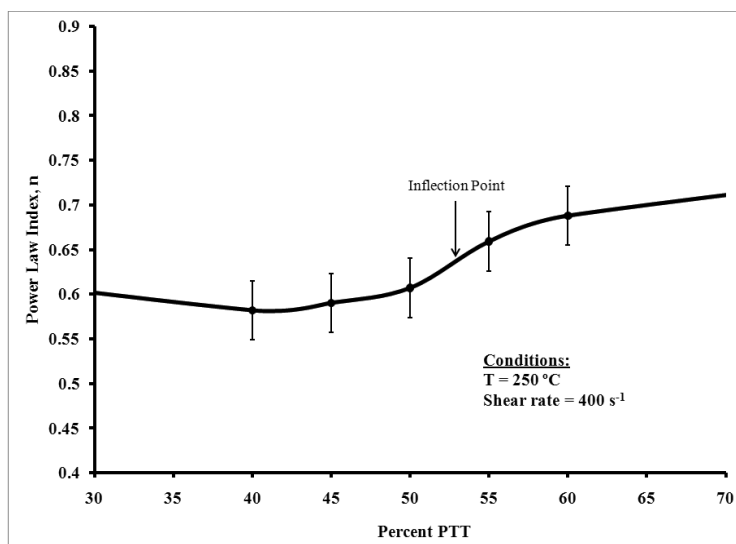


Figure 3. Variation of power law index with composition for PTT/PA6,10 blends obtained from parallel plate rheometry.

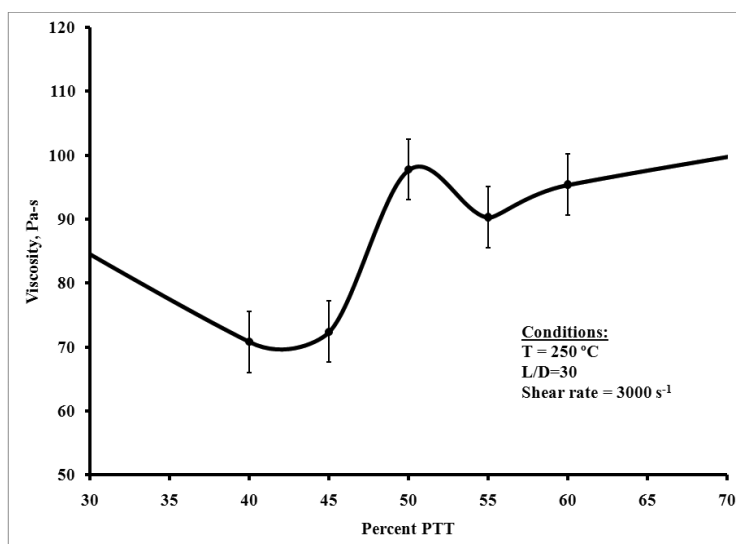


Figure 4. Viscosity composition relationships measured by capillary rheometry for PTT/PA6,10 blends.

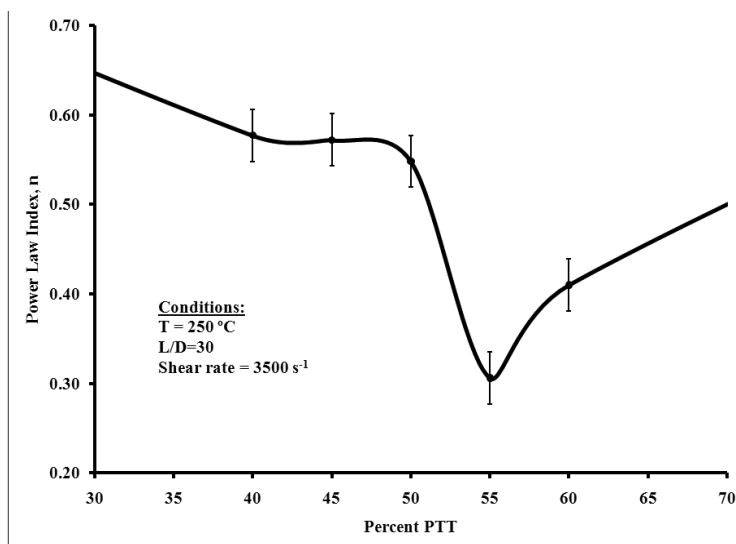


Figure 5. Variation of power law index with composition for PTT/PA6,10 blends obtained from capillary rheometry.

