INTRODUCTION

Extensive research has been employed in enlarging the scope of applications for polyesters and polyamides in the form of blends and composites to control and improve their properties. While early research focused on the investigation of the compatibility of base polyester/polyamide blends, such as PET blended with polyamide-6,6 (1–3) or polyamide-6 (4–6) and PBT/polyamide-6 blends (5, 7, 8), more recent reports have investigated the blends of polyamide with liquid crystal polyesters (9–12). Because of the immiscibility of the two parent polymers, numerous investigations have cited the use of compatibilizers, ranging from modification of one of the blend components (13, 14) to incorporation of a minor-component compatibilizer (9, 10, 12, 14–18), typically either an ionomer or copolymer, to improve the blend properties. Blend compatibilization is a very common technique utilized to decrease the interfacial tension between blend components and increase interfacial adhesion, thereby enhancing the blend mechanical properties (19).

For polyester/polyamide blends, the formation of polyester-polyamide copolymers through a reactive compatibilization process involving melt-phase ester-interchange reactions has been extensively investigated (20–23). The kinetics of the interchange reaction require the utilization of a catalyst, such as p-toluenesulfonic acid, in order to speed the reaction to a rate that is useful for an industrial process. The progress of the reaction has been followed using $^1$H and $^{13}$C NMR spectroscopy (23), and the thermal and mechanical properties of the copolymers have been fully characterized (21, 22). While the presence of the copolymers fosters improved compatibility and interfacial adhesion between blend components, thermal degradation and extensive interchange reactions were shown to degrade the mechanical properties of the blends (20, 22).
John and Bhattacharya have investigated the use of maleic anhydride–grafted PBT as a compatibilizer for PBT/polyamide 6,6 blends (13). The incorporation of the compatibilizer increased the interfacial adhesion, as evident by increases in the tensile, flexural, and impact strengths of the blends with increasing amounts of compatibilizer. Electron microscopy confirmed the influence of the compatibilizer on the blend morphology, and spectroscopy showed an interaction between the amide of the polyamide 6,6 and the grafted maleic anhydride functionality. Bifunctional epoxy resins have also been used to compatibilize PBT/polyamide (15–17) and polyamide 6,6/LCP blends (12). The in situ formation of PBT-epoxy-polyamide copolymers provides an internal compatibilizer that acts at the interface to reduce the domain sizes of the dispersed phase and greatly enhance the mechanical properties of the blends. Zheng and co-workers have investigated the use of other compatibilizers for polyamide 6/LCP blends, including styrene-maleic anhydride copolymers, polypropylene-glycidyl methacrylate and polypropylene-glycidyl maleic anhydride (9).

The use of ionomers as minor-component compatibilizers is well documented in the literature. Their effectiveness as a compatibilizer is related to the structure of the ionomer and the counterion used. Samios and Kalfoglou employed the use of Surlyn (Zn²⁺) as a compatibilizer for melt-mixed PET/polyamide 6 blends (18). The ionomer was shown to interact more strongly with the polyamide component, and effective compatibilization was not observed below ionomer loadings of 10%. Weiss and co-workers observed that the addition of sulfonated polystyrene (Zn²⁺) to blends of polyamide 6,6 and a liquid crystal polyester effectively compatibilized the blends through interactions between the sulfonate group and the amide linkage as well as intramolecular repulsive interactions along the ionomer (10). The addition of the compatibilizer reduced the dispersed domain sizes and enhanced the tensile modulus and stress at break.

In our previous studies, Boykin and co-workers focused on the use of polyester ionomers as minor-component compatibilizers in blends of PET or PBT and polyamide 6,6 (24–27). The results suggested compatibility due to specific interactions for the ionomer/polyamide 6,6 blends (27) and transesterification for the ionomer/PET blends (28). The compatibility was strongly dependent on the counterion type of the ionomer, with the divalent counterions (Zn²⁺ or Mn²⁺) showing enhanced compatibility compared to the monovalent form of the ionomer (Na⁺).

In this investigation, the Na⁺-form of sulfonated PETG (Na-SPETG) is used as a minor-component compatibilizer for amorphous polyester/polyamide 6 blends. The blending was performed both in solution and via twin-screw extrusion, and the morphology and thermal and mechanical properties of the blends were fully characterized. Without the complications associated with the existence of crystalline domains, the specific interactions in these amorphous blends between the sulfonate group and the amide linkage were isolated in order to explain the role of the ionic functionality in the compatibilization of the blends. While the Na⁺-form ionomer is shown to have a great effect on the morphology and properties of the blends, this research provides a framework for further studies involving various other counterions.

