

In Situ Compatibilization of PET/PS Blends through Reactive Copolymers

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SYNOPSIS

Polymer blends of poly(ethylene terephthalate) (PET) and polystyrene (PS) are immiscible and incompatible, which has been well recognized. Styrene-glycidyl methacrylate (SG) copolymer has been synthesized by suspension polymerization and employed in this study as an *in situ* compatibilizer for the polyblends of PET and PS. This copolymer contains reactive epoxy functional groups that are able to react with PET end groups ($-\text{OH}$ and $-\text{COOH}$) under melt conditions to form SG-graft-PET copolymer. The presence of a small amount of phosphonium catalyst (200 ppm) accelerates the graft reaction and results in a better compatibilized blend. The compatibilized PET/PS blend has a smaller phase domain and higher viscosity than does the corresponding noncompatibilized blend. Mechanical properties of the compatibilized blends have also been improved significantly over the corresponding noncompatibilized blends. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In a typical immiscible polyblending system, a satisfactory overall physicomachanical behavior will critically depend on the proper interfacial tension to generate a small phase size and strong interfacial adhesion to transmit applied force effectively between the component phases.¹ Methods to reduce interfacial tension and to improve phase adhesion between two immiscible phases have been a subject of considerable research activity, often of a proprietary nature. The synthesized block or graft copolymers as compatibilizers have successfully turned several otherwise incompatible blends into compatible and useful blending materials. The choice of a block or graft copolymer is based on the miscibility of its segments with the blend components and such a copolymer tends to concentrate at the interface as an emulsifier. However, such copolymers usually require a separate preparation step and certain block copolymers are difficult to obtain.

Recently, the *in situ*-formed compatibilizer in polyblends has attracted great attention as an al-

ternative to replace the conventional block or graft copolymers. Examples and selections of *in situ* compatibilization have been concentrated mainly in the polyblends of nylons and maleic anhydride (MA)-grafted polyolefins²⁻⁸ and relatively less on other systems.⁹⁻¹⁴ The *in situ* compatibilized polymer blends involving the reactive glycidyl methacrylate (GMA) monomer are even fewer, but have become important lately because of the versatile applications in many blending systems.¹⁵⁻²⁰

Both PET and PS are commodity polymers that possess unique properties individually. A polyblend of PET and PS (or HIPS) is expected to be highly desirable because of its great commercial potential. However, essentially no such commercial product is known to exist and very few studies on polyblends of PET and PS have been previously reported. Undoubtedly, this is due to the incompatibility of the system. McKay²¹ recently used polystyrene-*b*-polycaprolactone as a compatibilizer for the PET/PS blends. In our previous study, we employed the styrene-glycidyl methacrylate (SG) copolymer as the *in situ* compatibilizer for the PS/nylon blends.¹⁶ We also reported the styrene-acrylonitrile-glycidyl methacrylate (SAG) copolymer as an effective *in situ* compatibilizer in the polyblends of ABS with phenoxy resin,¹⁷ polyacetal,¹⁸ and nylon.¹⁹ In a con-

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tinuous program in our lab to study the *in situ* compatibilization of polyblends, this report will cover the *in situ* reactive compatibilizer SG in the PET/PS blends, their specific miscibility, and correlation with their physical properties.

EXPERIMENTAL

Materials

Polystyrene, MW-1-301, was obtained from Denki Co. of Japan. PET, Shin PET, I.V. = 1.0, was obtained from Shinkong Synthetic Fibers Inc. of Taiwan. The catalyst employed in this study, ethyl triphenylphosphonium bromide (ETPB), was purchased from Merck. Styrene-glycidyl methacrylate (SG) copolymers were prepared by suspension polymerization. Procedures for the preparation of SG5, 5% GMA in SG, are given as follows:

1. Dissolve 2.5 g poly(vinyl alcohol) (PVA) in 1200 cc water and raise the solution to 80°C in a stirrer glass reactor.
2. Add 380 g styrene, 20 g glycidyl methacrylate, and 2 g of BPO initiator into the reactor and let the reaction continue under agitation for 9 h.
3. The powder product is separated from water by filtration, washed with water thoroughly to remove PVA and unreacted monomers, and dried in a vacuum oven at 80°C overnight.

Melt Blending and Injection Molding

Melt blending was carried out by using a 30 mm corotating intermeshing twin-screw extruder with $L/D = 29$ and barrel temperatures between 260 and 270°C. The blended pellets were then dried in a vacuum oven and molded into $\frac{1}{8}$ in. standard test specimens by using an Arburg 3 oz injection-molding machine.

Torque vs. Time Measurements

To verify the reaction between SG and PET based on the viscosity increase (torque vs. time), 30 g sample (weight ratio, 1 : 1) was tested at 265°C and 60 rpm in a Brabender Plastic-Corder.

Mechanical Properties

Standard tests on Izod impact (ASTM-D256), tensile (ASTM-D638), flexural (ASTM-D790), and

instrumental falling weight impact were carried out at ambient conditions as described previously.^{22,23}

Others

Morphologies of the ambient cut and impact fracture surfaces were examined by scanning electron microscopy (SEM), Model S-570, Hitachi Co. of Japan. Portions of the samples were etched with THF solvent for 2 min to dissolve the PS phase out of the blends. Melt flow rates were measured at 255°C and 2.16 kg loading.

RESULTS AND DISCUSSION

Fundamental on *In Situ* Compatibilization

A synthesized graft or block nonreactive copolymer can be considered as a specific type compatibilizer because its structure and quantity are unchanged and independent of blending conditions. On the contrary, a reactive copolymer or a small multiple functional molecule can be considered as a nonspecific type *in situ* compatibilizer because the structure and quantity of the eventually formed copolymers will vary with the content of the reactive group, temperature, time, mixing efficiency, and presence of a catalyst. In this paper, the reactive copolymer (SG) itself cannot act as a phase compatibilizer for the polyblends of PS and PET. However, the reaction products between the epoxide groups in the SG copolymer and the PET end groups ($-\text{COOH}$ or $-\text{OH}$) will form various SG-*g*-PET copolymers that will function as the nonspecific compatibilizer.