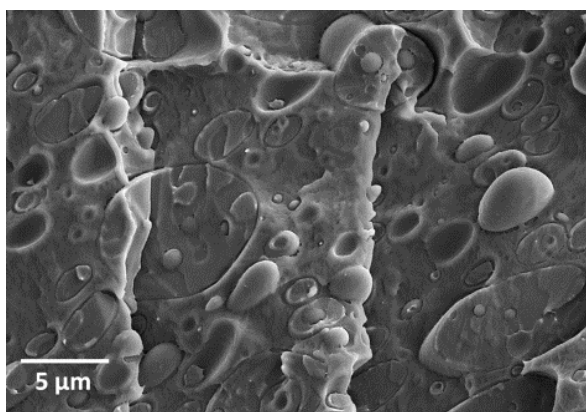


Figure 6a. Extruded 50% PTT and 50% PA6,10 blend, FESEM image.

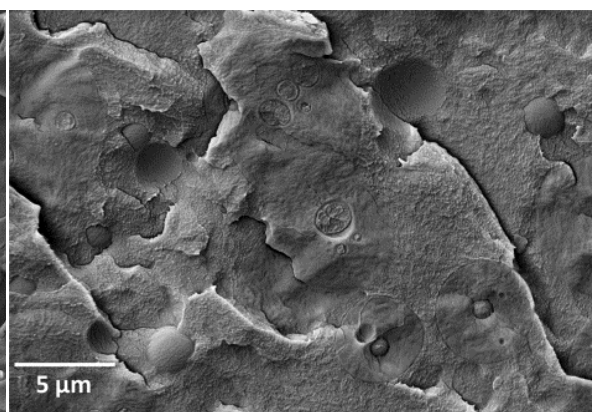


Figure 6b. Extruded 55% PTT and 45% PA6,10 blend, FESEM image.

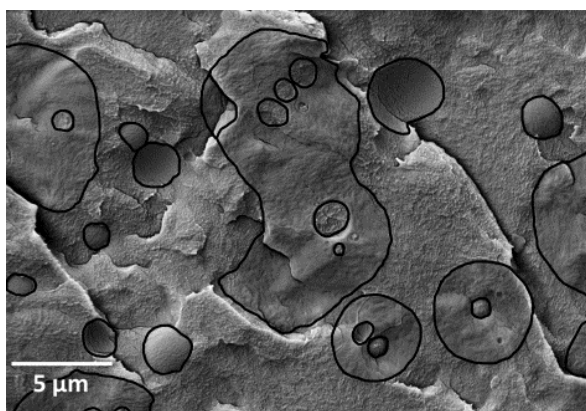


Figure 6c. Figure. 6b with domains traced for clarity.

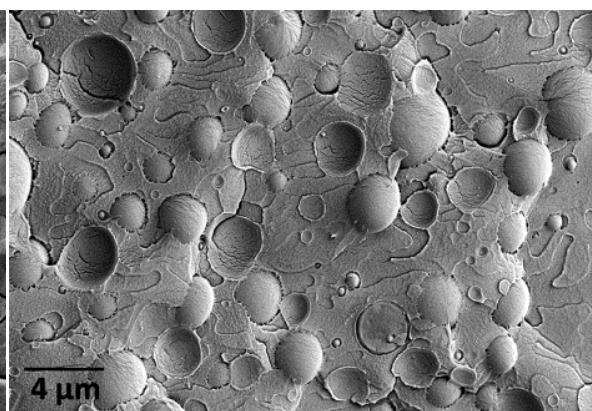


Figure 6d. Extruded 60% PTT and 40% PA6,10 blend, FESEM image.

Appendix VII

"In-situ formation of nano-scale PMMA network structures on the surface of immiscible polymer blends by solvent extraction and redeposition."