**EXPERIMENTAL**

**Materials**

The amorphous polyester (PETG 6763) and the analogous sulfonated Na⁺-forms of the amorphous polyester (SPETG) were supplied by Eastman Chemical Company. The PETG is composed of terephthalic acid and ethylene glycol with a portion of the glycol units substituted with cyclohexane dimethanol to render the polymer amorphous. The backbone of SPETG is similar to PETG with the exception of randomly placed sulfophthalic acid (SIP) units along the polymer chain incorporated at 1.9, 3.0 and 5.5 mole% of the total monomer units. The inherent viscosities of PETG, 1.9SPETG, 3.0SPETG and 5.5SPETG are 0.7, 0.516, 0.443 and 0.395, respectively. These numbers show that the molecular weight of the polyester decreases as the content increases. The amorphous polyamide—Durethan T40 from the Bayer Corporation—is composed of polyamide-6 with a small amount of aromatic units incorporated to eliminate the crystallinity. The common solvent 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was used as received from Fluorochem, and the esterified SIP monomer, dimethyl-5-sulfisosophthalate sodium salt (Na-mSIP), was chosen as a small molecule analog to the SPETG ionomers and used as received from Aldrich.

**Solution Blend Preparation**

The blends were prepared as a 1.5% (w/v) solution in HFIP, which is a common solvent for all the polymers. The desired ratio of polymers was simultaneously dissolved in HFIP and the solution was allowed to stir for at least 12 hours to ensure complete dissolution and mixing. The blend ratios were set at 50/50 (by weight) of Durethan T40/PETG. The SPETG was added at 2%, 5%, 10%, 15%, 20%, 25%, and 50% (by weight based on total blend weight) into the PETG portion of the blend to yield the desired ternary blend ratios: T40/PETG/SPETG 50/48/2, 50/45/5, 50/40/10, 50/35/15, 50/30/20, 50/25/25 and 50/0/50. Once fully dissolved, films of each of the solution blends were cast onto microscope slides in a HFIP environment under a crystallization dish.

**Extrusion Blend Preparation**

Similar ternary blend ratios were prepared by melt extrusion in a Prism 16-mm co-rotating twin-screw extruder. The polyester and polyester ionomers were dried in a vacuum oven at 65°C for 24 hours while the polyamide was dried in a vacuum oven at 80°C for 24 hours to ensure the polymers were dried to a 0% moisture.

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level. The pellets for each polymer were then dry-mixed at the desired blend ratio and fed simultaneously into the extruder. The barrel temperatures were set so that the melt temperature remained constant at 270°C throughout the length of the extruder, and the processing was carried out at 300 rpm, which yielded a residence time of ~30 seconds. The blend samples were collected as pellets after passing through a water bath and pelleting unit. The pellets were then dried at 70°C in a vacuum oven for 24 hours and molded into dogbone samples using a BOY 15S injection molder.

**Blend Characterization**

*Morphology of Solution Cast Blends*

The phase morphology of the solution-cast blends was characterized using phase contrast optical microscopy (PC-OM) and small angle light scattering (SALS). Microscopy was carried out with an Nikon Optiphot II scope operating in phase contrast mode using a Nikon Digital Eclipse DXM 1200 CCD camera for image acquisition. The SALS images were acquired using incident light from a 3 mW He-Ne laser (λ = 632.8 nm, Oriel Corp., model 6697). The resulting \( V_c \) scattering pattern was projected onto a sheet of paper and the image was collected using a Photometrics SenSys 1401E CCD camera interfaced with a computer.

*Thermal and Mechanical Properties*

The injection molded blend samples were analyzed using dynamic mechanical analysis and mechanical tensile testing. DMA was carried out on a Seiko DMS 110 operating in three-point bending mode at 1 Hz while the sample was heated from 25°C to 200°C at 4°C/min. Tensile testing of the blends was performed on a MTS Alliance RT/10 according to the standard protocol of ASTM 882.

*Morphology of Extruded Blends*

Environmental scanning electron microscopy (ESEM) was used to investigate the morphology of the extruded blends. Injection molded dogbone samples were freeze-fractured using liquid \( N_2 \), and the fracture surface was subsequently solvent-etched to remove the PETG and SPETG phases. The etching was carried out by dipping the fracture surface in chloroform, a preferential solvent for the polyesters, for 5 min. ESEM was performed using an FEI 200 electron microscope.

