Studies on Polymer Blends with Moderate Specific Interactions. 2. Phase Structure of Blends SAN/TPU and SAN/TPU/EVA

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Abstract: This paper deals with morphological studies of binary and ternary blends composed of poly(styrene-co-acrylonitrile) (SAN), polyurethane elastomer (TPU) and poly(ethylene-co-vinyl acetate) (EVA). Selective etching was found necessary to expose the morphologies of the blends. Chloroform or hot acetone, hexane/toluene (2/1 v/v) and NaOH/CH₃OH (1 wt%) were found to be selective etching agents for SAN, EVA and TPU, respectively. SAN and TPU form blends with fine dispersion structure, while SAN and EVA lead to rough phase structure with poor phase adhesion. These results are in accordance with the difference in the mechanical properties of SAN/TPU and SAN/EVA. In addition, for SAN/TPU/EVA blends, if TPU is only a minor component, it is preferentially located at the interphase, playing the role of a compatibilizer. As the amount of TPU increases, the compatibility is gradually improved.

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Key words: polymer blends, morphology, SEM, etching, polyurethane, poly(styrene-co-acrylonitrile), poly(ethylene-co-vinyl acetate).

INTRODUCTION

The morphology and mechanical properties of a polymer blend are governed mainly by the interactions between the component polymers. Usually, strong specific interactions dominating the unfavourable dispersion interaction lead to a single phase, while weak or no specific interactions cause multiphases lacking in interphase adhesion. Both these cases are undesirable for producing rubber-toughened plastics, for which a two-phase structure with low interfacial energy is one of the basic requirements. Based on this consideration, in this series of work it was found that by careful selection of polymer pairs with moderate specific interactions, it was possible to produce multiphase blends with proper phase adhesion. The brittle plastic poly(styrene-co-acrylonitrile) (SAN) and thermoplastic elastomers of different types, polyurethane (TPU) and poly(ethylene-co-vinyl acetate) (EVA), were used to produce binary (SAN/TPU and SAN/EVA) and ternary (SAN/TPU/EVA) blends. The research included the following main aspects: (1) mechanical properties of both the binary and ternary blends and their dependence on the blend composition and chemical structure of TPU; (2) the miscibility, morphology and rheological behaviour of the blends; (3) specific interactions and their dependence on the blend composition and structure determined using Fourier transform infrared (FTIR) band resolution and fitting technology; and (4) the effect on the miscibility and morphology of strengthening specific

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TABLE 1. Etching agents and the corresponding etching conditions for SAN, EVA and TPU

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Etching agent</th>
<th>Etching time (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAN</td>
<td>CHCl₃ or hot acetone</td>
<td>1</td>
</tr>
<tr>
<td>TPU</td>
<td>NaOH/CH₃OH (1%)</td>
<td>7</td>
</tr>
<tr>
<td>EVA</td>
<td>hexane/toluene (2/1 v/v)</td>
<td>1</td>
</tr>
</tbody>
</table>

interactions by introducing sulphonic and tertiary amine groups into SAN and TPU, respectively. As a part of this research, this paper concentrates on the morphology of the blends by developing etching techniques to reveal the phase structure properly.¹⁻³

Although there are many published papers dealing with blends containing TPU,⁴ only a few reports⁵⁻⁷ are related to SAN/TPU blends and no systematic studies on morphology of the blends have been reported.

Scanning electron microscopy (SEM) has been widely employed in studying morphologies of polymer blends because of the advantages of simplicity in sample preparation and direct observation. However, in the studies of blends, what is seen from an SEM micrograph is usually the features or topography of the fracture surface. This also depends on the phase structure and fracture mechanism. Usually, when a sample possesses a distinct two-phase structure with a spherical dispersed phase, protruding spheres and semi-spherical voids may be observed on the fracture surface reflecting the phase structure. However, in many cases the phase structure may be concealed by the complicated fracture patterns on the surface. Therefore, it is often necessary to explore the real phase structure by etching the surface to dissolve or destroy one of the phases. The selection of etching agent for each component and the etching conditions have been of great importance for proper observation of the morphologies.

It was found that blends of SAN/TPU show remarkable mechanical properties, while SAN/EVA presents poor properties.¹⁻² However, the properties of SAN/EVA blends were obviously improved when a small amount of TPU was incorporated. TPU itself

Fig. 1. SEM micrographs of TPU/SAN of different compositions, (a) TPU/SAN 10/90, (b) 20/80 and (c) 30/70, etched with NaOH/CH₃OH (1%), and EVA/SAN of different compositions, (d) EVA/SAN 10/90, (e) 20/80 and (f) 30/70, etched with hexane/toluene 2/1.
possesses microphase separation, which is affected by many factors. The morphologies of the blends, especially ternary ones containing TPU, are usually very complicated. In this paper, efforts have been made to find a suitable etching agent for each component. The morphologies of the blends over a broad composition range for both binary and ternary blends have been clearly observed and the morphologies show a distinct correlation with the mechanical properties.