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In-situ formation of nano-scale PMMA network structures on the surface of immiscible polymer blends by solvent extraction and redeposition

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ABSTRACT

A continuous open structured network with high surface area, low solids fraction, and nano-scale domain morphology was observed to grow from dissolved blend components on cold fractured surfaces of immiscible polymer blends when reacted with dimethyl formamide. In this work we showed that the network is comprised of PMMA with a strong glassy character similar to or even in excess of conventional PMMA pellets used in the preparation process, in contrast to the amorphous but not glassy PMMA produced when similar materials were synthesized away from the PMMA host. FTIR and DSC analyses confirmed the chemical and physical character of the network. This general network formation phenomenon, which was initially observed in PMMA/HDPE blends produced by conventional extrusion, PMMA/HDPE blends compression molded from powder precursors, and subsequently on bulk PMMA, produces a unique structure that has potential applications as an interfacial modification substance or as a functional material in biomaterials and catalysis.

INTRODUCTION

Binary blending selected immiscible polymers is a productive approach to producing novel polymeric materials without requiring the costly and arduous process of synthesizing new polymer compositions.[1,2] The domains in these unique blends are not chemically bonded[3] but when co-continuity is achieved near the phase inversion

composition, a complex and tortuous morphology is created with a large amount of interfacial surface area. Co-continuity forms a closely knit interconnected morphology that enables both phases to extend completely throughout the structure. In certain compositions, typically when one semicrystalline polymer is blended with an amorphous polymer, the thermally induced stresses result in a strong clamping action between these intertwined phases and excellent load transfer is achieved. This phenomenon, known as mechanical grafting,[4] yields excellent mechanical properties, rule of mixtures values in most cases and synergistic effects attributed to domain orientation. The mechanical properties of the composite tend to improve further as the scale of the two-phase morphology becomes finer in the micro-scale and nano-scale regions.[3] Overall, an ideal immiscible blend is homogenous at the macro scale but has good co-continuous dispersion of the domains to produce an intertwined micro- to nano-scale domain morphology with minimal regions where a droplet-in-matrix morphology is present,[5] although some dispersed blends show effective performance in dynamic properties such as impact resistance.

Typically, binary immiscible polymer blends are melt-processed directly from pellets of the two components, usually by extrusion or injection molding. When the polymers are thermally and shear sensitive,[6] low shear and short residence time processes such as compression molding[3] are used.

In this work we studied an interesting phenomenon observed in our laboratory, the formation of a nano-scale network of material on cold fracture surfaces of PMMA/HDPE composites during etching with dimethyl formamide, presumably by dissolution and redeposition of one or both of the polymer phases. Solution and

precipitation of polymers is strongly affected by the type of solvent, and DMF was the only one of several solvents tested that formed this structure. The resulting network is of particular interest due to the fine scale of the domains, the continuity and open structure of the network which suggest numerous applications.

METHODOLOGY

Thermoplastic immiscible polymer composites have been prepared successfully in our laboratories by melt processing. We have produced a range of materials and functional structures for applications ranging from bridges to biomedical scaffolding and implants.[4,7] Traditionally single screw extrusion is suitable for blending polymer pellets to produce immiscible blends with micrometer sized domains. Some polymer blends are fragile and cannot withstand the high shear and long residence times of extrusion. For such polymer blends a two-step process of powder blending followed by compression molding is effective.[8] Both routes achieve a fine scaled structure with similar levels of mixedness. In the present study PMMA/HDPE binary immiscible blends were prepared using both traditional pellet extrusion and the two-step powder method. Inorganic silica spheres were introduced to all blends at the 10 volume percent level as a means to assess homogeneity during SEM imaging.

Solvent etching of composites is effective in enhancing microscopic morphological features.[7] Solvents are selected based on solubility parameters. We have used dimethyl formamide [DMF], a suitable solvent with intermediate solubility parameter ($24.7 \text{ MPa}^{1/2}$),[9] for etching blends such as PMMA/PLLA and the present system PMMA/HDPE. In both instances PMMA, which has a solubility parameter of $22.7 \text{ MPa}^{1/2}$, [10] is the selectively etched phase. The blends studied in this paper were

analyzed by SEM and EDS spectroscopy to identify the domains in both the extrusion and compression molded specimens and these results have been reported.[3] Although solvent extraction was initially targeted as a way to confirm domain identification, a unique observation was made on nearly all of the specimens. A continuous, fine scale (~50-150 nm), self-assembled, network was discovered serendipitously on the etched surface of the immiscible blends. The network was notable to the authors for its fineness, continuity, and openness. This network structure possesses a high level of surface area and a morphology that will be useful in a range of applications such as catalytic substrates, biomaterials, or as a bonding layer for structural materials. These considerations prompted the present study in which we characterized the network using SEM, differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). In addition to characterizing the network formed on the PMMA/HDPE blend surfaces, we sought to reproduce the network on virgin pellets of PMMA.