*Spectroscopic Analysis*

FT-IR spectroscopy was used to investigate the interactions between the Na\(^+\)SO\(_3\)\(^-\) group of the ionomer and the polyamide in the compatibilized blends. In order to isolate the influence of the sulfonate functionality, Durethan T40 was blended with the Na-mSIP monomer at the following molar ratios (sulfonate: amide): 0.25:1, 0.5:1, 0.75:1 and 1:1. Films of each blend were cast onto a salt plate and IR spectra were obtained using a Nicolet Protégé 460 spectrometer.

**RESULTS AND DISCUSSION**

**Solution Blends**

The binary and ternary solution blends were cast to yield films approximately 5 \( \mu \)m thick, suitable for characterization by both phase contrast optical microscopy (PC-OM) and small angle light scattering (SALS). Binary blends of Durethan T40 with PETG or SPETG (50/50) were first analyzed by PC-OM and SALS in order to study the effect of the ionic groups on the phase domain sizes. However, while the T40/PETG blend showed two distinct phases with domain sizes around 13 \( \mu \)m, all of the binary blends of T40/SPETG were transparent. Therefore, ternary blends incorporating varying amounts of the SPETG (1.9, 3.0 or 5.5 mole% SIP) were investigated to determine the effectiveness of the ionomer as a minor component compatibilizer.

*Figure 1* shows a representative set of phase contrast optical micrographs for the solution-cast T40/PETG/1.9SPETG blends. As the amount of the ionomer in the blends increased, the domain sizes of the dispersed phase decreased. The results showed that the incorporation of 2% (by weight) of the 1.9% ionomer reduced the phase domain sizes from approximately 12 \( \mu \)m to 7 \( \mu \)m, and the sizes continued to decrease as the amount of ionomer in the blends increased. To accompany this, the contrast between the two phases decreased with increasing ionomer incorporation, which is indicative of phase mixing resulting in a decrease in the difference between the refractive indexes of the two phases. Similar decreases in the domain sizes and contrast were observed for the 3.0 and 5.5 mole% ionomers, with a greater size reduction for the higher-ion-content ionomers. While 25% incorporation of the 1.9% ionomer resulted in a transparent blend, only 20% incorporation of the 3.0% and 5.5% ionomer was required to yield a transparent blend. Future work will investigate the mechanism of the co-continuous morphology development.

Microscopy provides a means for real space analysis of structural features of a phase-separated blend, while small angle light scattering is a complementary technique analyzing structural features in reciprocal space. The two techniques have been used together extensively to fully characterize the morphology and phase-separation behavior (kinetics and mechanism) of many blend systems (29–36). Of particular interest to the current study, compatibilizing interactions between blend components including H-bonding (30, 36), ion-dipole interactions (34) and incorporation of a block copolymer or reactive functionality (31, 32) have been shown to have a significant effect on the morphology and phase-separation behavior as observed by microscopy and light scattering. The incorporation of specific interactions between blend components can slow the phase-separation process and result in a more stable morphology, often with reduced dispersed phase dimensions and contrast between phases.

Characterization of the solution-cast blend morphology by SALS reinforced the trends observed in PC-OM,
as shown in Fig. 2. The scattering patterns of the binary and ternary blends were acquired using the same films analyzed by microscopy. As the incorporation of the ionomer increased, the size of the scattering halo increased (at a constant sample-to-detector distance). This trend correlates to a decrease in the size of the phase-separated domains with increasing ionomer incorporation. Similar to PC-OM, the higher-ion-content ionomers resulted in a more significant reduction in the domain sizes, and transparent blends were observed at

Fig. 1. Phase contrast optical microscopy of T40/PETG/1.9SPETG solution blends. (A) 50/50/0; (B) 50/48/2; (C) 50/45/5; (D) 50/40/10; (E) 50/35/15; (F) 50/25/25. Scale bar = 10 μm.

Fig. 2. Small angle light scattering (SALS) images of T40/PETG/1.9SPETG solution blends. (A) 50/50/0; (B) 50/48/2; (C) 50/45/5; (D) 50/40/10; (E) 50/35/15; (F) 50/25/25.
25% incorporation of the 1.9% ionomer and 20% incorporation of the 3.0% and 5.5% ionomers. The SALS of the 50/30/20 blend with 1.9SPETG did not show a scattering halo at this sample-to-detector distance (SDD), though a scattering halo was observed for this blend at larger SDD.

