A New Class of Transparent Polymeric Materials. III. Miscible Blends of Poly(*N*-methylmaleimide-*alt*-isobutene) with Poly(acrylonitrile-*co*-styrene) and the Properties of the Blends

TORU DOI, SATOSHI YUKIOKA, HIROSHI INOUE, AKIRA AKIMOTO

Polymer Research Laboratory, Tosoh Corporation, 1–8 Kasumi, Yokkaichi, Mie 510, Japan

Received 31 May 1996; accepted 19 August 1996

ABSTRACT: The blend miscibility of poly(*N*-methylmaleimide-*alt*-isobutene) [poly(MeMI-IB)] with poly(acrylonitrile-*co*-styrene) (SAN) was investigated by means of measurement of the glass transition temperature of the blends. Poly(MeMI-IB) was found to be miscible with SAN of a specific range of acrylonitrile (AN) contents in the copolymer to produce transparent moldings. The refractive index changed from 1.58 to 1.53 and the dispersion decreased with increasing the amount of poly(MeMI-IB) in the blends. The stress optical coefficient of poly(MeMI-IB) was found to be reduced by the blending of SAN. The glass transition temperature, flexural modulus, and surface hardness of the blends increased with an increase in the amount of poly(MeMI-IB) in the blend. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 925–929, 1997

Key words: *N*-methylmaleimide; isobutene; alternating copolymer; poly(acrylonitrile-*co*-styrene); miscibility; stress optical coefficient

INTRODUCTION

Numerous studies on the copolymerization of maleimide derivatives with various vinyl monomers including styrene, methyl methacrylate, and vinyl chloride have been performed to improve the thermal stability of the products.[1–7] Recently, several polymer blends of various polymers with maleimide copolymers have been also investigated for the same purpose.[8–10] Aoki has reported the blend miscibility of poly(styrene-*co*-*N*-phenylmaleimide) with poly(acrylonitrile-*co*-styrene)(SAN) having various copolymer compositions in detail, and explained the miscibility by the strong repulsion between the two different kinds of monomer units in the copolymer.[10] Dean has reported the blend miscibility of poly(methyl methacrylate-*co*-*N*-phenylmaleimide) with SAN and the use as a heat distortion temperature modifier for SAN and ABS resins.[8] Although the incorporation of maleimide unit such as *N*-phenylmaleimide into the backbone of the vinyl polymers is a useful method to improve the thermal stability, it often caused problems of britleness and discoloration of the resulting copolymers at the same time. The blend of the maleimide copolymers with other polymers results in the same problems. In our previous articles,[13–16] we reported the synthesis and properties of the alternating copolymers of *N*-substituted maleimide with isobutene.Especially, poly(*N*-methylmaleimide-*alt*-isobutene) [poly(MeMI-IB)] was found to have a unique characteristics of optical, thermal, and mechanical properties, i.e., excellent transparency, high heat deformation temperature, and the highest modulus among the typical amorphous polymers. In this article, we reports the blend miscibility of poly(MeMI-IB) with SAN and the optical, thermal, and mechanical properties of the blends.

Correspondence to: Toru Doi

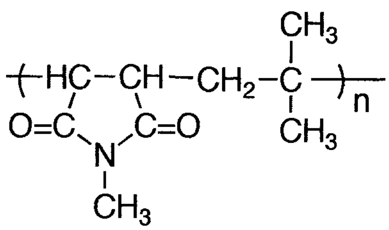
Table I Molecular Characteristics of Poly(MeMI-IB) and SANs

Sample	AN Content (wt %)	$M_n \times 10^{-5}$	M_w/M_n	Refractive Index
Poly(MeMI-IB)	—	1.30	2.1	1.53
SAN-05	6.0	1.20	2.2	1.58
SAN-10	11.3	0.56	2.5	1.58
SAN-20	20.0	0.52	2.5	1.57
SAN-25	25.0	0.67	2.4	1.57
SAN-30	30.0	0.74	2.1	1.56
SAN-45	45.8	0.34	2.2	1.55
SAN-55	56.6	0.16	1.8	1.54
SAN-65	65.6	0.13	1.9	1.53

EXPERIMENTAL

Materials and Procedures

Poly(MeMI-IB) was produced according to the method previously reported.[15] The copolymer thus obtained had an alternating structure of MeMI and IB, as is shown in Scheme 1.



