Properties of Immiscible Polymer Alloys without Compatibilizer

HIROSHI HACHIYA, SHIGEKI TAKAYAMA, KUNIHIKO TAKEDA

Department of Materials Science, Shibaura Institute of Technology, 3-9-14, Shibaura, Minato-ku, Tokyo 108, Japan

Received 11 November 1997; accepted 20 May 1998

ABSTRACT: The miscibility and properties of the alloys composed of polyphenylene ether (PPE), polystyrene (PS), and acrylonitrile-styrene (SAN) polymers have been studied. The heat distortion temperature and flexual strength decreased with increasing AN contents in SAN in PPE/SAN alloys because the mutual solubility was poor in the high-AN content region. However, PPE/PS/SAN alloys showed higher heat distortion temperature and higher flexural strength than the PPE/PS miscible alloy and the PPE/SAN immiscible alloy. Furthermore, the PPE/PS/SAN alloy has excellent fluidity. It is a kind of immiscible alloy without a compatibilizer, which shows the excellent properties. The results suggested that there is a so-called "entanglement phase" between two separated phases and PPE distributed to both phases, and this phase is superior to that in which compatibilizer was added to enhance miscibility. Moreover, it is very useful for recycling materials because it does not contain a sophisticated compatibilizer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2515–2520, 1998

Key words: alloy; blend; miscibility; compatibilizer; recycle; polyphenylene ether; polystyrene; acrylonitrile-styrene copolymer

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 alloy 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

Correspondence to: H. Hachiya (takedak@sic.shibaura-it.ac.jp).

Journal of Applied Polymer Science, Vol. 70, 2515-2520 (1998)

^{© 1998} John Wiley & Sons, Inc. CCC 0021-8995/98/122515-06



Table I Miscibility of PS, PPE, SAN, and Related Polymers

article is concerned with the immiscible polymer alloys by using the polymer distribution between the two polymer phases in place of a compatibilizer.

EXPERIMENTAL

Materials

PPE ($M_w = 56,000$, injection grade), PS ($M_w = 270,000$, injection grade commercially available), 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 and tensile tests were performed on an Instron (Model 1127, USA) in accordance with

ASTM D790 and D638, respectively, at room temperature. Heat distortion temperature (HDT) tests have been achieved by ASTM D648. The apparatus used to measure the viscoelastic properties was designed by Toyo Seiki Co., Japan. The data were calculated and listed into a personal computer as the temperature, storage modulus, loss modulus, and tan δ .¹⁴ The morphology of the alloys was observed by a scanning electron microscope (Topcon SEM 500, Japan).

RESULTS AND DISCUSSION

Before showing the results of this study, the mutual miscibility of PPE, PS, SAN, and related polymers is summarized and shown in Table I.

PPE is perfectly miscible with PS and partly miscible with SAN. SAN including 10 wt % or more AN is immiscible with PPE, which is hydrophobic, because the copolymerization of AN makes the copolymer hydrophilic. A similar tendency is observed in the case of PS, where PS is partly miscible with SAN. However, a small difference is observed in the case of PPE/SAN and PS/SAN, where \sim 7 wt % SAN is not miscible with PS, but miscible with PPE.

The HDT, which can represent a fundamental property of the alloys, was measured as a function of the AN content in SAN. The results are shown



Figure 1 HDT of PPE/SAN alloys as a function of AN contents in SAN.

in Figure 1. HDT fell in the region of AN 10% from 128°C to 102°C.

The flexural strength showed the same tendency as HDT as a function of AN contents in SAN copolymer. It fell from 130 to 72 Mpa, as shown in Figure 2.

Short shot pressure (SSP), the minimum filling pressure of the injection molding at a special mold, is shown in Figure 3.

SSP decreased from 8.6 to 4.2 Mpa with increasing AN content in SAN. The change was advantageous against the decreases of HDT and flexural strength adversely affected on the performance of the alloys. The changes were typically attributed to the phase separation in the alloy with increasing AN content in SAN. Two phases were observed by SEM. The two phases were not



Figure 2 Flexural strength of PPE/SAN alloys as a function of AN contents in SAN.