An excessively grafted copolymer will result in the highly branched SG-*g*-PET copolymers or even a cross-linked network, as shown in Figure 1(A). Such an excessively grafted copolymer has the branched PET chains effectively shielding the styrene sections of the SG copolymer and loses its role as a phase compatibilizer. Besides, the excessive grafted copolymers will drastically increase the viscosity of the blend and this is rheologically unfavorable to the blend. Therefore, the optimized degree of the *in situ* grafting is essential to achieve the greatest performance of the resulted blended product and this can be accomplished through proper adjustment of the GMA content in the SG copolymer, the presence of a suitable catalyst, and proper control of the blending conditions.

The lightly grafted copolymer is the one that can

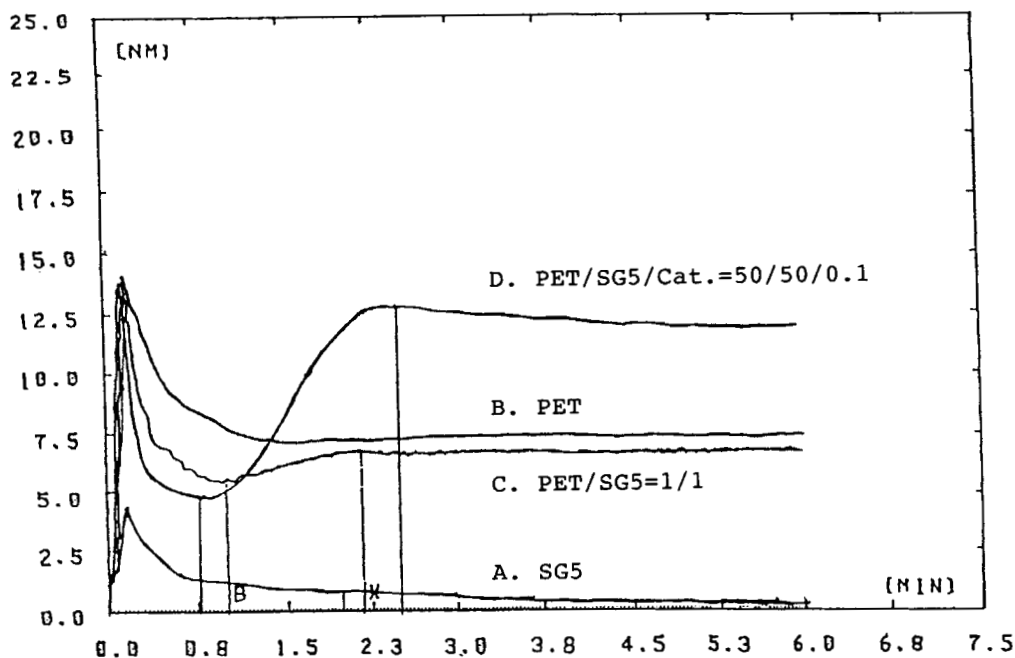


Figure 2 Plots of torque vs. time at 265°C and 60 rpm.

curves C and D in Figure 2 are essentially leveled out. This indicates the completion of the grafting reactions. If all the epoxide groups in SG are consumed only in the grafting reaction, whether or not in the presence of the catalyst, we would expect almost identical final torques from curves C and D.

However, curve D has a significantly higher final torque than that of curve C experimentally. Therefore, the presence of the catalyst in curve D is responsible for the greater degree of grafting than that from curve C. As mentioned previously, the competitive hydrolysis reaction will consume part of the

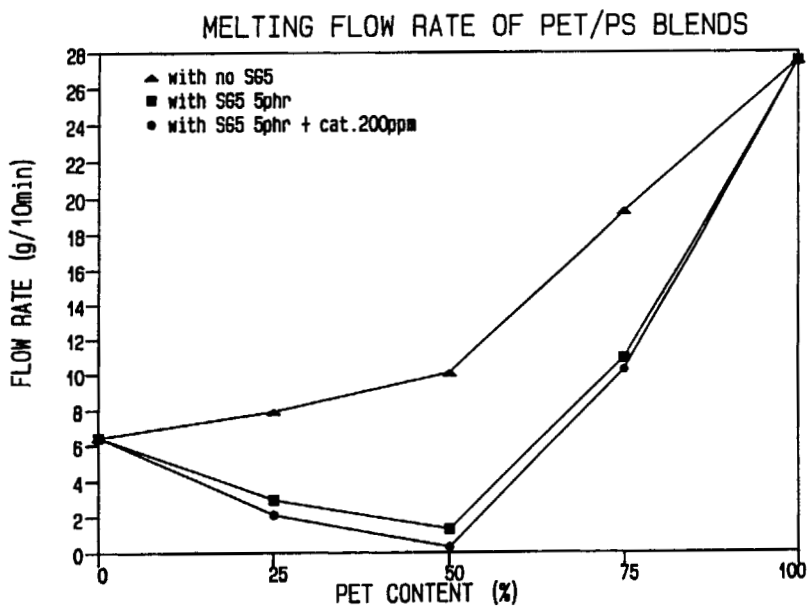


Figure 3 Effect of SG5 and catalyst on MFR of PET/PS blends.

epoxide groups and the presence catalyst may reduce the hydrolysis. This result provides evidence of the predicted grafting reaction and that the presence of the catalyst further increases the reaction rate.