SANs were supplied from Mitsubishi Chemical Co. Ltd. Molecular characteristics of these poly(MeMI-IB) and SANs used here are shown in Table I.

Blends of poly(MeMI-IB) with various SANs were prepared by a melt blending method using a brabender mixer (Laboplustmil, Toyo Seiki K.K.) equipped with a 100 cm^3 sample chamber at 230–250°C for 5 min under a nitrogen stream. Sample sheets were prepared by the hot pressing between steel plates in the range 200–230°C for 5 min and then quenched to room temperature.

Measurements

The number average molecular weight (M_n) and its distribution (M_w/M_n) of the polymers was determined by gel permeation chromatography calibrated with polystyrene standards using Tosoh RE-8000, RI-8000, and UV-8000 instruments equipped with TSK gel G-6000H, G-4000H, G-4000H, and G-2000H columns with chloroform or *N,N*-dimethyl formamide as the eluent at 38°C. The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC200, Seiko Corp.) in a nitrogen stream at a heating rate of 10°C/min. The refractive index and Abbe's number were determined by means of an Abbe refractometer (Atago). The Abbe's number (ν_D) is determined by the following equation:

$$\nu_D = \frac{n_D - 1}{n_F - n_C} \quad (1)$$

where n_C, n_D, and n_F represent the refractive index at 656, 589, and 486 nm, respectively. The birefringence was evaluated as the stress optical coefficient using the following equation:

$$\Delta n = C \cdot \sigma \quad (2)$$

where Δn is the birefringence value, that is, the difference in refractive index between the extensional direction and the crossed direction, C is the stress optical coefficient, and σ is the applied stress. The coefficient C was measured using an Optorheometer (model HRS-100, ORC Seisakusho) at constant strain rate of 1%/s at a temperature 50°C higher than the T_g. The mechanical strength and modulus were determined by means of a Tensile tester (Tensilon UTM-2.5, Toyo Baldwin Co., Ltd.) according to ASTM standards. The surface hardness was measured by means of a Rockwell hardness tester according to ASTM D-785 (M Scale). Water absorption of the polymers was evaluated according to the method of JIS K7114 (immersion in water at 23°C, Sample size; ϕ 50 × 3 mm).

RESULTS AND DISCUSSION

Blend Miscibility of Poly(MeMI-IB) with SANs

The blend miscibility of poly(MeMI-IB) with SAN having various acrylonitrile (AN) contents was

Table II Miscibility of Poly(MeMI-IB) with Various SANs[a]

Sample	T_g (°C)	Appearance
SAN-05	102, 155	Opaque
SAN-10	102, 151	Opaque
SAN-20	105, 151	Opaque
SAN-25	119	Transparent
SAN-30	121	Transparent
SAN-45	107, 147	Translucent
SAN-55	109, 151	Transparent
SAN-65	107, 152	Transparent

[a] Poly(MeMI-IB)/SAN = 1/1 (wt/wt).

investigated by measurement of the glass transition temperature (T_g) using differential scanning calorimetry. The results are summarized in Table II and the typical DSC curves of the blends are shown in Figure 1. The blends of poly(MeMI-IB) with SAN containing 25 and 30% AN exhibited a single T_g value and produced transparent sheets by press molding, while the other blends showed two T_g values. The transparency of the pressed sheets of the blends with SAN containing 55 and 66% AN was due to the matching of the refractive index of poly(MeMI-IB)[13] and SANs, not due to the miscibility. It is concluded from these results that poly(MeMI-IB) is miscible with SAN containing AN of the ranges 25–30 wt %. Figure 2 shows the relationships between the T_g values and the blend composition of poly(MeMI-IB) with SANs having 25 and 30% of AN. All blends showed single T_g value and the T_g of the blends increased monotonously with an increase in the amount of poly(MeMI-IB) in the blends. The solid

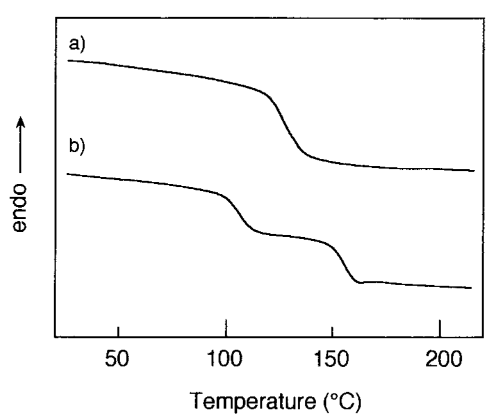


Figure 1 DSC curves of blends of poly(MeMI-IB) with SAN. (a) SAN-25; (b) SAN-55.