EXPERIMENTAL

Materials Selection

Polymethyl methacrylate and polyethylene blends have been prepared for numerous studies in our laboratory. This is a strongly immiscible system based on thermal and viscosity data previously published.[2,3] The blend component raw materials were obtained in both pellet form and as fine micrometer scale powders. Such powders are not available commercially as high quality materials since they are usually milled by conventional methods that often yield contaminated powders. To avoid this, PMMA pellets were cryogenically jet milled to particles of about 10 μm as measured by

SEM image analysis and dynamic light scattering techniques.[3] The HDPE and silica powders were generated through emulsion polymerization resulting in spherical particles of approximate size of 11 μm and 5 μm respectively. The inorganic silica was added to all blends at the 10 volume percent level as a marker for measuring mixedness in the blends. Table I lists all materials and their supply source.

Formulation and Solvent Extraction

Line series formulations were formulated in the approximate compositional space of co-continuity using pellet precursors for extrusion processing and micrometer size powder precursors for compression molding processing (Table II).[3] All melt processed specimens were cold fractured to obtain fracture surfaces without smearing of the HDPE. Specimens were static etched in DMF for 5 minutes (no ultrasonic agitation) followed by a rinse in ethanol to stop the etch process. Neither of the two constituent polymers is significantly soluble in ethanol at room temperature.[11]

To confirm the PMMA origin of the nano-scaled network and to obtain sufficient quantities for DSC and FTIR analysis, virgin PMMA pellets were used to synthesize quantities of the network in a separate experiment. One hundred grams of pellets were measured and washed in an ethanol bath for 2 minutes with mild stirring to remove any surface contamination from these commercial pellets. The pellets were then static leached in DMF for 5 minutes according to the same procedure described for the composite specimens.

After cursory SEM examination of the etched pellets to verify formation of the nano-network on bulk PMMA, methods were investigated to remove the network from the substrate. The interaction of the DMF with the PMMA pellets generates two types of

“synthetic” materials. One such material is firmly attached to the network and is not readily removed by rinsing or wiping, whereas a second type was not bonded to the network and was readily evolved into the DMF. Some of this latter material is clearly dissolved in the DMF but much of it appears as a sol that clouds the etch solution. First, we separated the DMF leach solution from the pellets and evaporated this liquid to dryness at ambient and retained the dry solids for analysis. The pellets were rinsed in ethanol and dried. To release and separate the adherent nano-network from the pellets we pulse ground small batches (10 g) of the pellets for a few seconds in a small analytical mill. A 20 mesh screen was used to separate the powder from the pellets. In this separation process the friable nano-network was readily separated from the harder, more durable pellets and no core pellet material was found in the removed nano-network specimens as assessed by electron microscopy.

Image Analysis

Extruded and compression molded DMF-etched specimens as well as virgin and etched PMMA pellets were mounted on SEM stubs. The two types of synthetic PMMA nano-networks synthesized were dispersed in ethanol and carefully smeared on a mount, taking care to maintain the integrity of the particle structure. All mounted specimens were coated with 10nm of gold to limit charging effects. A Zeiss Sigma FESEM was used for imaging with an 8.5mm working distance, an accelerating voltage of 5kV, and a 20 μ m aperture.

DSC and FTIR Analysis

Differential Scanning Calorimetry using a TA Instruments DSC Q1000 was performed on the two types of synthetic PMMA network powders obtained from the

virgin pellets. A standard DSC heat/cool/heat test was performed with a lower temperature of 30 °C to an upper temperature of 200 °C. The heating rate was 10 °C/min and the cooling rate was 5 °C/min. Specimens were approximately 7mg. The goal was to determine if the network was amorphous, glassy, or crystalline, and to compare the transition points with known values of standard materials.