Melt Flow Rates (MFR)

Figure 3 clearly shows that the presence of the 5 phr SG copolymer in any PET/PS blend is able to cause a significant drop in the MFR. The MFR is further decreased if the blend contains both SG and 200 ppm of the ETPB catalyst. As mentioned previously, the epoxy group in the SG copolymer is able to react with PET end groups under melt conditions and the rate of reaction increases with the presence of the phosphonium catalyst. The molecular weight increase through the grafting reaction is believed to be the major contributor to the viscosity increase of the blends. The *in situ*-formed SG-*g*-PET copolymer tends to concentrate at the interface and, therefore, raises the interfacial friction under shear stress. The increase of interfacial friction of the compatibilized blend than that of the noncompatibilized one is another reason for the observed higher viscosity. This explains why the greatest viscosity drop occurs in the blend when both phases are in a cocontinuous structure as shown in Figure 3. Figure 4 shows that SG copolymer with higher GMA content results in lower MFR of the blend than of the corresponding SG with lower GMA content, as

would be expected. All the MFR data are summarized in Table I.

SEM Morphologies

Figures 5(A)–(C) show the SEM micrographs of the cryogenic fracture surfaces without solvent etching of the PET/PS = 75/25 blends. The large dispersed and spherical PS particles with different dimensions can be easily identified from the noncompatibilized blend [Fig. 5(A)], whereas the phase contrast of the blends containing SG5 (5% GMA and 95% styrene), either with or without a catalyst [Fig. 5(B) and (C)], is not very clearly defined. Figure 6(A)–(C) shows the surface morphologies of the same set of blends cut by a regular knife at ambient temperature. The dispersed PS particles are well separated from the torn PET matrix and their sizes decrease with the presence of the SG compatibilizer and catalyst. Compared to Figure 5(A)–(C), the domain dimensions of the dispersed phase can be easily identified by this simple knife-cutting approach without relying on the solvent-etching procedure. This unusual approach to examine phase morphology is particularly useful, in certain blends, when a suitable etching solvent is not available. Figure 7(A)–(C) shows the cryogenic fracture surfaces of the same set of blends after solvent etching where the empty holes are the PS being etched out by solvent. Comparative surface morphologies from Figures 5–7 are based on the same blends but through

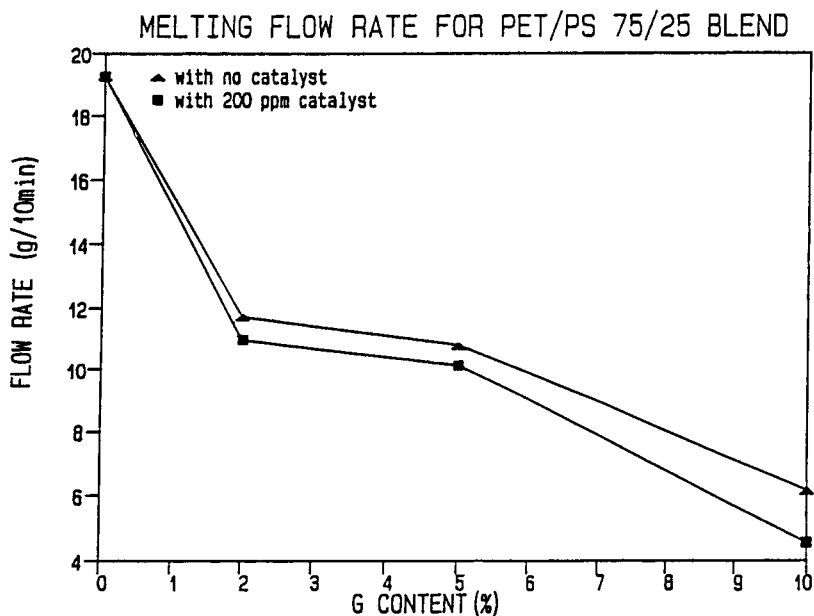


Figure 4 Effect of G content in SG copolymer on PET/PS = 75/25 blends.

Table I Summarized Properties of PET/PS Blends

Composition	MFR	Izod (J/M)	Falling Wt Impact (J)	Tensile		
				Modulus (MPa)	Yield Stress (MPa)	Elongation (%)
PET	27.46	18.7	—	512	52	—
PS	6.42	10.8	—	747	39	7.4
PET/PS = 75/25	19.25	6.2	0.99	551	38	7.5
PET/PS/SG2 = 75/25/5	11.76	9.3	1.63	556	45	9.0
PET/PS/SG5 = 75/25/5	10.81	9.1	2.04	569	49	10.6
PET/PS/SG10 = 75/25/5	6.14	12.1	1.30	544	46	9.6
PET/PS/SG2/Cat = 75/25/5/0.02	10.92	12.5	1.92	560	52	10.0
PET/PS/SG5/Cat = 75/25/5/0.02	10.14	12.7	1.38	584	55	10.6
PET/PS/SG10/Cat = 75/25/5/0.02	4.60	12.7	2.08	670	52	10.1
PET/PS = 50/50	10.06	3.4	—	588	42	7.9
PET/PS/SG2 = 50/50/5	3.48	9.3	—	587	48	9.4
PET/PS/SG5 = 50/50/5	1.34	7.3	—	597	47	8.8
PET/PS/SG10 = 50/50/5	1.15	8.9	—	583	36	8.2
PET/PS/SG2/Cat = 50/50/5/0.02	0.40	12.3	—	591	42	9.0
PET/PS/SG5/Cat = 50/50/5/0.02	0.34	11.9	—	619	47	8.7
PET/PS/SG10/Cat = 50/50/5/0.02	0.30	12.0	—	701	48	8.5
PET/PS = 25/75	7.89	3.1	—	622	38	7.9
PET/PS/SG2 = 25/75/5	3.65	10.2	—	614	38	7.9
PET/PS/SG5 = 25/75/5	2.95	10.3	—	531	33	7.1
PET/PS/SG10 = 25/75/5	2.62	11.4	—	628	28	5.7
PET/PS/SG2/Cat = 25/75/5/0.02	2.74	12.2	—	632	39	7.6
PET/PS/SG5/Cat = 25/75/5/0.02	2.21	12.3	—	605	35	7.3
PET/PS/SG10/Cat = 25/75/5/0.02	1.50	12.3	—	638	37	6.9

different treatments. The observed trend is very similar to the previous melt flow rate (MFR) in terms of the presence of SG and catalyst; the better compatibilized blend has a higher viscosity and a

smaller domain size. The *in situ*-formed compatibilizer reduces interfacial tension during melt blending and results in a smaller domain size of the dispersed-phase particles.