The angle of the maximum scattering intensity from the scattering halos was used to calculate the phase-separated domain sizes according to Eqs 1 and 2:

$$\tan \theta = \frac{r}{x}$$  \hspace{1cm} (1)

$$d = \frac{n \lambda}{2 \sin \theta}$$  \hspace{1cm} (2)

where $\theta$ is the scattering angle, $r$ is the radius of the scattering halo, $x$ is the sample-to-detector distance, $d$ is the domain size, $n$ is the order of reflection ($n = 1$) and $\lambda$ is the wavelength of incident light ($\lambda = 632.8$ nm). Figure 3 shows the results of the calculations, indicating the domain sizes of the ternary blends incorporating ionomer were smaller than the uncompatibilized blend in all cases, with the sizes decreasing as either ionomer composition in the blend or ion content increased. No scattering was observed in blends incorporating greater than 25 wt% of ionomer for all ion contents.

The anomalous behavior of the domain sizes at 5% ionomer loading, where the sizes are substantially smaller than both 2% and 10% loading, is unexpected yet reproducible. One possible explanation may involve a competition between ionic aggregation, as is typically observed with ionomers (37), and the interaction of the ionic groups with the polyamide. This phenomenon is similar to results observed by Beck Tan and co-workers with sulfonated polystyrene/poly(2-vinylpyridine) blends (38) and is currently under further investigation.

**Extrusion Blends**

**Thermal and Mechanical Properties**

As a result of strong phase separation, the base blend of 50/50/0 T40/PETG/SPETG was extruded with great difficulty and exhibited large die swell and very poor melt strength. However, incorporations of the SPETG as a minor-component compatibilizer even at loadings as low as 2% provided substantially better melt strength. While all of the ternary blends remained opaque, the extrusions were all carried out successfully, incorporating varying amounts of each of the ionomers as a minor-component compatibilizer.

Figure 4 shows the tan $\delta$ vs. temperature curves from the dynamic mechanical analysis of the T40/PETG/5.5SPETG ternary blends, illustrating the effect of incorporating SPETG as a minor-component compatibilizer on the $\alpha$-relaxation of the respective phases. The appearance of two distinct $\alpha$-relaxations for all blend compositions reflects the presence of a phase-separated morphology in the ternary blends. While the peaks are shifted slightly toward each other, indicating intermolecular interactions, no further shift in peak position is observed with increases in ion content or ionomer composition in the blend. However, investigation of the intensity and breadth of the tan $\delta$ peaks yields several interesting features.

The intensity of the tan $\delta$ peak has been shown to track with the breadth of the transition and the area under the loss modulus curve (39). For a constant tan $\delta$ peak area, an increase in the breadth of the tan $\delta$ peak coincides with a decrease in peak intensity, indicating a wider distribution of relaxation processes contributing to the overall transition (39–41). In the case where the tan $\delta$ peak area changes, a decrease in the area under the loss modulus curve (and corresponding intensity of the tan $\delta$ peak) correlates with a reduction in the main chain mobility of the polymer (39).
The data in **Fig. 5** depicts the intensity of the $\alpha$-relaxation of the PETG phase in the ternary compatibilized blends as a function of the amount of ionomer added. Two sets of data points are shown, illustrating the trends in peak intensity predicted by the rule of additivity (adding SPETG to PETG) and the actual intensity observed in the DMA curves. The calculations predict that as SPETG is added to PETG, the intensity of the $\alpha$-relaxation of the PETG phase should decrease slightly, with a larger decrease predicted for higher-ion-content ionomers. However, the actual peak intensities observed in the tan $\delta$ curves show interesting trends based on the ion content of the ionomer and the ionomer composition in the blend.

