Phase Distribution of Polymers in Immiscible Polymer Alloy without Compatibilizer

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ABSTRACT: The phase separation of PS/SAN/PPE (polystyrene/acrylonitrile-styrene copolymer/polyphenylene ether) immiscible alloy and the distribution of PPE into the separated phases in the alloy have been studied in detail. The profiles of the loss modulus clearly showed the phase separation, and the structure of the alloy could be designed by the assistance of the viscoelastic information. The immiscible alloy composed of PS, SAN, and PPE showed high distortion temperature, good fluidity, and high flexural strength even in the absence of the compatibilizer. PPE distributed into the two phases and played a role of a compatibilizer. The PS/PPE phase led to the high distortion temperature and the SAN/PPE phase brought about the high mechanical strength. The distribution constant of PPE in PS and SAN phases was measured and showed a constant value (K = 0.50) in the whole region of the alloy composition. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2521–2526, 1998

Key words: alloy; polymer; miscibility; polystyrene; polystyrene-acrylonitrile copolymer; polyphenylene ether; equilibrium constant; recycling

INTRODUCTION

Polymer alloys can be classified into two groups with respect to mutual miscibility of the polymers composed of the alloys.¹ One is a group of the miscible alloys, such as a polyphenylene ether (PPE)/polystyrene (PS) blend, and the other is the alloys which have been known as the immiscible alloys.² The immiscible alloys were considered to be very promising materials at the initial stage of the research, because the excellent characteristics of the plural polymers composed of the allow were expected to affect the properties. However, the defects have been gradually revealed as the years passed. Especially, they arose from the fact that the continuity of the two phases on the interface was indispensable for the alloy whose mechanical strength was high enough to apply to structural materials.^{3–5}

There have been many studies on the compatibilizers to improve the continuity between the two kinds of polymer phases.^{6,7} For example, the compatibilizer synthesized from a modified PPE polymer and polyamide (PA) by blending in the twin screw extruder is known as a successful one for the PPE/PA alloy.⁸ Generally speaking, the reactive process is more advantageous than preparing the compatibilizer prior to blending plural polymers, because a more sophisticated procedure is required to synthesize the compatibilizer.⁹

The preparation of the various polymer alloys by reactive processing and the structure of the interface between the immiscible polymers have been researched by our laboratory.¹⁰ This article is concerned with the detailed study of phase separation and distribution of component polymers in the immiscible polymer alloys.

EXPERIMENTAL

Materials

PPE (M_w = 56,000, injection grade), PS (M_w = 270,000, injection grade commercially avail-

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Figure 1 Schematic polymerization process of PPE.

able), and SAN (acrylonitrile-styrene copolymer, AN content = 5-25 wt %, test products) were provided by Asahi Chemical Industry Co., Ltd. (Japan).

Polymer alloys were prepared by blending in a 25-mm co-rotating twin screw extruder (Werner & Pfleiderer, Germany) at 110 rpm.^{11–13} Process temperatures were varied from 240 to 260°C depending on alloy compositions. Sheets of the press-molded polymers were prepared for tests, then cut into smooth dumbbell-shaped specimens. Before the specimens were used for tests, they were carefully polished by hand to avoid surface crazing.

Method of Mechanical Tests

Flexural tests were performed on an Instron (Model 1127, USA) in accordance with ASTM D790 at room temperature. The apparatus used to measure the viscoelastic properties was designed by Tokyo Seiki Co., Japan. The data were calculated and listed into a personal computer as the temperature, storage modulus, loss modulus, and tan δ .¹⁴ ¹H-NMR spectra were determined with 0.03 wt % PPE in CDCl3 using a JOEL (Japan) GX-400 spectrometer.

RESULTS AND DISCUSSION

Before showing the results of the properties and the phase separation of the alloy, the uniformity of the polymers used in this study will be demonstrated. The polymer structure of PPE is generally seen to be complicated because the polymerization of PPE is classified as an oxidizing polymerization.^{15,16} It is recognized in the field of organic synthesis that the various side reactions occur in oxidizing reactions because a radical process under which the high selectivity cannot be expected controls the oxidizing reactions. The schematic polymerization process of PPE is shown in Figure 1.

The process is summarized in Figure 1 where the monomer, 2,6-dimethylphenol, is polymerized under metal/amine catalyst and oxygen atmosphere. Oxygen does not participate in the polymerization, but regenerates the copper, which has worked as an electron acceptor from the monomer. Therefore, the polymerization does not proceed by a radical process, but by an ionic one. The selectivity of the polymerization to the side reaction by which bis-hydroquinone is synthesized is very high. The contents of hydroquinone and other by-products are generally < 1 wt % in the polymer solution. However, the polymer reactions such as graft polymerization of side methyl groups could possibly be side reactions; the relatively simple structure of the PPE main chain in this study was observed by ¹H-NMR, as shown in Figure 2.