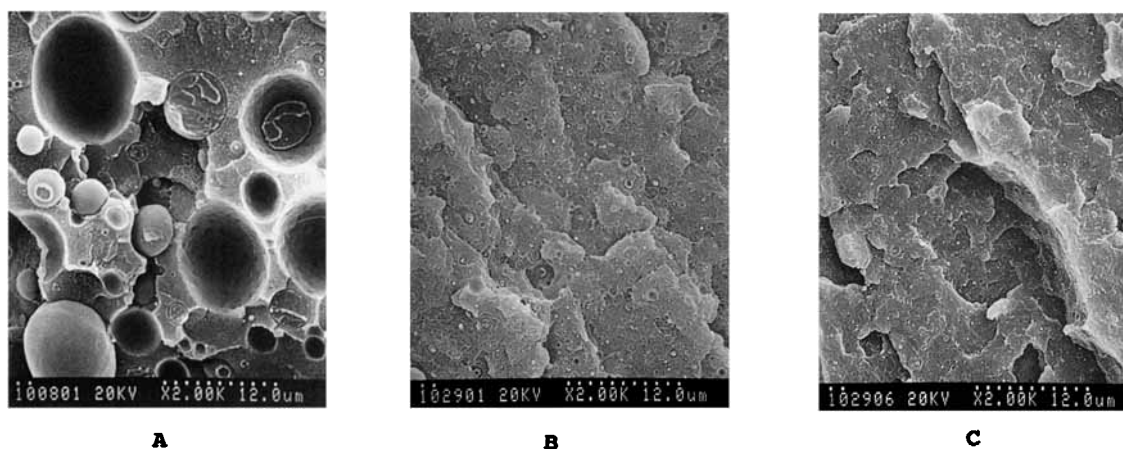


Figure 5 SEM micrographs of the cryogenic fracture surfaces of the compatibilized and noncompatibilized PET/PS = 75/25 blends: (A) PET/PS = 75/25; (B) PET/PS/SG5 = 75/25/5; (C) PET/PS/SG5/Cat = 75/25/5/0.02.

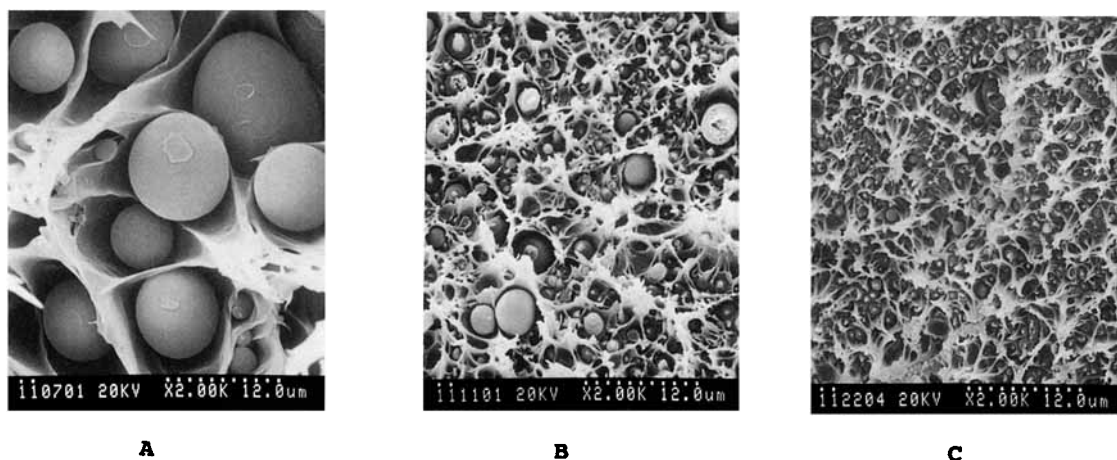


Figure 6 SEM micrographs of the ambient fracture cut surfaces of the compatibilized and noncompatibilized PET/PS = 75/25 blends: (A) PET/PS = 75/25; (B) PET/PS/SG5 = 75/25/5; (C) PET/PS/SG5/Cat = 75/25/5/0.02.

The presence of the catalyst results in further reduction in the size of the dispersed phase. Figure 8(A)–(C) shows the surface morphologies of the blends containing SG with different contents of GMA. The blend with SG2 (2% GMA) has a relatively larger dispersed PS domain [Fig. 8(A)], whereas the blends with SG5 and SG10 [Fig. 8(B) and (C)] both have a very small PS domain. Figure 9 shows the cryogenic fracture surfaces parallel to the flow direction of the noncompatibilized and compatibilized PET/PS = 50/50 blends. Again, only the noncompatibilized blend [Fig. 8(A)] shows the clear phase contrast. Figure 10(A)–(C) shows the same set of samples as shown in Figure 9 after

solvent etching and the compatibilized blends [Fig. 10(B) and (C)] have a much smaller phase domain. Figure 10(A)–(C) shows that the PET/PS = 50/50 blends, with and without a compatibilizer, are nearly in a cocontinuous structure, as would be expected.