Figure 3 SSP (short shot pressure) of PPE/SAN alloys as a function of AN contents in SAN.

connected by the compatibilizer, for it was not blended to the alloys. Many studies have already reported that the mechanical strength of the immiscible alloy dropped without a compatibilizer which can connect two phases.¹⁵ The decrease of SSP apparently resulted when the two phases separated in the injection mold and the structure of the alloy was destroyed by a very strong shear stress.

The three-component alloy was prepared after the blend ratio of those polymers had been attempted and the viscoelastic properties of the alloys had also been measured in order to consider the phase separation. The detailed study on viscoelasticity of the alloys elucidates the phase separation of PPE/SAN and PPE/SAN/PS alloys.¹⁶ When an alloy is perfectly miscible, the peak of the loss modulus is



Figure 4 Loss modulus of PPE, SAN (25 wt % AN), their alloys, and PPE/SAN/PS alloys.



Figure 5 HDT of PPE/SAN/PS alloys as a function of AN contents in SAN.

single. It splits into two peaks at an immiscible alloy. The loss modulus of four kinds of polymers and alloys are shown in Figure 4.

The temperature of SAN (25 wt % AN) was $\sim 115^{\circ}$ C and that of PPE could be recognized at \sim 215°C. The peak of PPE/SAN was split into two, one of which was near that of SAN (25 wt %AN) and another was not clearly seen, but it seemed to be near PPE peak, for the loss tangent increased with temperature from 180°C. Two peaks of PPE/SAN/PS 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, one of which is that of miscible PPE/PS and the other is that of 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.

The HDT of the PPE/SAN/PS alloys did not change in the range from 0 wt % to 25 wt % of AN contents in SAN, as illustrated in Figure 5, despite its decrease shown in Figure 1.

The tendency of the HDT seemed to represent a dramatic change in alloy structure compared to PPE/AS alloys. Flexural strength decreased slightly from 130 to 110 MPa (Fig. 6). It is much smaller than that in the case of PPE/SAN alloys, where the strength fell from 130 to 72 MPa.

The structure of the alloy affected the fluidity in the mold. The SSP decreased with increasing AN contents in SAN, as shown in Figure 7.

The fluidity is usually considered an industrial index of the plastics. However, the fluidity or



Figure 6 Flexural strength of PPE/SAN/PS alloys as a function of AN contents in SAN.

moldability is one of the fundamental properties because it is the great advantage organic materials have compared to metals and inorganic materials. Moreover, the fluidity depends strongly on the structure of the materials. It can be considered as a fundamental property rather than a thermal or mechanical property.

The balance of the properties is illustrated in Figure 8.

The line in Figure 8 represents the property balance of PPE/PS alloys. The fluidity is inversely proportional to the heat distortion temperature because the content of PPE increases in order to raise the heat distortion temperature, and the fluidity of PPE is low. The heat distortion temperature simply depends on the content of the polymer which has higher glass temperature for such miscible alloys. On the contrary, the property bal-



Figure 7 SSP of PPE/SAN/PS alloys as a function of AS contents in alloy.



Figure 8 Relation between thermal property and fluidity of PPE/SAN/PS alloys.

ance of PPE/SAN/PS alloys was apart from that of miscible alloys, as shown in Figure 8. The triangles show the properties of PPE/SAN/PS alloys and the figures on the shoulders show AN contents in SAN copolymer. The remarkable results have been obtained and they were beyond expectations from the ordinary structures of various alloys.

The reason why HDT and flexural strength did not change, and SSP did change by the phase separation in the case of PPE/SAN/PS alloys, is not easily elucidated without detailed analyses of the structure and chemical measurement. However, we can try to imagine the structure of the alloys and the reason for the high performance balance by considering the solubility of the components and the studies on the characteristics of other immiscible alloys.^{17,18} Generally speaking, the diameter of the dispersed phase and the interface bonding of the different phases are very important in designing the immiscible alloy having a high performance balance.¹⁹⁻²¹ For example, PPE and polyamide66 (PA66) alloy, which is one of the famous immiscible alloys, is indispensable to the entanglement phase between the two phases.^{22–25} The entanglement phase is from 20 to 40 nm thick between two phases for the alloy.²⁶ The hard particle made by PPE disperses in the PA66 matrix and hinders the distortion under load. On the contrary, PA66 matrix easily flows at higher temperature because the glass transition temperature of PA66 is relatively low, and the viscosity of the semicrystalline polymer is low at elevating temperature.