To obtain FTIR spectra, a Perkin Elmer Spectrum RX I FTIR Spectrometer in conjunction with a MTEC photoacoustic model 300 detector was used. The spectrometer scan was from 600 cm^{-1} to 4000 cm^{-1} with a 150 scan count. All spectra were normalized and adjusted with background correction. Multiple spectra of each sample were acquired to assure consistent results. The two types of synthetic PMMA network were analyzed in powder form while virgin pellets were analyzed as a control. The goal of the FTIR analysis was to confirm the chemical nature of the network.

DISCUSSION

The nano-scale network structure, as shown in Figure 1 was initially noticed on PMMA/HDPE composites regardless of the processing technique after DMF etching and was assumed to be PMMA. Generally a uniform thick layer of the network was observed, particularly on the extruded blends, as shown in Figure 1b. Considerably less network was observed to form on the compression molded blends as seen in Figure 1a even though the compression molded blend contained 70% (volume) PMMA and the extruded blend (Fig 1a) contained only 50%. The images in Figure 1a and 1b are representative of the networks formed on all blend compositions. Even though the DMF etch time for the compression molded specimens was half that of the extruded blends, the amount of network formation on the compression molded specimens was consistently

disproportionately less than on the extruded blends. Considering that these two melt processes yield similar results with regard to homogeneity and morphology[3] the reduced generation of the nano-network on the compression molded specimens is most likely attributable to the powder precursors. The PMMA powder was prepared from the PMMA pellets by cryo-grinding and should be virtually identical to the pellets since the cryo-grinding is an autogeneous process that induces virtually no contamination. Nonetheless, the PMMA powder did undergo this additional processing step and some change in the property of the material cannot be ruled out. The HDPE used in the compression molding was a different material than that used in the extrusion (see Table I) and it, too, may have had an effect. Nonetheless, the character of the nano-network on both composites appears the same, just the quantity varies.

Of particular interest is the fineness of the domains of this network (~50-150nm), the continuity of the network as large amounts are formed on the surface, and the relative uniformity of the domains and the voids of the network. The network appears to grow as a web-like structure extending over the surface of the composite and builds a multi-layer thickness on the order of micrometers. Interestingly, each layer of the network growth process builds on the underlying network to form a uniform open structure rather than filling in the voids. Although no mercury intrusion porosimetry has been conducted to date, planar image analysis suggests pores in the range of 150 – 900 nm with an average pore size near 500 nanometers. The void volume fraction is approximately 75%. The appearance in Figure 1a of the nano-network appearing on the silica marker spheres and the HDPE domains shows that the network is not epitaxial to the partially PMMA based

substrate, but grows on any surface in the composite, including the silica, by a heterogeneous process of amorphous growth.

To understand more about this nano-network and to generate sufficient quantities for further analysis, we sought to systematically synthesize this network directly from virgin PMMA pellets. PMMA pellets from the same batch as those used in the extrusion process DMF etched in the same manner as the immiscible blends. Electron microscopy (Fig 2) confirmed that this network self-assembles on the surface of a virgin pellet that was previously virtually feature free. The two synthetic materials, one generated on the PMMA pellet surface (“surface network”) and the other generated by evaporating the etch solution to dryness in a glass dish (“solution solids”) were also examined by SEM. The network formed on the pellets (Fig 3b) appears similar to those formed on the polymer blends and consists of network rings comprised of and connected by thin strands of polymer. Conversely, the material dried from the DMF solution has a much more nodular texture with fewer open rings and less of a network structure. Moreover, this material does not exhibit the thin strands of connective material evident in the other networks.

Differential scanning calorimetry (DSC) analyses were useful in determining that the two synthetic materials were amorphous non-crystalline materials and that the synthetic network grown on the pellets was a glassy material with a T_g at 103° C. This T_g compares favorably with the measured T_g of the virgin pellets at 104° C. First heat data, prior to erasure of the thermal history, were used to indicate the structure of the materials as-formed rather than the quasi-equilibrium DSC behavior reflected by the reheat curves. Thus, the similarity of the two values is remarkable considering the pellets

and the surface network film have very different polymer histories. Furthermore, the surface network film gives a strong endothermic enthalpic signal at T_g with the heat flow shifting 59 mW/g, a 14% greater shift than observed for the pellets, indicating the strong glassy nature of the surface network.