Impact and Tensile Properties

In general, the compatibilized polyblend (finer phase dispersion) does not necessarily guarantee toughness improvement, as we mentioned previously.¹⁶ The way the compatibilizer affects the inherent properties of the constituent matrices needs also to

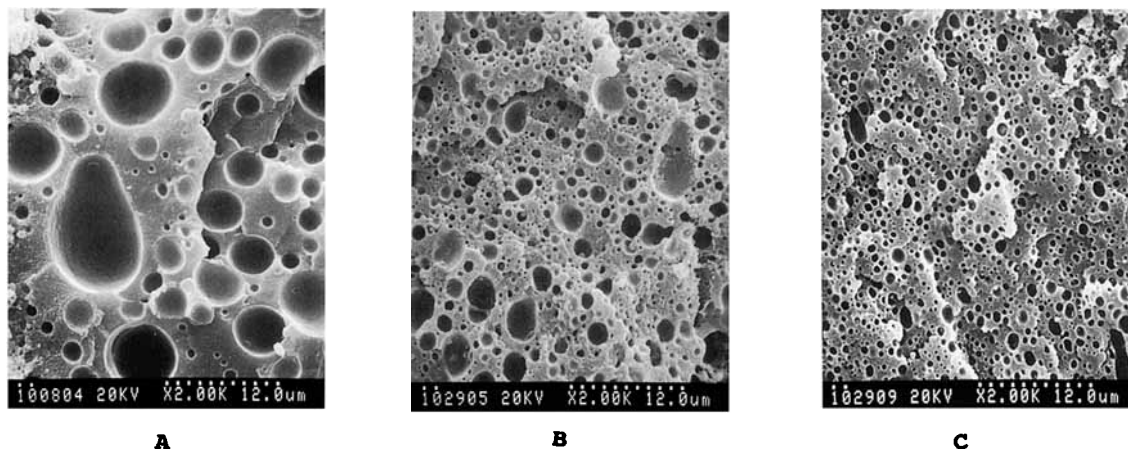


Figure 7 SEM micrographs the etched cryogenic fracture surfaces of the compatibilized and noncompatibilized PET/PS = 75/25 blends: (A) PET/PS = 75/25; (B) PET/PS/SG5 = 75/25/5; (C) PET/PS/SG5/Cat = 75/25/5/0.02.

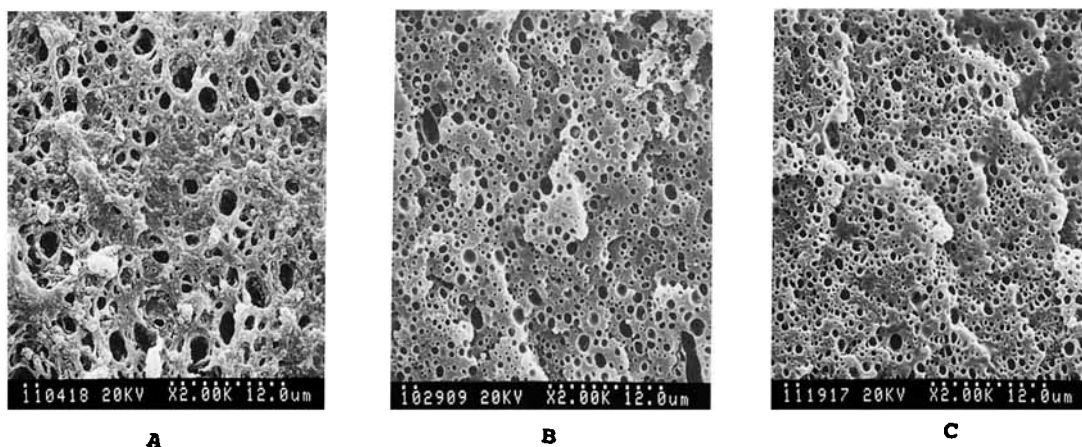


Figure 8 SEM micrographs of the solvent-etched cryogenic fracture surfaces of the PET/PS/SG5/Cat = 75/25/5/0.02 blends by varying GMA content in SG: (A) SG2, 2% G in SG; (B) SG5, 5% G in SG; (C) SG10, 10% G in SG.

be taken into consideration. Polystyrene-*b*-polycaprolactone indeed functions as a phase compatibilizer for PET/PS blends in terms of phase dispersion but it fails to improve the resulted mechanical properties.²¹ The overall property improvements for the blends containing SG copolymer and catalyst have been clearly demonstrated in this study and the results are summarized in Table I.

Figure 11 shows significant improvement of the Izod impact strength due to the presence of SG5 and catalyst in the polyblends of PS/PET with various component ratios. The property improvement of the compatibilized blends over the noncompatibilized blends is particularly drastic for those blends with

25 and 50% of PET, which coincides with the previous MFR results. Figure 12 shows the impact strengths of the blends are almost independent of the GMA content in the SG copolymers. As mentioned earlier (Figs. 1 and 4), higher GMA content in SG may produce an excessively grafted copolymer, which is considered to be less effective. Lower GMA content in the SG copolymer has the advantage of producing lightly grafted copolymer but has the tendency to produce fewer numbers of the grafted copolymers. The presence of SG or SG plus the catalyst shows the definite trend of higher modulus (Fig. 13) and higher yield strength (Fig. 14) for those blends containing 75% PET, but such a trend is not very