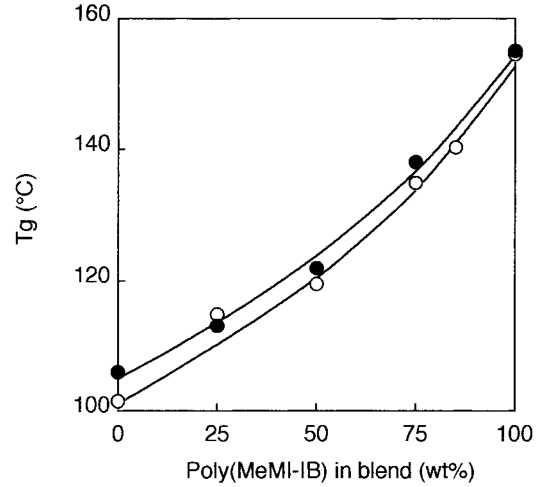


Figure 2 Relationships between T_g and blend compositions. (○) SAN-25; (●) SAN-30.

lines in Figure 2 are the calculated ones according to the Fox relation.[17]

$$T_{gb}^{-1} = w_1 T_{g1}^{-1} + w_2 T_{g2}^{-1} \quad (3)$$

where T_{gb}, T_{g1}, and T_{g2} are T_g of blends, SAN, and poly(MeMI-IB), and w_1 and w_2 are weight fraction of SAN and poly(MeMI-IB), respectively.

These results indicate that the blend systems are completely miscible over the full range of polymer blend compositions.

Optical Properties of the Miscible Blends of Poly(MeMI-IB) with SAN

The miscible blends of poly(MeMI-IB) with SAN containing 25–30% AN in the copolymer gave

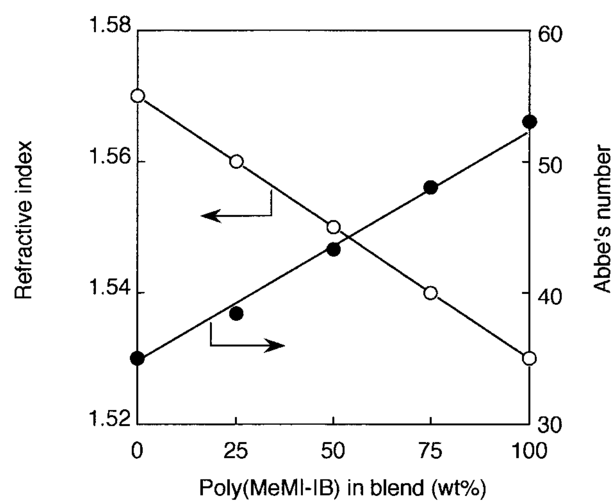


Figure 3 Effect of blend compositions on refractive index and Abbe's number of the blend.

Table III Stress Optical Coefficient of the Blend

Blend Composition (wt%)		Stress Optical Coefficient (Pa^{-1})
Poly(MeMI-IB)	SAN[a]	
100	0	$+2.2 \times 10^{-9}$
80	20	$+9.2 \times 10^{-10}$
60	40	$+2.6 \times 10^{-10}$
0	100	-1.6×10^{-9}

[a] 25% AN.

