Effect of Rubber Content in Acrylonitrile–Butadiene–Styrene and Additional Rubber on The Polymer Blends of Polycarbonate and Acrylonitrile–Butadiene–Styrene

Jiann-Shing WU,* Shu-Chen SHEN, and Feng-Chih CHANG

Institute of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, Republic of China

ABSTRACT: Higher ABS rubber content in the polycarbonate (PC)/acrynitrile–butadiene–styrene (ABS) blend resulted in toughness improvement in terms of tensile, Izod impact and strain energy release rate at a cost of higher melt viscosity. The extra-added core-shell rubber particles with poly(methyl methacrylate) (PMMA) or acrylonitrile–styrene (SAN) outer shell resided mainly in the ABS phase and further improved the resulted blends toughness. The addition of styrene–maleic anhydride (SMA) copolymer in the PC/ABS blends caused severe coagulation of the rubber particles in the ABS phase and left a greater fraction of the SAN phase without presence of rubber. The toughness improvement by increasing rubber content must be compensated by the increase of melt viscosity and this fact has to be taken into consideration in selecting the starting materials of the PC/ABS blends.
KEY WORDS Polymer Blend / Polycarbonate / Acrylonitrile–Butadiene–Styrene / Rubber Distribution / Toughness /

The development of rubber-toughened thermoplastic resins is an important contribution to the commerical polymer industry. A small amount of discrete rubber particles in a glassy plastic can significantly improve the crack and impact resistance of normally brittle plastic. Polymer blends of polycarbonate (PC) and acrylonitrile–butadiene–styrene (ABS) provide products with a improved balanced properties at reduced cost in comparison to that of PC. In a typical PC/ABS blend, PC contributes toughness and heat distortion temperature. Besides lower cost, ABS also contributes to improve low temperature toughness, improved physical aging, lower sensitivity to thickness and notch radius, and most importantly-processability.

Since the appearance of the first PC/ABS patent issued nearly three decades ago,[1] blends and alloys of PC/ABS have been some of the most successful commerical polyblend prod-ucts. Numerous key patents have issued[2-12] specifically dealing with many aspects of properties, such as heat distortion temperature, low temperature impact strength, processability, or flame resistance. Fundamental studies of PC/ABS blends in terms of miscibility, mechanical, rheological, morphological, also have been extensively reported in open literature.[13-32] Most literature does not give reasons why the particular PC or ABS was selected in their studies. Selection of these two blending components certainly will influence essentially all the above mentioned properties of the resultant PC/ABS blends. Two of the most important variables in ABS component are the acrylonitrile (AN) in acrylonitrile–styrene (SAN) phase and rubber contents. AN content of the SAN portion of the ABS affects compatibility between PC and ABS and the best compatibility in PC/ABS blends is at approximately 25% AN in SAN although a

---

* To whom correspondence should be addressed.

wider AN range has also been claimed.[20,31] We have reported the effect of PC molecular weight in the PC/ABS blends.[32]

Addition of rubber particle in a binary A/B polyblend will result in several possibilities: in phase A, in phase B, along the interface, or in any of the above combination. The mutual miscibility between rubber and blend components are the most important factor to control the rubber distribution. Processing condition such as sequence of blending can also change the rubber distribution. Rubber distribution is important in dictating the final properties of the resultant blending products and this area has drawn great attention lately. We first discovered the methyl methacrylate–butadiene–styrene (MBS) particles distributed exclusively in PC phase in the polyblends of PC and poly(ethylene terephthalate) (PET) regardless of blending sequence.[33] Hobbs *et al.*[34,35] identified the methyl methacrylate–butadiene–styrene (MBS) rubber particles distributed exclusively in PC phase in PC/PBT blend. We also found the MBS rubber distributed in the styrene–maleic anhydride (SMA) phase in the PC/SMA blends[36] and the thermoplastic polyurethane elastomer (TPE) distributed at the polyacetal–PC interface in the PC/Polyacetal blends.[37] Paul *et al.* found the MBS particles to locate in the interfacial region of a blend of high impact polystyrene (HIPS) and ABS.[38] They later studied the effect of mixing technique and sequence on the distribution of MBS particles in the PS/SAN blend and found that the rubber particles had a strong tendency to locate at the PS–SAN interface.[39] Paul *et al.* again reported MBS rubber particles distributed in SAN or at the PC–SAN interface depending on AN content in SAN in the PC/SAN/MBS blends.[31] Recently we reported the control of the core-shell butylacrylate rubber particles in either PC, PET, or both phases in the PC/PET/rubber blends by incorporating small amount of the reactive glycidyl methacylate monomer (GMA) in the shell portion of the rubber particles.[40] By a similar approach,

we were able to control the rubber particles distributed in PC, nylon, or both in the polyblends of PC/Nylon by employing the MBS rubber with and without containing maleic anhydride monomer in the shell.[41]