In PPE/SAN (AN content < 9 wt %)/PS alloys, PS is perfectly immiscible with SAN and PPE is soluble to both phases. There are two separated phases composed of PS and AS in the initial stage of the processing for preparing the alloys. PPE distributes to both phases by diffusion. PPE is considered not to distribute perfectly to the phases and partly remains and forms the interface region between the two phases. Figures 1 and 2 clearly demonstrate such structure if the relation between the structure and the property is the same as that of the immiscible alloys.

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 more suitable for recycling systems of waste plastics than that using the reactive compatibilizer, because the reactive compatibilizer is difficult to re-use.

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 AS phases which were mutually immiscible. It showed high distortion temperature, high flexual strength, and good fluidity in injection molding. The property balance of the alloy as a structural material improved compared to the miscible alloy relation. The entanglement phase seemed to exist on the boundary of both phases.

The authors are grateful to the research team of the Xylon Development Group in the Asahi Chemical Industry Co., Ltd. for assisting with the measurement and preparation of the alloys.

REFERENCES

 L. A. Utracki, *Two-Phase Polymer Systems*, Hanser Publisher, New York, 1991.

- L. E. Nielsen and R. F. Landel, Mechanical Properties of Polymers and Composites, Marcel Dekker, Inc., New York, 1994.
- C. I. Poser et al., J. Colloid Interface Sci., 69, 539 (1979).
- I. M. Ward, Mechanical Properties of Solid Polymers, John Wiley & Sons, New York, 1971.
- 5. C. B. Bucknall, *Toughed Plastics*, Applied Science Publishers, London, 1977.
- P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
- T. Inoue, J. C. Angoro, Y. Fujita, and T. Sakai, J. Polym. Sci., 26, 807 (1988).
- S. Y. Hobbs, M. E. J. Dekkers, and V. H. Watkins, J. Mater. Sci., 24, 2025 (1989).
- J. L. White, W. Szydlowski, D. Min, and M. H. Kim, Adv. Polym. Tech., 7, 295 (1987).
- S. Takayama and K. Takeda, Advanced Materials '93, 15A, 191 (1994). 194, (1994).
- 11. L. A. Utracki, Polym. Eng. Sci., 22, 1166 (1981).
- H. E. H. Meijer, P. J. Lemstra, and P. H. M. Elemans, Macromol. Chem., Macromol. Symp., 16, 19 (1988).
- J. L. White and K. Min, Macromol. Chem., Macromol. Symp., 16, 19 (1988).

- 14. S. Takayama, A. Ishikawa, and K. Takeda, *Kobunshi Ronbunshu*, **54**, 61 (1997).
- M. Ishikawa, Polymer Preprints, Japan, 41, 3894– 3896 (1992).
- K. Takeda, S. Takayama, and M. Kinoshita, "Polymer Blend and Polymer Composites," 137, 100–106 (1997).
- T. Ohnaga, T. Sato, and S. Nagata, Polymer Preprints, Japan, 42, 3890–3892 (1993).
- 18. N. Ogata, et al., J. Mater. Sci., 28, 3228 (1993).
- C. I. Poser et al., J. Colloid Interface Sci., 69, 539 (1979).
- 20. F. J. Brochard et al., *Macromolecules*, **16**, 1638 (1983).
- 21. S. Wu, J. Appl. Polym. Sci., 35, 549 (1988).
- 22. P. I. Vincent, Polymer, 15, 111 (1974).
- A. F. Yee, Am. Chem. Soc., Div. Polym. Chem., 17, 145 (1976).
- 24. S. Wu, J. Polym. Sci., Part B: Polym. Phys., 27, 723 (1989).
- 25. S. Wu, J. Appl. Polym. Sci., 46, 619 (1992).
- 26. S. Takayama and K. Takeda, Kobunshi Ronbunshu, **50**, 919 (1993).