The blends incorporating 1.9SPETG as the minor-component compatibilizer show an increase in the intensity of the $\alpha$-relaxation of the PETG phase as the ionomer composition increases. Based on the inherent viscosity data discussed in the **Experimental** section, the ionomers are predicted to have a lower molecular weight, which decreases with increasing ion content, compared to the unmodified PETG. While the intensity of the $\alpha$-relaxation of 1.9SPETG predicts it to have a slightly lower mobility than PETG, blending the two seems to result in the ionomer’s acting as a low-MW analog of the PETG, increasing its mobility through a plasticization effect. As the ion content of the ionomer increases to 3.0%, an increase in the ionomer composition in the blends results in only a very slight increase in the mobility of the PETG phase. While the MW of 3.0SPETG is lower than 1.9SPETG, a less significant plasticization effect is observed with this ion content. This trend may be attributed to the higher ion content, leading to more intermolecular interactions between the PETG phase and the less-mobile T40 phase. Further increase in the ion content to 5.5% results in a greater decrease in the intensity of the PETG $\alpha$-relaxation than that predicted by the calculation. At this ion content, the intermolecular interactions between PETG and T40 are sufficient to overcome any plasticization effect, and the lower MW of the ionomer allows it to more easily diffuse to the interface. Though not shown, analysis of the $\alpha$-relaxation of the T40 phase shows the opposite behavior with an increase in its mobility as the ion content of the ionomer increases.

Tensile testing of the SPETG compatibilized blends illustrates the effect of compatibilizer on the mechanical properties of the blends. The modulus, strain at break and yield stress for the compatibilized blends are all increased compared to the uncompatibilized blend (**Table 1**). Though the ionomer has a modulus comparable to PETG and a very low strain at break ($< 2\%$), incorporation of ionomer into the blends as a compatibilizer increases the modulus of the blend to a value just below that of pure T40 and also increases the strain at break of the immiscible blends. The effectiveness of the ionomer as a compatibilizer increases with increasing ion content. While the mechanical properties of the ternary blends with 1.9 and 3.0SPETG as the compatibilizer drop off above 10% ionomer incorporation, the enhanced

![Fig. 5. Calculated (from additivity) and actual intensity of the $\alpha$-relaxation of the PETG phase in T40/PETG/SPETG blends as a function of ionomer composition in the blends and ion content. (●) Calculated–1.9, (▲) Calculated–3.0, (■) Calculated–5.5, (♦) Actual–1.9, (▲) Actual–3.0, (●) Actual–5.5.](image)

**Table 1. Mechanical Properties of SPETG Compatibilized T40/PETG Blends.**

<table>
<thead>
<tr>
<th>Blend System</th>
<th>% Ionomer</th>
<th>Modulus (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>Strain at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durethan T40</td>
<td>—</td>
<td>1200 ± 10</td>
<td>99 ± 0.9</td>
<td>63 ± 19</td>
</tr>
<tr>
<td>PETG</td>
<td>—</td>
<td>820 ± 5</td>
<td>49 ± 0.2</td>
<td>119 ± 11</td>
</tr>
<tr>
<td>T40/PETG</td>
<td>0</td>
<td>1040 ± 10</td>
<td>52 ± 1.0</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>T40/PETG/1.9SPETG</td>
<td>2</td>
<td>1130 ± 10</td>
<td>61 ± 0.7</td>
<td>20 ± 1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1130 ± 10</td>
<td>58 ± 0.4</td>
<td>21 ± 6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1120 ± 10</td>
<td>58 ± 0.9</td>
<td>20 ± 7</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1125 ± 20</td>
<td>41 ± 9</td>
<td>5 ± 2</td>
</tr>
<tr>
<td>T40/PETG/3.0SPETG</td>
<td>2</td>
<td>1150 ± 10</td>
<td>60 ± 4</td>
<td>12 ± 5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1140 ± 10</td>
<td>60 ± 1</td>
<td>19 ± 4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1130 ± 30</td>
<td>51 ± 6</td>
<td>6 ± 1</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1150 ± 5</td>
<td>60 ± 1</td>
<td>11 ± 3</td>
</tr>
<tr>
<td>T40/PETG/5.5SPETG</td>
<td>2</td>
<td>1130 ± 10</td>
<td>62 ± 0.4</td>
<td>18 ± 3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1140 ± 10</td>
<td>64 ± 0.5</td>
<td>24 ± 3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1130 ± 10</td>
<td>63 ± 0.8</td>
<td>23 ± 5</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1170 ± 5</td>
<td>67 ± 0.4</td>
<td>20 ± 3</td>
</tr>
</tbody>
</table>
mechanical properties observed with 5.5SPETG are maintained up to 25% incorporation.

**Blend Morphology**

The phase morphology of the injection molded blends was characterized using ESEM with the PETG/SPETG phase etched using chloroform after freeze-fracturing. Figure 6 illustrates the effect of ionomer composition in the blend on the domain sizes of the dispersed phase as shown by ESEM. The uncompatibilized T40/PETG blend showed gross phase separation with a wide range of domain sizes centered around 10 μm. The wide distribution of domain sizes is indicative of an uncontrolled morphology without the incorporation of a compatibilizer.