The main objective of this study is to get a better understanding the effect of changing rubber content in ABS and thus to provide better guidance for proper selection of ABS in the PC/ABS blends. The other purpose of this study is to understand the phase distribution of the extra added rubber and the resulted toughness improvement.

EXPERIMENTAL

Materials

Natural grade polycarbonate Calibre with melt flow rate (MFR) of 15 was obtained from Dow Chemical Company which was considered as the general purpose product. SAN and three grades of ABS (ABS1, ABS2, and ABS3) with S/AN ratiof 72/28 were kindly donated from Grand Pacific Petrochemical Corp. of Taiwan. Rubber content and other useful information from the supplier are given in Table I. ABS2 and ABS3 were the blended products from SAN and ABS1 by the producer and the ABS4 was from our own laboratory blend by 1 : 1 weight ratio of ABS3 and SAN. Therefore all the ABS products employed in this study contain, more or less, the free and ungrafted SAN. MBS core-shell rubber, Metablend CS-223, was from M & T Chem. HABS, Blendex from Du Pont, is an ABS type rubber that contains 75% butadiene. Other core-shell rubber, EXL 3386, contains acid functional group in the shell which was obtained from Rohm & Haas Co. SMA, Dylark 232, with 11 wt% maleic anhydride is from ARCO Chem. Co.

Melt Blending and Specimens Preparation

Melt blending was prepared by a co-rotating 30 mm diameter twin screw extruder with L/D ratio of 29. The standard ASTM 1/8 inch

Table I. Summarized ABS and SAN Properties from producer

	ABS1	ABS2	ABS3	ABS4	SAN
Rubber content/%	25.5	18.0	12.5	6.3	0
Tensile yeild strength/MPa	38	45	51	—	71
Flexural modulus/GPa	1.91	2.40	2.75	—	3.53
Izod impact notched/JM^{-1}	529	431	216	—	21
Melt flow index ASTM D-1238	0.4	1.1	1.6	—	2.2

[a] Data extracted from materials spec. of the producer, Grand Pacific Petrochemical Corporation.

specimens were prepared by an Arburg 3 oz injection molding machine. The temperatures of extrustion and injection molding were adjusted to give the optimized processing conditions according to the blending compositions and the materials selected. Component weight ratio, PC/ABS = 65/35, was close to most commercially available products and was chosen to study the effect ABS rubber content in this study.

Characterizations

Melt rheology measurements were carried out using a capillary rheometer, model Rheograph 2001, Gottfert, Germany. Detailed procedures for various mechanical properties, tensile, flexural, notched Izod impact at different temperatures, and the critical strain energy release rate (G_c) were described in our previous reports.[42-44] Phase morphologies of the blends were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The specimen fracture surfaces were examined by SEM after etching with 30% KOH aqueous solution up to a maximum of 30 min, rinsing with water, and coating with gold. The TEM thin layer specimens were cut by a microtome and stained with a 2% OsO$_4$ solution for six hours.

RESULTS AND DISCUSSION

Rheological Properties

Considerably studies have been conducted on the rheological properties of polymer blends in the melt state. The rheological properties of polymer blend are important information to optimize processing conditions such as melt extrusion or injection molding. The presence of ABS2 in PC, even at as low as 20%, is able to reduce the melt viscosity significantly and the presence of 35% or higher ABS2 in the PC15/ABS2 blends results in viscosity close or even lower than ABS2.[32] Figure 1 shows the effect of rubber content in ABS by the plots of viscosity *vs.* shear rate of the blends, PC15/ABS = 65/35. Higher rubber content in ABS has a relatively higher viscosity itself and in the corresponding blends. Due to a serious die-swelling problem encountered, the viscosity data obtained from the PC15/ABS4 and PC15/SAN blends were irregular and are not included here.