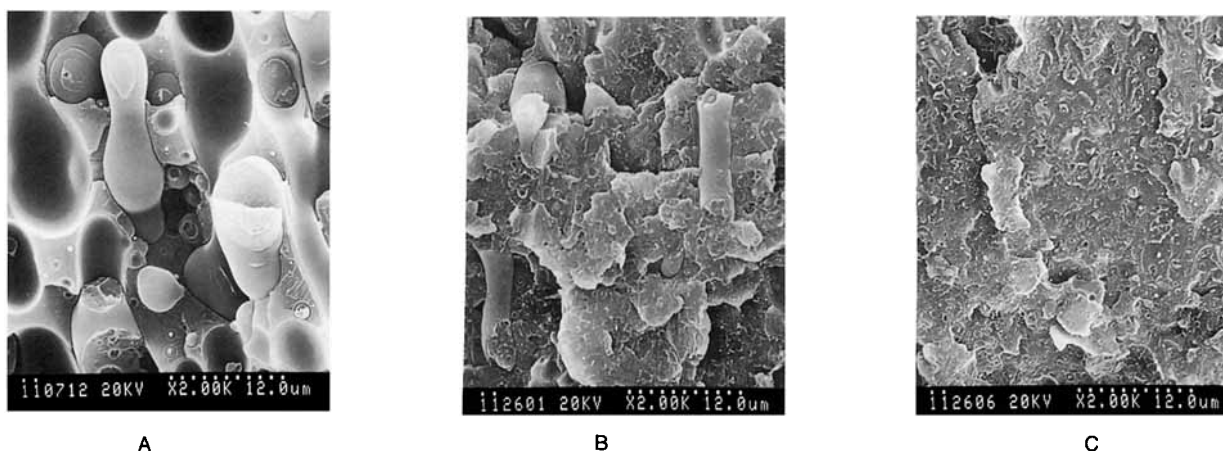


Figure 9 SEM micrographs of the cryogenic fracture surfaces of the compatibilized and noncompatibilized PET/PS = 50/50 blends: (A) PET/PS = 50/50; (B) PET/PS/SG5 = 50/50/5; (C) PET/PS/SG5/Cat = 50/50/5/0.02.

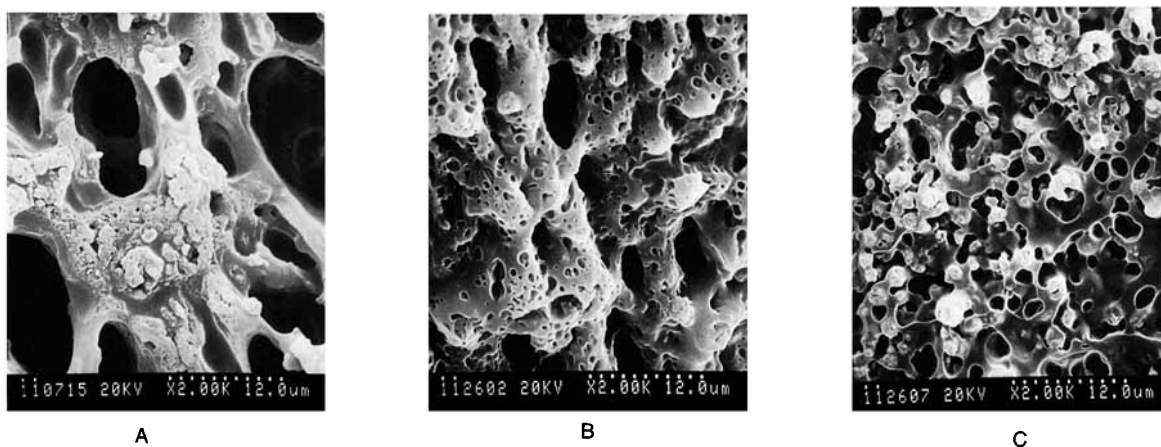


Figure 10 SEM micrographs of the solvent-etched cryogenic fracture surfaces of the compatibilized and noncompatibilized PET/PS = 50/50 blends: (A) PET/PS = 50/50; (B) PET/PS/SG5 = 50/50/5; (C) PET/PS/SG5/Cat = 50/50/5/0.02.

consistent for the blends with 50 and 25% PET. Figure 15 shows the effect of the presence of the catalyst and GMA content in SG on yield strength of the PET/PS = 75/25 blends. The presence of the catalyst appears more important than the GMA content in SG (as long as it is greater than 2%) to raise the resultant yield strength. Overall, the compatibilized blend has higher yield strength over the corresponding noncompatibilized blends. The trend of tensile elongation due to the presence of compatibilizer and catalyst is not very clearly defined,

as shown in Table I. Table I also shows definite improvement in the falling weight impact energy for the compatibilized blends.

SUMMARY

Polyblends of PET and PS are immiscible and incompatible with poor interfacial adhesion and large phase domains and are difficult to process. The SG copolymer itself does not function as a compatibil-

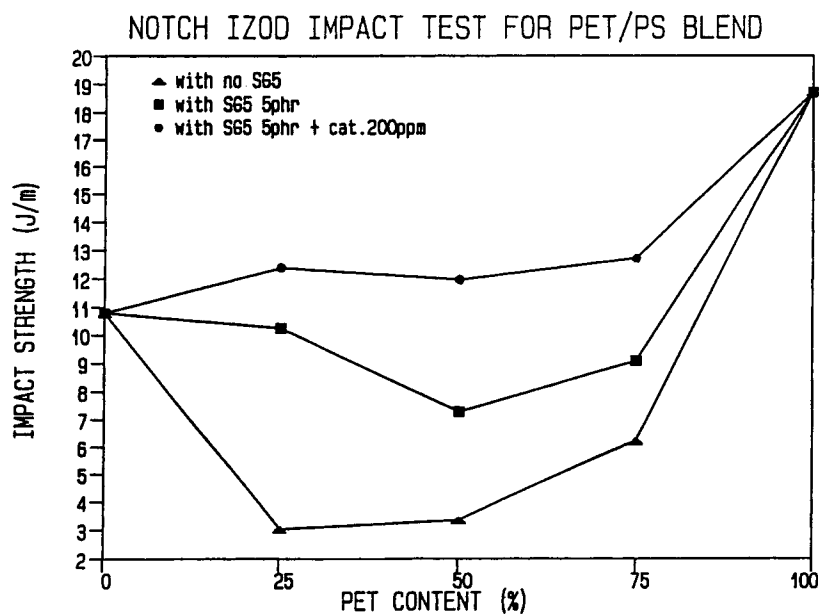


Figure 11 Effect of SG5 and catalyst on impact strength of various PET/PS blends.