transparent moldings described above. The effect of the blend composition on the optical properties of the blend was evaluated. The refractive index linearly decreased from 1.58 to 1.53, with an increasing in the amount of poly(MeMI-IB), while the Abbe's number increased from 32 to 52 (Fig. 3). One of our interests in this blend system is to reduce the birefringence of poly(MeMI-IB). Optical birefringence of polymers is an undesirable property, especially in the optical use such as optical lenses and compact discs. It is well known that large birefringence is one of the disadvantages of polycarbonate (PC) compared with that of poly(methyl methacrylate)(PMMA).[18] The stress optical coefficient of poly(MeMI-IB) was the same level as that of PMMA in glass region, and between those of PMMA and PC in rubbery region.[15] It has been reported that miscible blend of positive birefringence polymer ($n_{\parallel} - n_{\perp} > 0$) with negative one ($n_{\parallel} - n_{\perp} < 0$) gives a birefringence-free polymer blend at the specific blend composition.[19,20] Therefore, we also applied this concept to reduction of the birefringence of poly(MeMI-IB). The copolymers of styrene with *N*-substituted maleimides such as *N*-phenyl maleimide and *N*-cyclohexylmaleimide were reported to have negative birefringence value.[20] On the contrary, we reported that poly(MeMI-IB) has a positive stress optical coefficient, that is, positive birefringence in the previous paper.[15] SAN is known to have a negative birefringence.[20] Table III summarized the stress optical coefficient (C) of the blends of poly(MeMI-IB) with SAN-25 measured at the rubbery region (T_g + 50°C). SAN-25 was confirmed to have a negative C value and the absolute value was almost same level of that of poly(MeMI-IB). The C of the blend of poly(MeMI-IB) with SAN-25 was found to decrease with an increasing the amount of SAN-25 and the C of the blend containing 40% SAN-25 was one-ninth of that of poly(MeMI-IB).

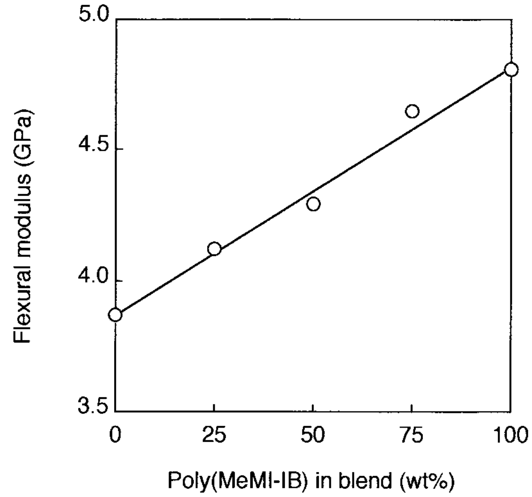


Figure 4 Effect of blend compositions on fluxural modulus.

Other Properties

The other properties of the blends with SAN-25 were also evaluated. The flexural strength, flexural modulus, and surface hardness of the blends are summarized in Table IV and the dependence of the blend composition on the flexural modulus was illustrated in Figure 4. The highest flexural modulus among the common amorphous plastics

Table IV Mechanical Properties of the Blends

Blend Composition (wt %)		Flexural Strength (MPa)	Flexural Modulus (GPa)	Surface Hardness
Poly(MeMI-IB)	SAN			
0	100	95	3.87	83
25	75	112	4.12	91
50	50	128	4.29	96
75	25	130	4.65	100
100	0	137	4.81	103

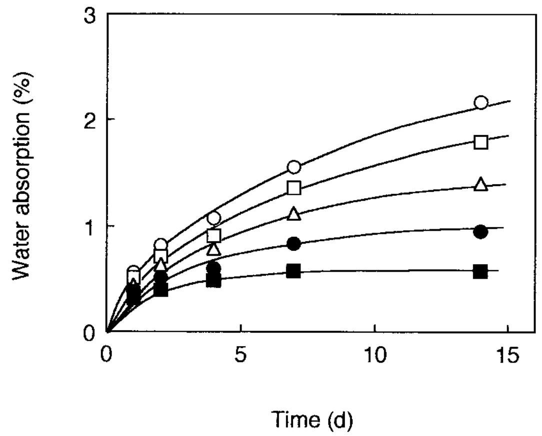


Figure 5 Dependence of immersion time on water absorption at 23°C. [poly(MeMI-IB)]/[SAN-25] = (○) 100/0, (□) 75/25, (△) 50/50, (●) 25/75, (■) 0/100.

is a remarkable feature of poly(MeMI-IB) and the modulus of the blends linearly increased with an increase of poly(MeMI-IB) contents of the blends as well as the flexural strength. Surface hardness of plastics is one of the important practical properties relating the scratch resistance. The surface hardness of SAN was also improved by blending poly(MeMI-IB). Figure 5 shows the time dependence on water absorption of the blends with various blend compositions. Poly(MeMI-IB) showed relatively high water absorption, while SAN showed lower water absorption and saturated within 7 days. The water absorption of poly(MeMI-IB) was found to be improved by blending SAN.