SEM Morphologies of the Blends

Melt blended immiscible polymer blends possess complicated phase morphologies depending on factors such as interfacial tension, viscosity ratio, viscosity and elasticity of the two phases, volume fraction, temperature and the extent of the applied shearing during melt blending. Breakup of a droplet occurs easier
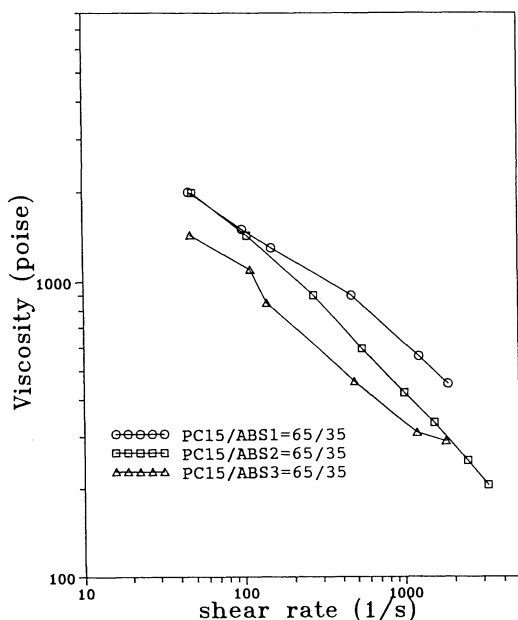
Figure 1. Melt viscosity *vs.* shear rate of PC15/ABS blends by varying rubber content in ABS at 250°C.

when the interfacial tension is low and the viscosity of the continuous phase is high. Large droplets can be broken easier into smaller droplets when the viscosity ratio is close to 1.[45,46] Pieces of one polymer may be drawn into filaments which may remain as filaments or break up into smaller droplets or connect to each other to give an interconnected network. Thus rheologically related morphologies of polymer blends are very complex. By careful control of the solvent etching conditions, the features of phase domains of the blends can be obtained. In our previous paper, we reported the SEM morphologies of the PC15/ABS2 blends with various component ratios and the blends with 65 and 50% PC15 were in co-continuous structure.[32] Figure 2 shows the co-continuous morphologies of the PC15/ABS = 65/35 blends for which the rubber content in the ABS was varied. The more ductile blend with higher rubber content shows finer texture of the ambient fracture surface. Greater surface shear yielding of the more ductile blend reflects in the resultant finer

texture of the etched surface morphology. Besides the above mentioned complex factors dictating the phase morphology, the presence of rubber in this triple blend was reported previously to promote compatibility between PC and SAN.[26]
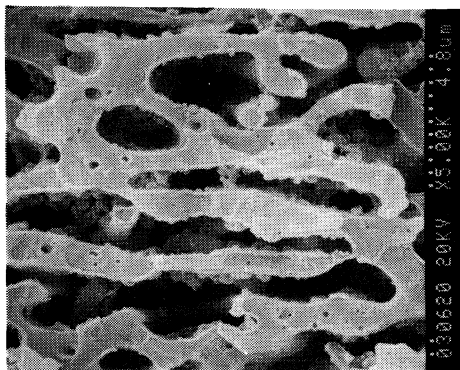
Tensile and Flexural Properties

Table II shows the tensile and flexural properties of the blends, PC15/ABS = 65/35, with various rubber contents in ABS. The higher ABS rubber content in the blend results in lower modulus and lower yield strength but higher elongation to break. The flexural properties obtained have the same trend as the tensile properties as illustrated in Table II.