FTIR further confirmed that the nano-network on the composite blends and the synthetic pellet surface network were comprised of PMMA (Fig 5) and revealed nearly identical FTIR fingerprints with a strong absorbance peak at 1470 cm^{-1} and a lesser one at 1495 cm^{-1} both of which can be attributed to the bending asymmetry of CH_2 found in PMMA.[12, 13, 14] The solution solids fingerprint contained the same main absorption peak but major discrepancies were noted at other wavenumbers. This type of FTIR behavior is typical of oligomers where the main features of the compound are present but the full polymer fingerprint is absent. Thus, the solution solids, in addition to not exhibiting a glass transition, appear to be comprised of oligomers rather than true PMMA. This is an interesting outcome, suggesting that the morphology of the blend or the pellet surface is needed to synthesis network structures of polymeric, glassy, PMMA.

The ability of these nano-scale PMMA domains to self-assemble on the surface of the binary PMMA/HDPE composites and the network nature of the structure suggests multiple areas of use. As an in-situ formed surface phase with high surface area and co-continuous access to the surface, this network has potential in numerous applications. One such application, if the network layer is bonded to the domains or can be made to bond to the domains via thermal treatment above T_g , is to provide an interfacial bonding enhancement agent for polymer/polymer or bio-polymer composites. Naturally, the degree of adhesion to the originating base structure and the integrity of the network itself

are critical for this application. Furthermore, this nano-scale network, comprised of a relatively high elastic modulus polymer, will be an effective reinforcement phase when impregnated with low viscosity precursors of a matrix polymer that can be polymerized in-situ, thus generating a strong wear resistant coating on the surface of these blends. The high surface area and semi-ordered structure of this network also suggest applications in the fields of catalysis, biomaterials, and energy applications such as fuel cells and batteries.

SUMMARY AND CONCLUSIONS

Immiscible polymer blends of PMMA/HDPE with SiO₂ marker spheres were blended and melt processed near the phase inversion point using both traditional extrusion melt processing and a novel powder system processed via compression molding. Composites produced by the two systems were morphologically quite similar with comparable levels of homogeneity and domain size. As part of a DMF solvent etching process, the appearance of an intricate, high surface area nano-scale network was observed, apparently resulting from an extraction/redeposition process of PMMA. Characterization of this network by FTIR and DSC revealed that the network is comprised of PMMA and has a glass transition nearly identical to the PMMA pellets used in processing the composites. SEM image analysis was essential in characterizing the network in terms of domain size (approximately 50-100nm), morphology (open continuous network of rings and links), and volume fraction solids (approximately 25%). Such a network can work as an interfacial bonding enhancement agent for polymer/polymer or bio-polymer composites provided the network layer is or can be made to bond to the domains.

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VITAE

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Form	Material	Product/Supplier	Density (g/cm ³)	Processing Method
Pellet	PMMA	Altuglas V045I	1.15	Extrusion
Pellet	HDPE	Exxon D7960	0.95	Extrusion
Powder	PMMA	Altuglas V045I (cryo jet milled)	1.15	Compression Mold
Powder	HDPE	Kobo Products CL-2080	0.92	Compression Mold
Powder	SiO ₂	Kobo Products MSS-500/3N	2.4	Extrusion & Compression Mold

Table I. Selected Materials

Composition percentages by volume (weight)				
Blend	HDPE	PMMA	SiO ₂	Process
1A	20(14.8)	70(65.5)	10(19.5)	Compression Molded
1B	30(22.9)	60(57.2)	10(19.9)	Compression Molded
1C	50(39.7)	40(39.7)	10(20.7)	Compression Molded
2A	35(30.4)	55(47.72)	10(21.9)	Extruded
2B	45(39.0)	45(39.0)	10(21.9)	Extruded
2C	55(47.7)	35(30.4)	10(21.9)	Extruded