**EXPERIMENTAL**

**Materials**

Poly(styrene-co-acrylonitrile) (SAN) was from Gaoqiao Chem. Co. with 24.5 wt% of acrylonitrile; poly(ethylene-co-vinyl acetate) (EVA) was from Bayer Co., with 40 wt% vinyl acetate; thermoplastic polyurethane elastomer (TPU) was from Bayer Co., with hard segments based on 4,4'-methylene bis(phenyl isocyanate) (23.1 wt%) and 1,4-butandiol and soft segments based on poly(tetramethylene adipate).

**Blend preparation and SEM observation**

Blending was performed using a two-roll mill at 180–190 °C for 10 min followed by compression moulding at 160 °C and 60 kg cm⁻². The blend samples were fractured after cooling in liquid nitrogen. Observations of the fracture surface were made after treating the samples with the corresponding etching agents using an Hitachi S-520 scanning electron microscope.

**RESULTS AND DISCUSSION**

**Selection of etching agents and etching conditions**

An ideal etching agent should only dissolve or destroy one of the polymer components without any influence on the others. All of the blend components in the present case, i.e. SAN, TPU and EVA, have polar groups showing similar solubility in many solvents. After tedious solubility testing, it was found that hexane/toluene (2/1 v/v) would dissolve EVA only, without any effect on SAN and TPU, while trichloromethane and hot acetone would dissolve SAN only. However, we failed to find a solvent capable of dissolving TPU selectively. Taking advantage of the hydrolysis of the polyester segment of TPU, we succeeded in using NaOH–methanol solution (1 wt%) as the chemical etching agent.

Besides the selection of etching agent for each component, it is also important to find suitable conditions for etching, i.e. concentration of the agents and etching time. Based on a series of tests the best conditions for each component were found and are summarized in Table 1.

**Phase structure of binary blends of TPU/SAN and EVA/SAN**

The morphology of the blends of TPU/SAN over the whole composition range was observed. The etching agents NaOH/CH₃OH and CHCl₃ were used for the cases when TPU and SAN were minor components, respectively. Some typical results for the former case are shown in Figs 1a–c. For the blend of TPU/SAN 10/90, there are many very small holes, about 0.2–0.3 μm in size, randomly dispersed. This indicates fine dispersion of the TPU phase. An apparent increase in both the density and size of the dispersed TPU phase can be observed when the content of TPU increases to 20% (Fig. 1b). Although most of the holes remain spherical in shape, some show a certain degree of deformation. Further change can be seen in the blends with 30% TPU, where most of the dispersed domains become short strips of 0.5–5 μm in size, and some holes reach about 2 μm (Fig. 1c). For blends with TPU as the major component, the etching process with NaOH–CH₃OH may lead to collapse of the surface morphology. Therefore, the blends with TPU as a major component were treated with trichloromethane prior to SEM observation. For the blend TPU/SAN 60/40, the SAN forms a dispersed phase with irregular shape. The length of some of the big domains may reach about 3 μm, while the small ones are less than 0.5 μm. In the blends containing 20% SAN, most of the dispersed domains assume a spherical shape and a size less than 0.5 μm.

With either TPU or SAN as the minor component, the blends always show uniform morphology with fine dispersion of the minor component. The size of the dispersed phase is of the order of a micrometre or less. This fine dispersion is associated with certain specific interactions between the components leading to relatively low interfacial energy. It was reported that blends with TPU ranging from 10% to 30% showed excellent tensile behaviour, giving a favourable combination of hardness and toughness. These outstanding properties can obviously be attributed to the fine two-phase structure revealed by SEM. FTIR and differential scanning calorimetry (DSC) have been used to explore the nature of the interactions and the results will be reported in forthcoming papers.

Since both TPU and EVA are saturated thermoplastic elastomers with polar groups, it is hardly expected...
that blends of EVA/SAN should show much poorer mechanical properties than those of TPU/SAN. Morphology studies of both of the systems have proved helpful for understanding the difference.

Figures 1d–f show the morphologies of EVA/SAN after etching with hexane/toluene. It can be seen that, as in TPU/SAN, EVA forms the dispersed phase when the elastomer is the minor component. However, the phase size is almost one order of magnitude larger than that in TPU/SAN. The phase size increases rapidly and the distribution of the dispersed domains becomes broader as the EVA content increases.