Izod Impact Properties

The ductile-brittle-transition temperature (DBTT) reflects the low temperature toughness of a material. Figure 3 shows the plots of impact strength *vs.* temperature of the blends, PC15/ABS = 65/35 by varying rubber content in ABS. Higher rubber content in ABS results in lower DBTT and greater impact strength. The blend with SAN (no rubber) fractured in brittle mode even at 40°C. Similar to the rubber-toughened polycarbonates,[43] two separate modes, plane-strain localized energy dissipations and plane-stress mass shear yielding, function simultaneously in the PC/ABS blends. The localized energy dissipations take place mainly near the fracture surfaces with relatively less volume involved. This localized energy dissipations dominate at low temperature plane-strain fracture which may include crazes, rubber cavitations, rubber–matrix or matrix–matrix de-bonding, and localized tear yielding.[47] On the contrary, the mass shear yielding ductile failure dominates at high temperature plane-stress conditions which involves significantly greater volume but less extension ratio relative to the brittle failure.[43]
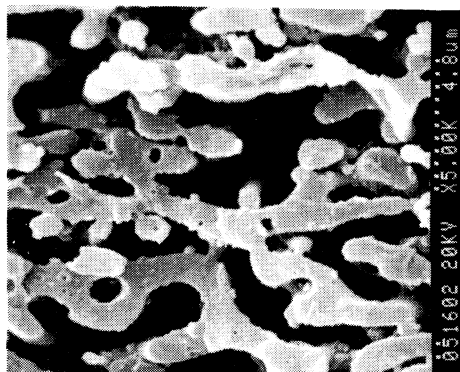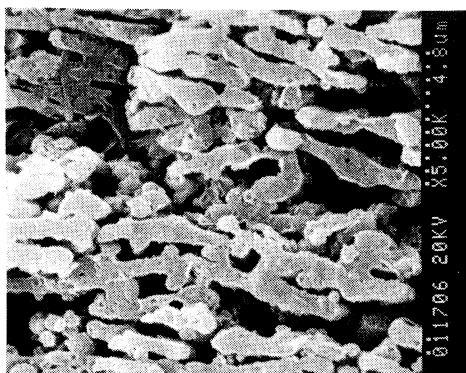
36
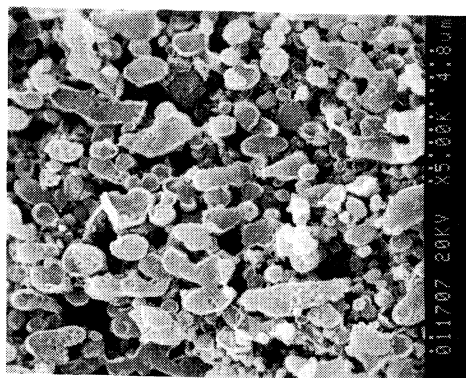
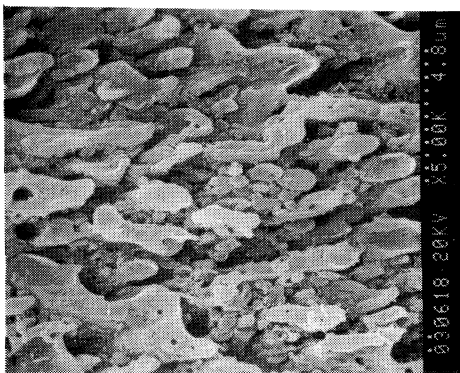2C. ABS3, BR = 12.5%, cryogenic

2F. SAN, BR = 0%, ambient
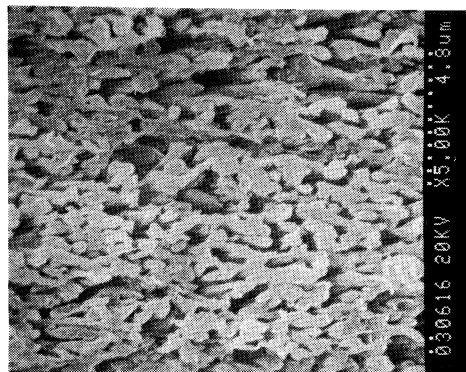
2B. ABS1, BR = 25.5%, ambient

2E. SAN, BR = 0%, cryogenic

2A. ABS1, BR = 25.5%, cryogenic

2D. ABS3, BR = 12.5%, ambient

Figure 2. Cryogenic and ambient fracture surfaces of PC15/ABS = 65/35 blends with various rubber contents in ABS.

Table II. Tensile and flexural properties of PC15/ABS = 65/35 with various rubber content in ABS

	% rubber in ABS				
	0.0	6.25	12.5	18.0	25.5
Tensile testing					
Modulus/MPa	1940	2010	2000	1850	1730
Yield str./MPa	70	67	65	63	57
Elongation/%	32	27	29	35	56
Flexural testing					
Modulus/MPa	2260	2060	2065	2020	1790
Yield str/MPa	97	90	86	84	77
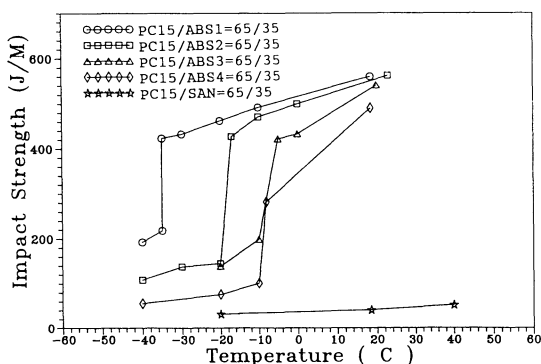
Figure 3. Izod impact strength *vs.* temperature of PC15/ABS = 65/35 blends with various rubber contents in ABS.
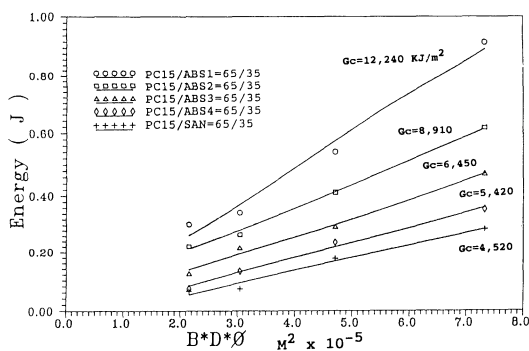