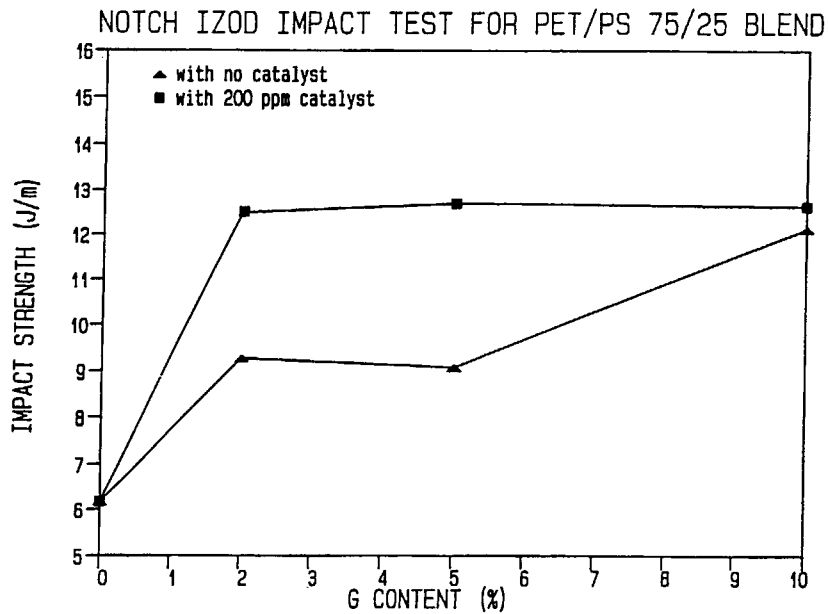


Figure 12 Effect of G content in SG copolymer on impact strength of the PET/PS = 75/25 blends.

izer, but will become one after reacting with PET end groups during melt blending. The presence of the SG copolymer, with or without a catalyst, improves the melt processability of the incompatible PET/PS blend. The toughness of the compatibilized blends increases with the expected improvement of interfacial adhesion and the observed finer phase

domains. These *in situ*-formed copolymer molecules tend to reside along the interface but not exclusively; some of them will dissolve in both blend components. Distribution of the compatibilizer molecules depends on several factors such as chemical structure, processing conditions, molecular weight, and type of copolymer. The compatibilizer distributed

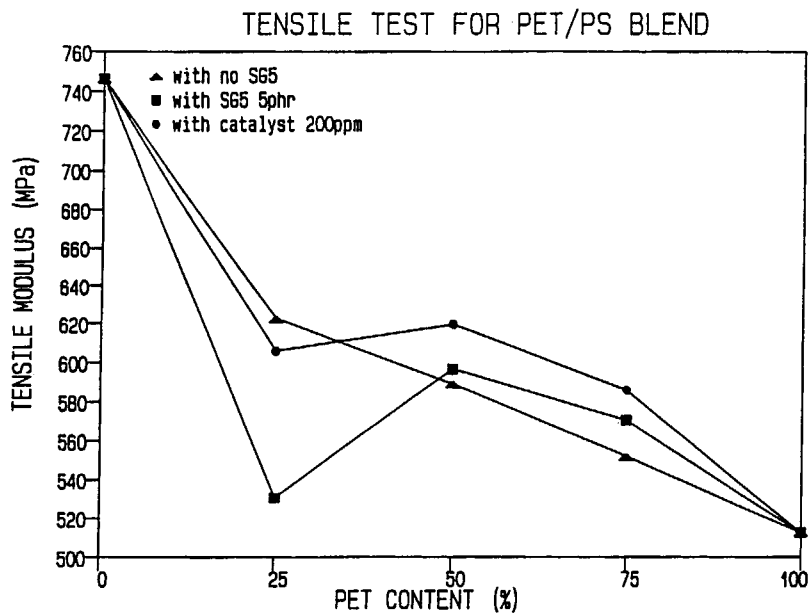


Figure 13 Effect of SG5 an catalyst on tensile modulus of various PET/PS blends.

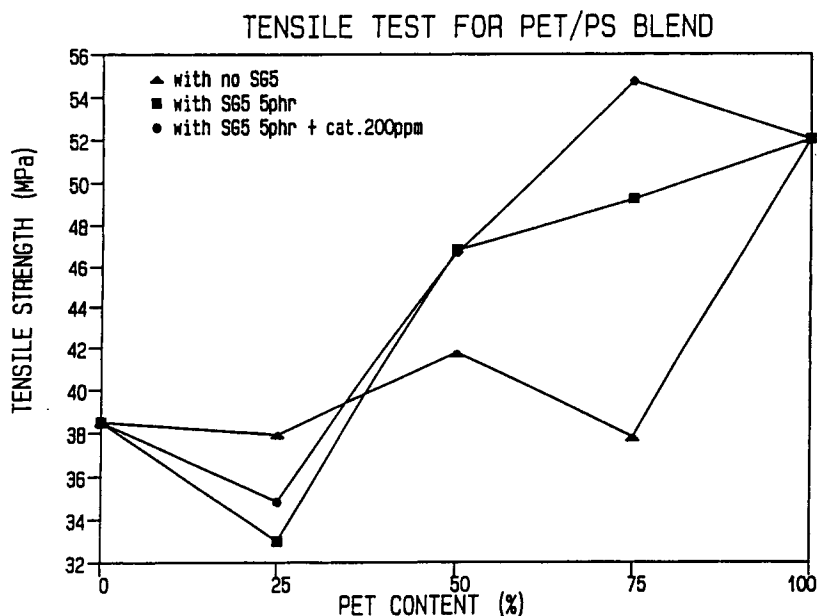


Figure 14 Effect of SG5 and catalyst on tensile strength of various PET/PS blends.