The peaks owing to six methyl protons and two phenyl protons are clearly observed and other proton signals are too small to find in such an NMR chart.¹⁷

The uniformity of SAN copolymerization is also important for this study because the miscibility depends on the AN contents in an individual SAN polymer chain as well as the average contents in the whole copolymers. The radical reactivity ratio, which is generally represented as r1 and r2, should be taken into account in order to prepare the uniform copolymerization.¹⁸ The common



Figure 2 ¹H-NMR chart of PPE.



Figure 3 AN content distribution in copolymer polymerized by a tapping method.

method by which the uniform SAN can be prepared is a tapping method, where styrene and AN are fed to the reactor to keep the theoretical AN contents calculated using the reactivity ratio. The AN content distribution of the copolymer is shown in Figure 3.

The AN content was nearly 12 wt %, which was the target content of the polymerization. Figure 4 shows the same chart where SAN was polymerized by a continuous feedback method.

The AN content distribution in copolymer polymerized by a continuous feedback method was much more narrow than by a tapping method. It illustrates the distinct regulation is required when the uniform structure of SAN copolymer is necessary, such as this article.

The miscibility can be easily observed by viscoelastic measurement. Two obvious peaks are recognized when two polymers are perfectly immiscible and the peak shifts and peaks when the polymers are miscible. Figure 5 shows the typical viscoelastic chart where three loss modulus curves represent the temperature dependence on



Figure 4 AN content distribution in copolymer polymerized by a continuous feedback method.



Figure 5 Loss modulus peaks of PPE, PS, and PPE/PS = 50/50 alloy.

the loss modulus of PPE, PS, and PPE/PS alloy. The PPE/PS alloy is a typical example of perfectly miscible alloys and the loss modulus has a narrow single peak.

AN 9 wt % SAN is known as the miscible polymer with PPE, as described in our previous article. The shift of the loss modulus peaks was measured and illustrated in Figure 6.

The peak temperatures shifted from $\sim 115^{\circ}$ C to 215° C with increasing PPE contents in the alloy. Each peak is single, which means the alloy is miscible in the whole region of PPE and SAN contents. As the AN contents in SAN copolymer increase, the mutual relation between these two polymers changes from miscible to immiscible, and the loss modulus peak splits into two peaks, as shown in Figure 7.

Six peaks could be recognized in Figure 7. The peaks of neat polymers, PPE and SAN, were



Figure 6 Shift of loss modulus in the case of PPE/SAN alloys where AN content in the SAN is 9 wt %.



Figure 7 Loss modulus peaks of PPE/SAN alloys.

sharp. Peaks of PPE/SAN (AN 4.9–9.5 wt %) were single, but the peak of PPE/SAN (AN 12 wt %) is double (123°C and 212°C). The peaks of the alloys in SAN in which AN contents were < 10 wt % are single. However, the widths of the peaks were broader than those of neat polymers, PPE and SAN, suggesting that the structures of the alloys were less uniform than the neat polymer because the width means the distribution of the chains.

During these studies on the viscoelastic measurements, we found that the profiles of the phase separation could be controlled by using SAN of high AN contents and adding PS in the alloy. For example, SAN composed of 25 wt % AN is immiscible both with PPE and PS. So, there were two peaks of the loss modulus in the case of PPE/SAN (25 wt % AN) and PS/SAN (25 wt % AN). When the same amounts of PS and SAN (25 wt % AN) were blended and successively the same amounts of the alloy and PPE were blended, the two peaks were observed as illustrated in Figure 8.

The temperature of SAN (25 wt % AN) was 115°C and that of PPE could be recognized at $\sim 215^{\circ}$ C. The peak of PPE/SAN/PS alloy was split into two, one of which was near that of SAN (25) wt % AN) and another was not clearly seen, but it appeared to be near the PPE peak for the loss modulus increased with temperature from 180°C. Two peaks of PPE/SAN/PS (called PAP in this article) were observed and considered to be corresponding to two phases in the alloy, whereas PPE and PS are immiscible with SAN, and PPE and PS are mutually miscible. Namely, two peaks, miscible PPE/PS and SAN, were predicted. However, the peak at lower temperature was not the same as the SAN peak. It was necessary to clarify the compositions of the two phases by chemical analysis or other relevant methods.



Figure 8 Loss modulus peaks of PPE/SAN/PS alloy and related polymers.

Various blends have been attempted, and one of the best compositions was selected: it was PAP (PPE/SAN/PS = 50/25/25) where SAN contained 9 wt % AN, which was miscible with PPE and immiscible with PS. The loss modulus curves are shown in Figure 9.

The two peaks for each PAP alloy were observed. The peak at lower temperature was due to the chain motion in the AN phase because the height was proportional to AN contents in the PAP alloy. The higher peak was due to that in the PS phase for the same reason. It can be predicted from the profiles that the phase separation can be controlled by contents of AN in the SAN copolymer and each polymer in the PAP alloy. Figure 10 shows the flexual strength of PAP alloys as a function of AN contents in SAN.