Table II. Formulations and Processing

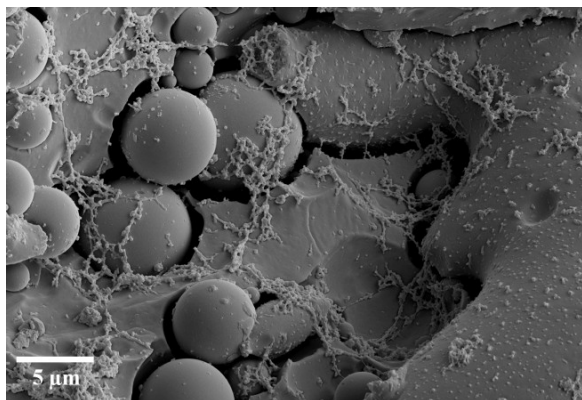


Figure 1a. SEM image of Blend 1A.
Etched in DMF, 1 min.

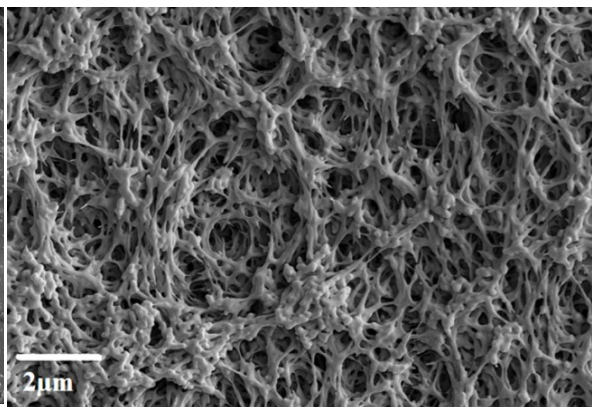


Figure 1b. SEM image of Blend 2B.
Etched in DMF, 2 min.

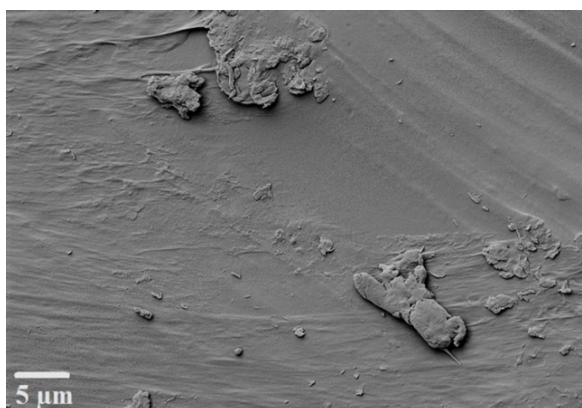


Figure 2a. SEM image of PMMA virgin
pellet, unetched.

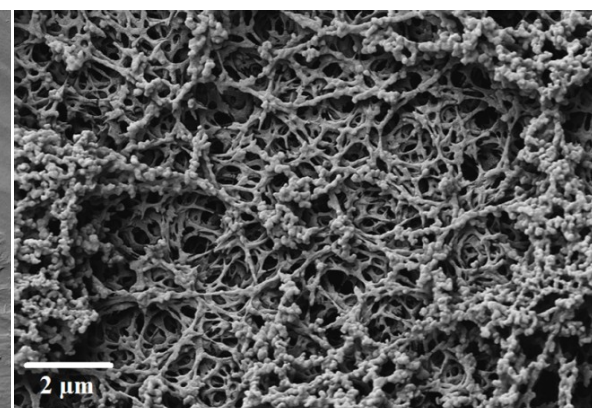


Figure 2b. SEM image of PMMA virgin
pellet. Etched in DMF etched, 5 min.

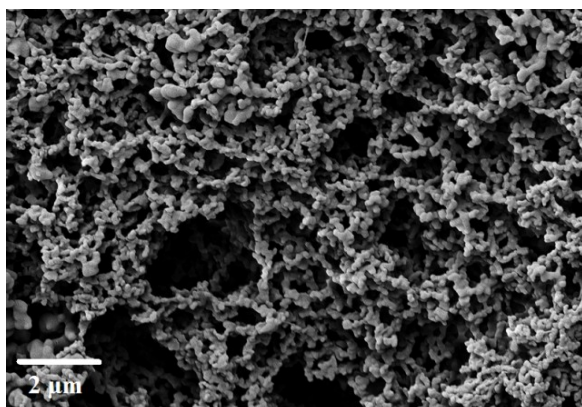


Figure 3a. SEM images of network from
PMMA pellet, DMF 5 min reaction. Non-
glassy network formed in solution.