Figure 4. Plots of impact energy *vs.* $B \times D \times \phi$ for PC15/ABS = 65/35 blends with various rubber contents in ABS.

Critical Strain Energy Release Rate, G_c

A fracture mechanics approach by notched impact testing was independently developed by Brown[48] and Marshall *et al.*[49] by assuming the specimen to exhibit bulk linear elastic behavior. The experiments were purposely carried out at low temperature ($-40°C$) and with a sharper notch (0.125 mm notch radius) to meet the criteria of this method as close as possible. Figure 4 shows the plots of fracture energy *vs.* $B \times D \times \phi$ of the blends, PC15/ABS = 65/35, by varying rubber content. B, D, and ϕ are the thickness, width and geometric factor of the specimen. The slope of the straight line is the corresponding strain energy release rate (G_c). The higher rubber content of the blend results in greater G_c as clearly shown in Figure 4. Since

this method was carried under plane-strain brittle fracture conditions, the obtained G_c values of the blends are in the same order as Izod impact strength at brittle mode as shown in Figure 3.

Additional Rubber to Toughen the PC/ABS Blends

The purpose of this part of study is to gain additional toughening effect of the PC/ABS blends and to determine phase distribution of the added rubber. Figure 5 shows the impact strengths of the MBS modified PC15/ABS2 = 50/50 blends at different temperatures. The added MBS rubber indeed decreases the DBTT of the blend and also raises the fracture energy. Figure 6 shows the TEM morphology of the
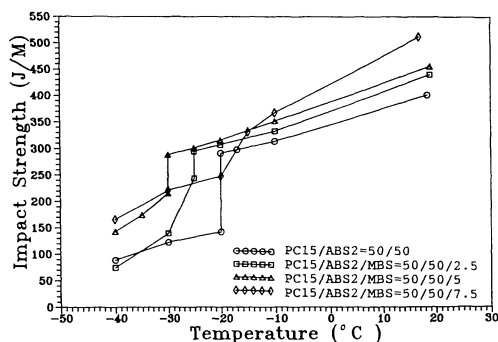
Figure 5. Effect of the extra-added MBS rubber on the Izod impact strength of the PC15/ABS2 = 50/50 blends.

Figure 7. TEM micrograph of PC15/ABS2/MBS = 50/50/7.5 blend.

Figure 6. TEM micrograph of PC15/ABS2 = 50/50 blend.

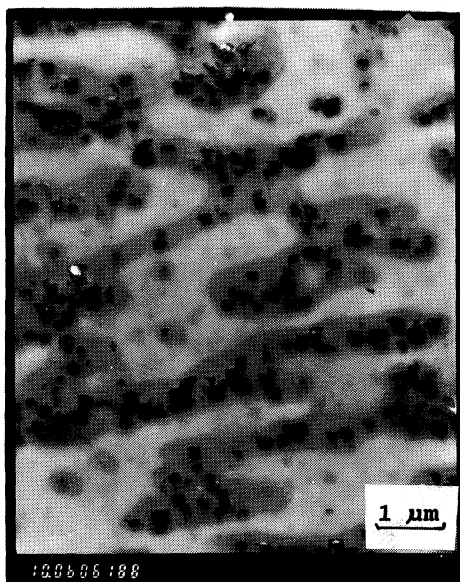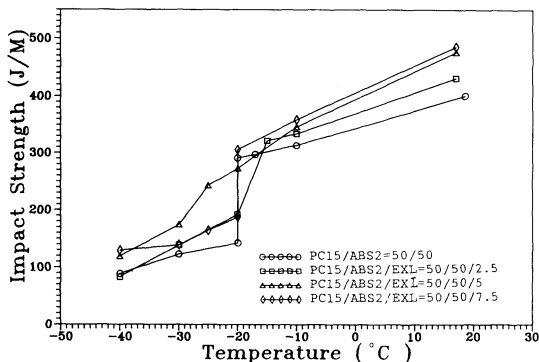**Figure 8.** Effect of the extra-added EXL3386 rubber on the Izod impact strength of the PC15/ABS2 = 50/50 blend.