CONCLUSION

Poly(MeMI-IB) was found to be miscible with SAN containing 25–30 wt % AN in the copolymer over the full ranges of the polymer blend composiitons. The resulting blends gave transparent moldings. The refractive index and the Abbe's number are controllable by the selecting blend compositions. It has been demonstrated that the properties of poly(MeMI-IB) and SAN compensate with each other. Namely, the stress optical coefficient and the water absorption of poly(MeMI-IB) were reduced by polymer blend with SAN, and to the contrary, poly(MeMI-IB) improved the thermal resistance, flexural strength, modulus, and surface hardness of SAN.

The authors wish to thank Dr. Akikazu Matsumoto, Osaka City University, for useful discussions during this work. The authors acknowledge Mr. Satoshi Fujii for his excellent technical support and Mr. Kazunori Hagimura for his DSC measurements.

REFERENCES

1. P. O. Tawney, R. H. Snyder, R. P. Conger, K. A. Leibbrand, C. H. Stiteler, and A. R. Williams, *J. Org. Chem.,* **26,** 15 (1961).
2. R. C. P. Cubbon, *Polymer,* **6,** 419 (1965).
3. M. Otsuka, K. Matsuoka, K. Takemoto, and M. Imoto, *Kogyo Kagaku Zasshi,* **73,** 1062 (1970).
4. J. M. Barrales–Rienda, J. I. Gonzales De La Campa, and J. Gonzales Ramos, *J. Macromol. Sci.-Chem.,* **A11,** 267 (1977).
5. M. Urushizaki and H. Aida, *Kobunshi Ronbunshu,* **36,** 447 (1979).
6. M. Z. Elsabee, M. W. Sabaa, and S. Mokhtar, *Polym. J.,* **15,** 429 (1983).
7. A. Matsumoto, T. Kubota, and T. Otsu, *Macromolecules,* **23,** 4508 (1990).
8. B. D. Dean, *J. Appl. Polym. Sci.,* **30,** 4193 (1985).
9. B. D. Dean, *J. Appl. Polym. Sci.,* **33,** 2259 (1987).
10. Y. Aoki, *Macromolecules,* **21,** 1277 (1988).
11. R. Bharel, V. Choudhary, and I. K. Varma, *J. Appl. Polym. Sci.,* **49,** 31 (1993).
12. V. Usha, I. K. Varma, G. C. Bhayani, and T. J. M. Sinha, *Angew. Makromol. Chem.,* **221,** 1 (1994).
13. T. Doi, A. Akimoto, A. Matsumoto, and T. Otsu, *J. Polym. Sci., Polym. Chem. Ed.,* **34,** 367 (1996).
14. T. Doi, A. Akimoto, A. Matsumoto, Y. Oki, and T. Otsu, *J. Polym. Sci., Polym. Chem. Ed.,* **34,** 2499 (1996).
15. T. Doi, Y. Sugiura, S. Yukioka, and A. Akimoto, *J. Appl. Polym. Sci.,* **61,** 853 (1996).
16. T. Doi, N. Ishikawa, and A. Akimoto, *J. Appl. Polym. Sci.,* **61,** 859 (1996).
17. T. G. Fox, *Bull. Am. Phys. Soc.,* **1,** 123 (1956).
18. M. Emmelius, G. Pawlowski, and H. W. Vollmann, *Angew Chem. Int. Ed. Engl.,* **28,** 1445 (1989)
19. B. R. Hahn and J. H. Wendorff, *Polymer,* **26,** 1619 (1985).
20. H. Saito and T. Inoue, *J. Polym. Sci., Polym. Phys. Ed.,* **25,** 1629 (1987).