in the blend components certainly will alter the inherent toughness of these components. The compatibilized blend may increase or decrease its toughness depending on the competition between the advantages from better adhesion and dispersity and the disadvantage from the loss of inherent toughness of blend components. Therefore, a good

compatibilizer in a binary blend does not warrant the improvement of its mechanical toughness and this point of view has been virtually neglected previously. In the present blending system, the possible toughness loss in the PET phase is less than the increase of toughness due to better adhesion and dispersity.

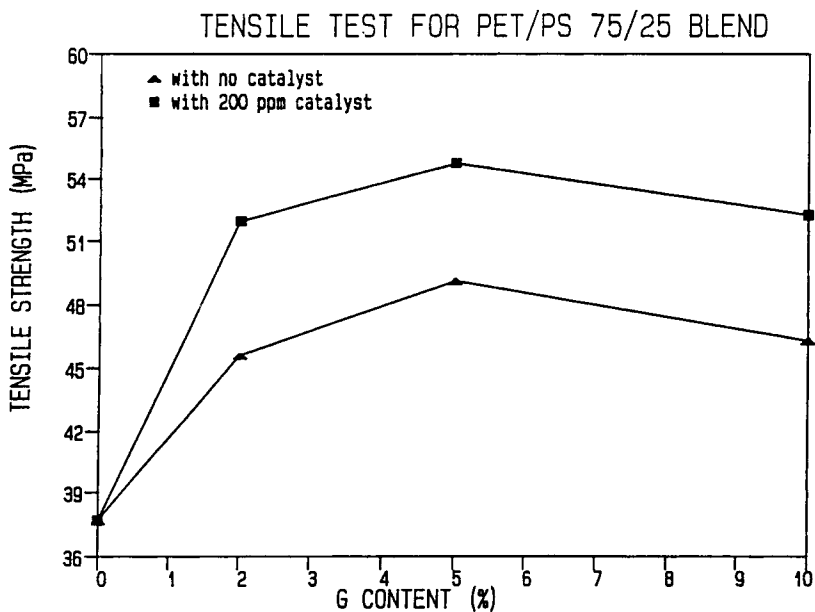


Figure 15 Effect of GMA content in SG copolymer on tensile strength of the PET/PS = 75/25 blends.

REFERENCES

1. J. W. Barlow and D. R. Paul, *Polym. Eng. Sci.*, **24**, 525 (1984).
2. F. Ide and A. Nasegawa, *J. Appl. Polym. Sci.*, **8**, 963 (1974).
3. C. D. Han, Y. J. Kim, and H. B. Chin, *Polym. Eng. Rev.*, **4**, 177 (1984).
4. E. A. Flexman, *Polym. Eng. Sci.*, **19**, 564 (1979).
5. S. Wu, *Polym. Eng. Sci.*, **27**, 335 (1987).
6. R. J. M. Borggreve and R. J. Gaymans, *Polymer*, **30**, 63 (1989).
7. S. Y. Hobbs, R. C. Bopp, and U. H. Watkins, *Polym. Eng. Sci.*, **23**, 380 (1983).
8. R. Greco, M. Malinconico, E. Martuscelli, G. Ragosta, and G. Scarinzi, *Polymer*, **28**, 1185 (1987).
9. M. Saleem and W. E. Baker, *J. Appl. Polym. Sci.*, **39**, 655 (1990).
10. A. Y. Coran and R. Patel, *Rubber Chem. Technol.*, **56**, 1045 (1983).
11. W. E. Baker and M. Saleem, *Polymer*, **28**, 2057 (1987).
12. W. E. Baker and M. Saleem, *Polym. Eng. Sci.*, **27**, 1637 (1987).
13. M. Hajian, C. Sadrmoaghegh, and G. Scott, *Eur. Polym. J.*, **20**, 135 (1984).
14. L. J. Pillon and L. A. Utracki, *Polym. Eng. Sci.*, **24**, 1300 (1984).
15. J. Y. J. Chung and R. P. Carter, Jr., U.S. Pat. 4,554,315 (1985).
16. F. C. Chang and Y. C. Hwu, *Polym. Eng. Sci.*, **31**, 1509 (1991).
17. S. H. Chen and F. C. Chang, in *Proceedings of the 15th ROC Polymer Symposium 1992*, Taiwan, 1992, pp. 445-448.
18. B. S. Chang and F. C. Chang, in *Proceedings of the 15th ROC Polymer Symposium 1992*, Taiwan, 1992, pp. 425-428.
19. H. H. Chang, J. S. Wu, and F. C. Chang, in *Proceedings of the 4th Asian Chem. Congress*, Beijing, August 1991, p. 699.
20. S. Suzuki and T. Yamamoto, *Plastics (Jpn)*, **41**(6), 116 (1990).
21. I. D. McKay, *J. Appl. Polym. Sci.*, **43**, 1593 (1991).
22. F. C. Chang and M. Y. Yang, *Polym. Eng. Sci.*, **30**, 54 (1990).
23. F. C. Chang, J. S. Wu, and L. H. Chu, *J. Appl. Polym. Sci.*, **44**, 491 (1992).

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