As observed with the solution blends, the utilization of SPETG as a minor-component compatibilizer had a significant effect on the domain sizes of the dispersed phase in the injection molded blends. With all three ion contents, an increase in the incorporation of the ionomer in the blends resulted in a continued decrease in the dimensions of the dispersed phase down to approximately 1–2 μm. To accompany this, the distribution of domain sizes became narrower with increased ionomer incorporation, indicating a more stable, controlled morphology. The domain sizes decreased to submicrometer dimensions with the incorporation of 25% ionomer.

The ESEM micrographs in Fig. 7 show the effect of ion content on the morphology of the compatibilized blends. At constant ionomer composition in the blend, the domain sizes decreased with an increase in the ion content of the ionomer. These results indicate that the ionomeric functionality yields a decrease in the phase-separated domain sizes, which may be attributed to a reduction in the interfacial tension between the blend components as the ionomer acts as an interfacial compatibilizer. While all the blends with 1.9 and 3.0SPETG showed a matrix/droplet morphology, incorporation of 5.5SPETG above 5 wt% resulted in the disintegration of...
the samples in the etching solvent. This behavior is attributed to a pronounced shift in the morphology to a co-continuous structure as seen in Fig. 7D.

The observation of a co-continuous morphology in blends containing the 5.5SPETG ionomer may be rationalized through a consideration of the relationship between interfacial tension and co-continuity. The effect of interfacial tension and incorporation of a compatibilizer on blend morphology has been studied in several reports (42–47). While early theories predict a phase inversion point (in the vicinity of a 50/50 volume ratio) based on the viscosity ratio of the two blend components (48–51), Willemse and co-workers have recently developed a model that predicts a co-continuous region (range of compositions) based on geometrical and micro-rheological requirements (42, 43). In this model, the formation of a co-continuous network requires the dispersed phase to be depicted by a series of randomly oriented rod-like particles at their maximum packing density and where coalescence has occurred at all cross-over points. The lower limit of volume fraction of the minor phase necessary for phase co-continuity ($\phi_{cc}$) can be calculated by combining the equations for the maximum packing density of randomly oriented rods with the capillary number describing the stability of elongated structures:

$$\frac{1}{\phi_{cc}} = 1.38 + 0.0213*\left(\frac{\eta_m \gamma}{\sigma} R_o\right)^{4.2}$$  \hspace{1cm} (3)

where $\eta_m$ is the matrix viscosity at the blending conditions, $\gamma$ is the shear rate, $\sigma$ is the interfacial tension and $R_o$ is radius of the minor phase. With the lower limit for phase co-continuity proportional to the interfacial tension, a decrease in the interfacial tension leads to a broader co-continuous region. Experimental confirmation, with PS/PE and PE/PA6 blends, has shown that the incorporation of a compatibilizer reduces the phase domain sizes and can shift the morphology from droplet/matrix to co-continuous owing to a reduction in the interfacial tension between blend components (44, 45).

Fig. 7. Electron micrographs showing effect of ionomer ion content on blend morphology for 50/45/5 (T40/PETG/SPETG) blends. (A) No ionomer; (B) 1.9SPETG; (C) 3.0SPETG; (D) 5.5SPETG. Scale bar = 10 \(\mu\)m.
Scott and Macosko (52) have also described the formation of a co-continuous morphology in terms of the formation of sheets or ribbons that subsequently break up into a lace-like structure through capillary, flow, and interfacial tension effects. The lace structure then continues to break up into elongated particles that further break into spherical domains. A decrease in the interfacial tension increases the capillary number and, thus, the lifetime of the lace-like and elongated structures, resulting in a co-continuous morphology. Thus, conclusions from both of these models can be used to accurately describe the behavior of the ionomer-compatibilized blends in the present study. As both the ion content and ionomer loading increase, a shift in the morphology is observed from droplet/matrix to co-continuous. The ionomer serves to reduce the interfacial tension between blend components, resulting in longer lifetimes and enhanced stability of thread-like structures, which form a co-continuous morphology.