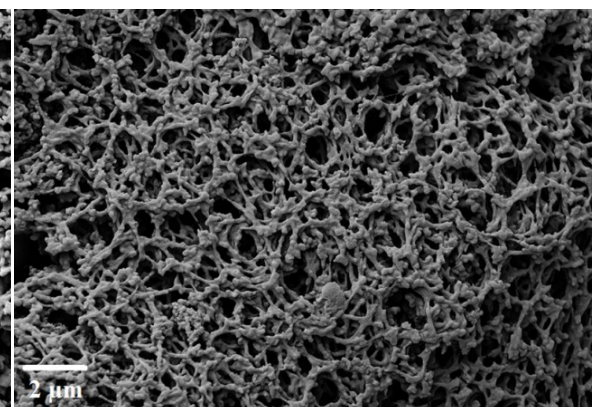


Figure 3b. SEM images of network from
PMMA pellet, DMF 5 min reaction.
Glassy network formed on pellet surface.

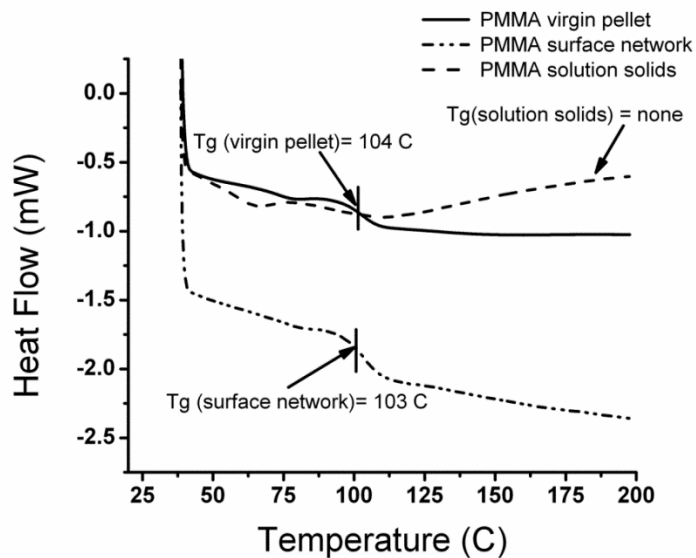


Figure 4. First heat DSC traces of PMMA virgin pellets, PMMA etch released network and PMMA etch grind released network. Ordinate is exothermic up.

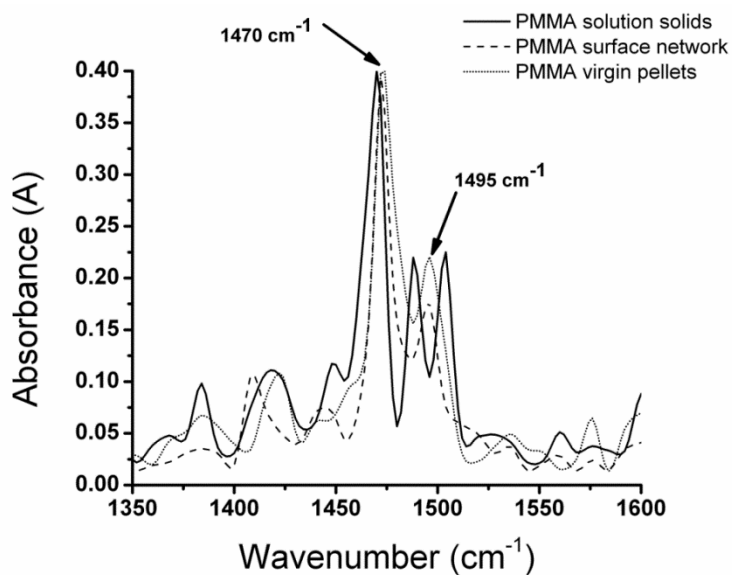


Figure 5. FTIR spectra of PMMA virgin pellets, PMMA etch released network and PMMA etch grind released network.