PC15/ABS2 = 50/50 blend where the rubber particles are located only in ABS2 phase as expected but the rubber particle distribution in SAN phase is not perfectly even. As we mentioned previously that the ABS2 is thé blended product of ABS1 and SAN by the producer and the ABS1 is the product directly come from the polymerization reactor. Therefore, significant amount of free SAN (not bonded to rubber) in this ABS2 is expected. Figure 7 shows the TEM micrograph of the

blend, PC15/ABS2/MBS = 50/50/7.5 where the MBS rubber particles are crowded within the SAN phase. Figure 8 shows the plots of impact strengths of the EXL 3386 rubber modified PC15/ABS2 = 50 blends. The shift of DBTT becomes less clear after the addition of EXL 3386 (core-shell rubber contains acid functional groups in shell). Figure 9 shows the TEM micrograph of the blend, PC15/ABS2/EXL3386 = 50/50/5, where the rubber particles are also distributed in SAN phase.
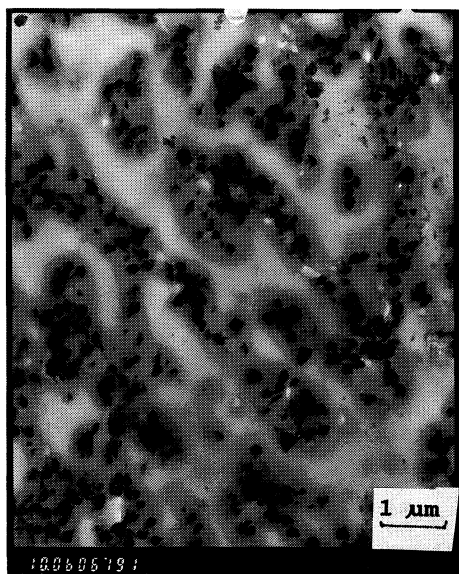
39

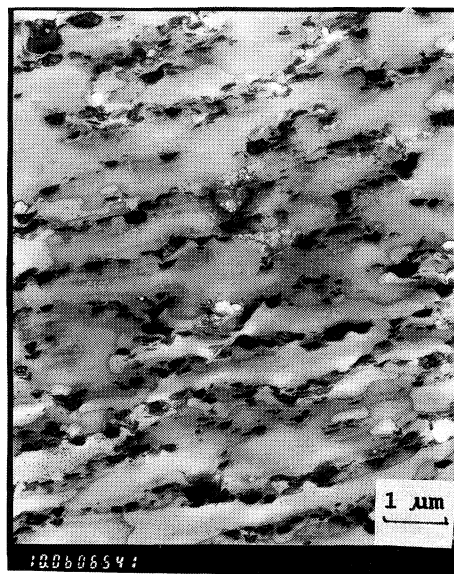**Figure 9.** TEM micrograph of PC15/ABS2/EXL3386 = 50/50/5 blend.

Figure 11. TEM micrograph of PC15/ABS2/HABS = 50/50/5 blend.
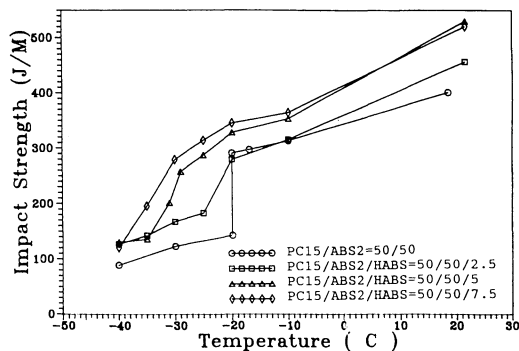

Figure 10. Effect of the extra-added HABS rubber on the Izod impact strength of the PC15/ABS2 = 50/50 blend.