**Blend Interactions—Spectroscopic Analysis**

The role of the sulfonate group in the compatibilization of the T40/PETG blends was evaluated using FT-IR spectroscopy. The interaction was isolated by blending T40 with the Na-mSIP monomer since the concentration of sulfonate groups in the SPECTG is below the detection limit of FT-IR. Previous work by Weiss and co-workers used a similar experimental approach to characterize the structure and relative strength of the interactions between the metal sulfonate group of sulfonated polystyrene and the amide groups of a polyamide (14, 53). While the ionic groups aggregate in the neat ionomer, blending with the polyamide homogeneously disperses the sulfonate groups as a result of a complexation between the metal sulfonate group and the amide linkage through an electron redistribution where electron density is transferred from the nitrogen to the sulfonate through the amide carbonyl (14, 53).

The IR spectra of the model T40/m-SIP system are shown in Figs. 8 and 9. In the neat Durethan T40, two carbonyl stretching vibrations (amide I and amide II) are observed at 1650 and 1550 cm$^{-1}$, respectively, as illustrated in Fig. 8A. As the molar ratio of sulfonate to amide approaches 1:1 in the blends of Na-mSIP and T40, the intensity of another peak at 1610 cm$^{-1}$ begins to increase. The region where the new shoulder appears is expanded in Fig. 8B. The spectral behavior shown here is consistent with the results observed by Weiss and co-workers, indicating an interaction involving the carbonyl of the polyamide. As the sulfonate group of the ionomer pulls electron density through the carbonyl group, the polarization of this bond decreases, resulting in a shift of the vibration to lower wavenumbers.

The N-H stretching vibration region is shown in Fig. 9B, and analysis of the spectrum indicates that a large majority of the hydrogens are involved in H-bonding in neat Durethan T40. However, as the polyamide is blended with Na-mSIP, the intensity of the H-bonded N-H stretch at 3300 cm$^{-1}$ decreased while the free N-H stretching vibration at 3550 cm$^{-1}$ increased. With more of the carbonyl groups involved in the ion-dipole interaction with the sulfonate groups, fewer proton acceptor sites are available for H-bonding, resulting in the presence of more free N-H units.

**Mechanism of Blend Compatibilization**

The results of this investigation indicate the ionomer plays a significant role in the compatibilization of immiscible polyester/polyamide blends. The utilization of ionomers as minor-component compatibilizers for immiscible blends creates sites of specific interactions between the blend components, reduces domain sizes, and enhances ultimate mechanical properties. In the
compatibilization of T40/PETG with SPETG, the ionomer has the ability to form interactions with both blend components, lending itself well to serving as a compatibilizer for the inherently immiscible parent blend. The SPETG is PETG modified by adding small amounts of the SIP monomer to incorporate the ionic functionality. The blends of PETG with SPETG are miscible, regardless of ionic content up to 5.5 mol%, owing to favorable interactions between the similar polymer backbones.

Through spectroscopic analysis, an interaction between the amide linkage of T40 and the sulfonate group of the ionomer and its counterion was observed. The interaction involves electron redistribution where electron density is transferred from the nitrogen to the sulfonate group through the carbonyl and counterion. The ionomer acts as a compatibilizer for the T40/PETG through the presence of specific interactions between the ionomer sulfonate group and counterion and the amide linkage of the T40. The Na\(^{+}\)-form of the SPETG ionomer has been shown to have significant effects on the phase morphology and mechanical properties of immiscible polyester/polyamide blends.

**CONCLUSIONS**

The utilization of SPETG as a minor-component compatibilizer has a significant effect on the phase morphology and mechanical properties of PETG/Durethan T40 blends. An increase in the ion content and/or ionomer incorporation results in reduced phase-separated domain sizes as well as increased interphase mixing that restricts the mobility of the PETG-rich phase and increases the mobility of the T40-rich phase. The ionomer also enhanced the ultimate mechanical properties of the blends as a result of increased interfacial adhesion. The utilization of SPETG as a minor-component compatibilizer in the extrusion blends decreased the dimensions of the dispersed phase and shifted the morphology from matrix/droplet to a co-continuous structure at higher incorporations of the 5.5SPETG.

The ionomer acts as a compatibilizer for the T40/PETG through the presence of specific interactions between the ionomer sulfonate group and counterion and the amide linkage of the T40. The Na\(^{+}\)-form of the SPETG ionomer has been shown to have significant effects on the phase morphology and mechanical properties of immiscible polyester/polyamide blends.

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**REFERENCES**

Influence of Ionomeric Compatibilizers

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