PPE and PS are immiscible with SAN containing more than 10 wt % and 5 wt % AN, respec-



Figure 9 Loss modulus of PS/SAN/PPE alloy for four compositions.



Figure 10 Flexural strength of PPE/SAN alloys and PAP alloys as a function of AN contents in SAN.

tively. The flexural strength of the PPE/SAN alloys fell rapidly in the region where the phase separation occurs because the weak bonding between the two phases separated as the result of a nonconnecting compatibilizer. However, the decrease of the strength for PAP alloys was much less than that for the PPE/SAN alloy, as shown in Figure 10. The much smaller decrease represents the existence of an interface region by which two phases are bonded strongly because the tensile and flexual strength are the most strongly dependent on the interface structure of the immiscible alloys. The stress has to transfer across the interface in order to avoid the fracture.

The structure and separation process can be inferred from the results of viscoelastic and mechanical properties. PS and SAN phases separate by mutual immiscibility, and PPE distributes into the two phases. PPE does not perfectly diffuse into two phases and the residue of PPE exists in the interface region, which acts as the compatibilizer.

The distribution constant of PPE in two phases was measured and listed in Table 1.

In Table I, C1 and C2 are the ratios of PPE/ SAN and PPE/PS in the SAN and PS phases, respectively. The equilibrium constant (K) was obtained by C2 dividing C1, and was approximately constant in the whole region; thus the activity coefficients of the three polymers were constant in the melting state. This result includes several important suggestions. For example, it shows the principle of the distribution of the polymer into the separated phases, the thermodynamic property of a melted polymer, and the possibility of a new method for analyzing the structure. These issues will be the focus of future investigation.

PPE can be called a compatibilizer for a PAP alloy as well as one of the major components in the alloy, but this is not suitable. The definition of a compatibilizer is a chemical, such as a surface activation reagent, by which a polymer that is inherently immiscible can disperse into the matrix of another polymer. It is not a major component, of course. So, PAP is one of the immiscible alloys without a compatibilizer.

One of the purposes of this article is the preparation of an "immiscible alloy without compatibilizer." It is very useful for the reduction of production cost and recycling materials.

Two concepts should be emphasized. One is that commonly used polymers such as PS and SAN are generally added to engineering plastics such as PPE because the cost of the alloy decreases by adding lower-priced plastics. However, PPE is added to the PS/SAN immiscible alloy here. It causes the cost to increase, but the alloy is very valuable in the industrial field. The mixing procedure is one of the main costs in producing plastic alloys, not the cost difference of component polymers.

The other is that the alloys without compatibilizer are expected to be suitable for recycling systems of waste plastics. Generally speaking, the chemical structure of the compatibilizer is so com-

| Composition (wt) | | | (PPE + PS) Phase | | | (PPE + SAN) Phase | | | $(\mathbf{DDF} \perp \mathbf{DS})$ |
|------------------|-----|----|------------------|-----------------|------|-------------------|-------|-------------|------------------------------------|
| PPE | SAN | PS | T_{g} | PPE/PS Ratio | C2 | PPE/SAN Ratio | C1 | $C1/C2^{a}$ | $\frac{(PPE+PS)}{(PPE+SAN)}$ |
| 50 | 40 | 10 | 182 | 73/27 = 27 /10 | 0.73 | 23/40 | 0.365 | 0.500 | 37/63 |
| 50 | 30 | 20 | 172 | 64/36 = 36 /20 | 0.64 | 14/30 | 0.318 | 0.497 | 56/44 |
| 50 | 25 | 25 | 170 | 61/39 = 39 /25 | 0.61 | 11/25 | 0.306 | 0.502 | 64/36 |
| 50 | 15 | 35 | 164 | 56/44 = 44.5/35 | 0.56 | 5.5/15 | 0.268 | 0.479 | 80/20 |

Table I Distribution Constants of PPE in Two Phases

^a Distribution coefficient; average = 0.495.

plex that it can not be re-used. The procedure of using the compatibilizer is very complicated, which increases the cost. For this reason, the alloys without compatibilizers are very useful for recycling systems.

The further study of the alloys is expected to elucidate the structure and to be an incentive for preparing other alloys and polymer materials.

CONCLUSION

An immiscible alloy without a compatibilizer could be prepared by controlling the distribution of PPE in PS and SAN phases which were mutually immiscible. PPE distributed into the two phases and played a role of a compatibilizer. It showed high distortion temperature and high flexural strength. The PS/PPE phase led to the high distortion temperature and the SAN/PPE phase brought about the high mechanical strength. The distribution constant of PPE to PS and SAN phases was observed, and it shows a constant value (K = 0.50) in the whole region of the alloy composition.

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