Further FTIR studies have found no indication of specific interactions between the components. It is clear that the EVA/SAN blends show such rough phase structure because of lack of interfacial adhesion. TPU/SAN blends exhibit much finer phase structure, which is caused by the moderate specific interactions between the constituents as evidenced by FTIR and DSC studies.

**Ternary blends of EVA/TPU/SAN**

The phase structure of ternary blends is more complicated than that of binary ones. Many factors, including the composition and interactions of each component pair, affect the final morphology. For simplicity, the morphologies of a series of blends with a constant ratio of 20/80 EVA/SAN, which is called SE20, and different amounts of TPU have been systematically studied with SEM.

Figure 2 shows the morphology of TPU/SE20 over a broad TPU composition range (5 to 80 wt%) after treatment with hexane/toluene to expose the EVA phase. In all cases, EVA (4–19 wt%) forms a spherical dispersed phase. It is interesting to find that as the relative content of EVA decreases by adding TPU, the size of the dispersed EVA phase apparently decreases from 2.0 to 0.2 μm and the particle density increases. This abnormal variation, i.e. phase particle density increasing with decreasing content of the component, can be attributed to the improvement of the compatibility between SAN and EVA because of addition of TPU. It means that in the ternary blends with a minor content of TPU, the TPU plays the role of a compatibilizer. This is probably associated with some degree of hydrogen bonding between urethane groups and carbonyl groups of EVA, leading to lower interfacial energy between EVA and TPU than that between EVA and SAN. DSC studies of enthalpy relaxation in the EVA/TPU blends have presented evidence of some degree of compatibility.

The TPU phase structure of the ternary blends is clearly revealed by etching with NaOH/CH₃OH, as shown in Fig. 3. TPU forms a spherical dispersed phase when it constitutes the minor component. As the

![Fig. 2. SEM micrographs of TPU/SE20 of different compositions showing EVA phase structure: (a) TPU/SE20 5/95; (b) 15/85; (c) 20/80; (d) 40/60; (e) 60/40; (f) 80/20. Hexane/toluene (2/1 v/v) was used as etching agents.](image-url)
Studies on polymer blends, part 2

Fig. 3. SEM micrographs of TPU/SE20 of different compositions showing TPU phase structure: (a) TPU/SE20 5/95; (b) 15/85; (c) 20/80; (d) 30/70; (e) 40/60; (f) 60/40. NaOH/CH$_3$OH was used as etching agent.

content of TPU increases, in general the particle density increases and size decreases. The particles are mostly under 0.5 μm for TPU contents ranging from 5 to 30%. This means that TPU/SAN blends possess low interfacial energy leading to a fine dispersion. The most remarkable feature of this series of micrographs is shown in Fig. 3a, where TPU content is only 5%. After etching, besides some semi-spherical voids, there are a lot of rings, which surround dispersed spheres on the sample surface. Since here only TPU can be destroyed and extracted, it is reasonable to conclude that the remaining spheres surrounded by the void rings are associated with the EVA phase. The presence of the rings provides a clear indication that TPU is preferentially located between the EVA dispersed phase and the SAN matrix. The formation of this kind of phase structure is believed to be caused by the decrease of the interfacial energy. As TPU content increases to 15%, spherical voids become dominate (Fig. 3b). This indicates that, besides being present between the phases, TPU forms its own dispersed phase. From Figs 3a–d it is clearly seen that the dispersed phase becomes smaller and smaller as the TPU content increases from 5 to 30%. For TPU contents of 40 and 60%, the density of the voids apparently increases, indicating the tendency to form a continuous phase of TPU. For TPU as the major component, etching may cause denudation of the surface, so the micrograph of Fig. 3f may not reflect the true phase morphology.

Figures 4a–f show the phase structure of the blend TPU/SE20 over the whole composition range with emphasis on the location and shape of the SAN phase. For the blends with SAN as the major component, sequential etching with hexane/toluene and NaOH/CH$_3$OH was used to remove both EVA and TPU. The main feature shown in Figs 4a–d is that the size of the dispersed phase apparently decreases with increasing total amount of the elastomers and the relative content of TPU to EVA. As discussed above, this size variation reflects two factors. Firstly, TPU possesses much better compatibility with SAN than does EVA and secondly, TPU can play the role of compatibilizer for EVA and SAN. In the cases where SAN is the minor component, etching with hot acetone exposes the SAN phase structure (Figs 4e and f). For the case shown in Fig. 4e, TPU at 60 wt% is believed to form a continuous phase. The dispersed phase of SAN (32 wt%) possesses an irregular shape showing a tendency towards continuity. As the amount of the dispersed component, SAN, diminishes further to 16 wt%, it forms
spherical domains with size mostly less than 1 μm. This is further evidence of the good compatibility of TPU and SAN.

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REFERENCES