The acid functional groups in this EXL 3386 rubber appear to have little influence to change the mutual miscibility with PC or SAN. Figure 10 demonstrates the low temperature toughness improvement by adding HABS rubber (high rubber content ABS) in the PC15/ABS2 = 50/50/5, blends. Figure 11 is the TEM morphology of the blend, PC15/ABS2/HABS = 50/50/5, where the rubber particles are coagulated within the SAN phase. That means the rubber phase of the ABS2 and
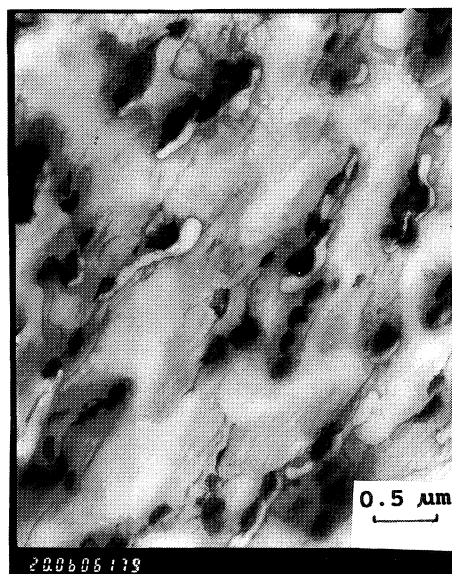

Figure 12. TEM micrograph of PC15/ABS2/SMA = 50/50/7.5 blend.

HABS may not be effectively surrounded by the grafted SAN and therefore causes the observed rubber coagulation. SMA copolymer has been used to raise the heat distortion

40

temperature (HDT) of PC/ABS blends.[6] We also added SMA in the PC15/ABS2 = 50/50 blend and the results show only slight toughness improvement of this blend (data not shown). Figure 12 shows the interesting morphology of the PC15/ABS2/SMA = 50/50/7.5 blend. Pieces of SMA reside within the SAN phase but close to the PC–SAN interface while the ABS rubber particles are severely coagulated and attracted by the SMA. The presence of SMA causes great fraction of the SAN phase without rubber presence because essentially all the rubber particles are being attracted by SMA as shown in Figure 12. This interesting observation indicates that the rubber has greater affinity to SMA than to SAN. The distribution of a minor third component C in a A/B blend is highly complex and the mutual miscibility (or affinity) may not be the only decisive factor, sometime blending sequence and viscosity ratio are also important.

CONCLUSIONS

Higher rubber content in the PC/ABS blend resulted in toughness improvement in terms of tensile, Izod impact and strain energy release rate but increases the melt viscosity. Additional core-shell rubber such as MBS, EXL 3386, or HABB was distributed in the ABS phase and resulted in additional toughening of the PC/ABS blends. The addition of SMA co-polymer in the PC/ABS blends caused severe coagulation of the rubber particles and resulted in a greater fraction of the SAN phase without the presence of rubber. The toughness advantages by increasing rubber cotent in the PC/ABS blends must be compensated by the viscosity increase and this fact has to be taken into consideration in selecting the starting materials.

REFERENCES

1. T. S. Grabowski (to Borg-Warner Corp.), U.S. Patent 3,130,177 (1964).
2. H. Keskkula and A. A. Pettis (to Dow Chemical Co.), U.S. Patent 3,239,582 (1966).
3. S. Furukawa, Y. Sonoyama, and A. Ohi (to Daicell Co., Ltd.), Japan Kokai 73 43,750 (1973).
4. H. Sakano, M. Kodama, A. Ito, and M. Terada (to Sumitomo Naugatuck Co. Ltd.), U.S. Patent 4,299,929 (1981).
5. E. Yonemitsu, S. Kamiyama, T. Kaneda, and M. Miura (to Mitsubishi Gas Chemical Co.), Japan Kokai 75 85,651 (1975).
6. D. E. Henton (to Dow Chemical Co.), U.S. Patent 4,367,310 (1983).
7. D. E. Henton (to Dow Chemical Co.), U.S. Patent 4,218,544 (1980).
8. D. Margotte, H. Peters, and J. Buekers (to Bayer A.G.), Ger. Offen. 3,002,662 (1981).
9. P. Y. Liu (to General Electric), U.S. Patent 4,263,415 (1981).
10. P. Y. Liu (to General Electric), U.S. Patent 4,390,657 (1983).
11. P. Y. Liu and N. R. Rosenquint (to General Electric), U.S. Patent 4,456,725 (1984).
12. U. R. Grogo, N. R. Lazear, and M. W. Witman (to Mobay Chemical Co.), U.S. Patent 4,472,554 (1984).
13. K. C. Rusch and R. H. Beck, J. Polym. Sci., C, No. 30, 447 (1970).
14. D. Stefan and H. L. Williams, J. Appl. Polym. Sci., 18, 1451 (1974).
15. J. I. Equiazabal and J. Nazabal, Polym. Eng. Sci., 30, 527 (1990).
16. S. L. Cohen and N. R. Lazear, Plastics Engineering, 23, August (1982).
17. M. T. Shaw, Polym. Eng. Sci., 22, 115 (1982).
18. T. Kurauchi and T. Ohta, J. Mater. Sci., 19, 1699 (1984).
19. H. Suarez, J. W. Barlow, and D. R. Paul, J. Appl. Polym. Sci., 29, 3253 (1984).
20. D. Keitz, J. W. Barlow, and D. R. Paul, J. Appl. Polym. Sci., 29, 3131 (1984).
21. K. Koo, T. Inoue, and K. Miyasaka, Polym. Eng. Sci., 25, 741 (1985).
22. G. Weber and J. Schocps, Angew Makromol. Chem., 136, 45 (1985).
23. R. E. Skochdopolc, C. R. Finch, and J. Marshall, Polym. Eng. Sci., 27, 627 (1987).
24. W. Y. Chiang and D. S. Hwung, Polym. Eng. Sci., 27, 632 (1987).
25. W. K. Chin and J. L. Hwung, "Advances in Polymer Blends and Alloys Technology," Vol. 1, M. A. Kohudic, Ed., Technomic Publishing Co. Inc., Lancaster 1988, p. 154.
26. W. N. Kim and C. M. Burns, Polym. Eng. Sci., 28, 1115 (1988).
27. K. W. Mclaughlin, Polym. Eng. Sci., 29, 1560 (1989).
28. D. Quintens, G. Groeninckx, M. Guest, and L. Aerts, Polym. Eng. Sci., 30, 1474 (1990).
29. J. J. Herpels and L. Mascia, Eur. Polym. J., 26, 997

(1990).

30. M. Ishikawa and I. Chiba, *Polymer*, **31**, 1232 (1990).
31. T. W. Cheng, H. Keskkula, and D. R. Paul, *Polymer*, **33**, 1606 (1992).
32. J. S. Wu, S. C. Shen, and F. C. Chang, *J. Appl. Polym. Sci.*, **50**, 1379 (1993).
33. F. C. Chang, Company internal report, Dow Chemical Company (1985).
34. S. Y. Hobbs, M. E. J. Dekkers, and V. H. Watkins, *Polym. Bull.*, **17**, 341 (1987).
35. S. Y. Hobbs, M. E. J. Dekkers, and V. H. Watkins, *J. Mater. Sci.*, **23**, 1219 (1988).
36. R. C. Chen and F. C. Chang, *Polym. Networks and Blends*, **3**, 107 (1993).
37. F. C. Chang, M. Y. Yang, and J. S. Wu, *Polymer*, **32**, 1394 (1991).
38. H. Keskkula, D. R. Paul, K. M. McCreedy, and D. E. Henton, *Polymer*, **28**, 2063 (1987).
40. K. P. Lin and F. C. Chang, *Polym. Networks and Blends*, to appear.
41. T. C. Chou and F. C. Chang, Proceedings of the 1993 Annual Conference of the Chinese Society for Material Science, Hsinchu, Taiwan, 1993, pp. 3–39.
42. F. C. Chang and M. Y. Yang, *Polym. Eng. Sci.*, **30**, 543 (1990).
43. F. C. Chang, J. S. Wu, and L. H. Chu, *J. Appl. Polym. Sci.*, **44**, 491 (1992).
44. F. C. Chang and Y. C. Hwu, *Polym. Eng. Sci.*, **31**, 1509 (1991).
45. H. J. Karam and J. C. Bellinger, *Ind. Eng. Chem. Fund.*, **7**, 576 (1968).
46. S. Wu, *Polym. Eng. Sci.*, **27**, 335 (1987).
47. F. C. Chang and H. C. Hsu, *J. Appl. Polym. Sci.*, **47**, 2195 (1993).
48. H. R. Brown, *J. Mater. Sci.*, **8**, 941 (1973).
49. G. P. Maeshall, J. G. Williams, and E. E. Turner, *J. Mater. Sci.*, **8**, 949 (1973).