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Interfacial enrichment of a compatibilizing graft copolymer in a partially miscible polymer blend

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Poly(alkyl acrylate-g-caprolactone) graft copolymers were prepared and applied as compatibilizing graft copolymer in polycarbonate (PC)/poly(acrylonitrile-butadiene-styrene) (ABS) blends. Incompatible poly(alkyl acrylate) segments were incorporated into the graft copolymer in order to localize the copolymer at the PC/ABS interface. The blend containing 1 part of copolymer per hundred of resin (phr) showed an improvement in impact strength as well as percentage elongation at break. Impact improvement was quite prominent with a thinner test specimen of 3 mm thickness. A morphological study showed that the presence of the graft copolymer led to smoother PC/ABS interface due to interfacial enrichment of the graft copolymer. © 1997 Elsevier Science Ltd.

(Keywords: graft; copolymer; blend)

INTRODUCTION

Block and graft copolymers have received much attention because of the emulsification or compatibilization effects of these copolymers on immiscible polymers[1–3]. The ultimate goal is usually to obtain a polymer blend with good mechanical (or chemical) properties by using a minimum amount of compatibilizer. In order to be used as an efficient compatibilizer, the copolymer has to satisfy a couple of requirements—i.e., it has to be located at the interface with large surface area coverage, and has to intimately mix with the corresponding polymer component of the blend at the interface.

For the interfacial enrichment of a block or graft copolymer in an immiscible polymer blend, the copolymer has to have a well-balanced structure. Molecular weight and weight ratio of each block in a diblock copolymer, for example, has to be in a proper range[4–6]. Otherwise obtained properties of the blend will be deteriorated due to the solubilization of the copolymer into a bulk phase of the blend components, and the amount of compatibilizer needed will be greater. Even when the requirement is satisfied, the block copolymer may behave as 'dry brush' or 'wet brush' depending on the molecular alignment (assembly) at the interface. With a block copolymer of sufficiently large molecular weight, an efficient mechanical coupling will be achieved if each block of the copolymer mixes with corresponding polymer component of blend (wet brush). Large molecular weight also has an additional advantage. Thomas and Prud'homme reported that as the molecular weight of a compatibilizing block copolymer increases, surface coverage of the block copolymer increases, and a lesser amount of block copolymer is needed for a sufficient surface coverage[7].

Although conformation restrictions for the solubilization of the components of the blend tend to favour block copolymers for use as compatibilizers[3], in practice graft copolymers are preferred owing to the easier routes available to tailor their chemical composition to meet specific requirements. Furthermore, graft copolymers can be produced in bulk, from readily available macromonomers, by simple reaction processing methods. Besides the above-mentioned advantages, graft copolymer may have other advantages. If one places a comb-shaped graft copolymer at the interface along the interfacial line, then a reduced number of graft copolymer molecules will be needed for a sufficient interfacial coverage. Also, at the curved interface, graft copolymers with a specific architecture will be assembled together to give a less strained arrangement in molecular scale.

Alignment of a graft copolymer at the blend interface, on the other hand, may simulate that of a block copolymer. Depending on the molecular structure of the graft copolymer 'dry brush' or 'wet brush' situations may occur. An efficient mechanical coupling will only be achieved if grafts as well as main chain segments intimately mix with corresponding polymer components of blend (wet brush). If the number of grafts per chain is too much, or the molecular weight of graft is too short, then graft copolymer and molecular chain of the blend cannot interpenetrate each other.

However, preparation of a block or graft copolymer with well-balanced molecular structure is quite difficult even with low molecular weighted copolymers, and an easier approach is needed for practical applications. This situation is true even in the preparation of a graft copolymer.

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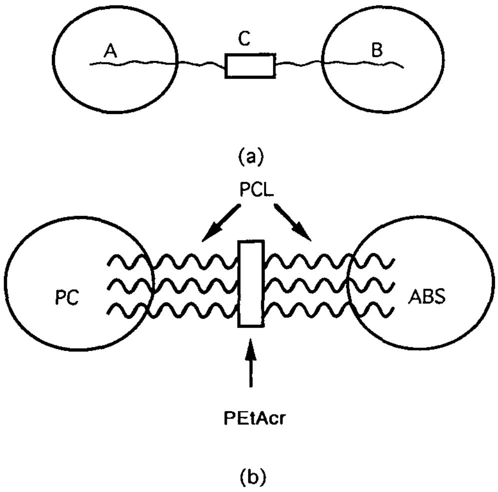
In order to situate a block or graft copolymer at the interface, therefore, it is desirable to use a somewhat different type of block or graft copolymer as a compatibilizer. That is, if one uses an ACB type block copolymer as a compatibilizer for A and B homopolymer mixtures, then the block copolymer will have a tendency to be enriched at the interface if C block is incompatible for both A and B (*Scheme 1a*). In this case repulsion forces caused by the presence of C block may be enough to alleviate the strict requirement of A/B block length ratio, which is needed for the localization of an ordinary AB block copolymer at the interface. With this ACB triblock copolymer, the weight fraction of C block has to be in a proper range if the triblock copolymer is designed to be used as a compatibilizer. Large weight fraction of C block will cause a separate C phase in a polymer blend[8] and result in poor performance as a compatibilizer.

Likewise, if one adds a graft copolymer with an incompatible main chain backbone and compatible grafts to the immiscible polymer mixture, then the graft copolymer will have a better chance to be situated at the interface due to the repulsion between the backbone polymer and immiscible polymers (*Scheme 1b*). In this case a small amount of compatibilizer will be enough to change the properties of the blend.

In this research we prepared poly(ethyl acrylate)-grafted polycaprolactone (PEtAcr-g-PCL) as a compatibilizer and applied this to a partially miscible poly(acrylonitrile-co-butadiene-co-styrene) (ABS) and polycarbonate (PC) blend which was selected for experimental convenience as well as for industrial interest. Polycaprolactone (PCL) segment is known to have negative enthalpy of mixing with both ABS and PC, and poly(ethyl acrylate) (PEtAcr) is known to be immiscible. Blends of PC/ABS with different ratios were prepared and their mechanical properties were analysed in order to see whether this concept of compatibilization worked.



Scheme 1 Localization of copolymer at the interface: (a) block copolymer; (b) graft copolymer

EXPERIMENTAL

Materials

ε-Caprolactone (from Aldrich, USA) was fractionally distilled over CaH$_2$ and the middle cut was used. 2-Hydroxyethyl methacrylate (HEMA) (from Aldrich) was used after distillation over CaH$_2$ under reduced pressure. Ethyl acrylate, *n*-butyl acrylate, and *t*-butyl acrylate were used after passing through activated alumina. Polycarbonate (from Samyang Co., Korea, Triex 3025A, $M_n = 15\,500$, $M_w/M_n = 1.75$ based on g.p.c. with polystyrene standard in THF), and ABS copolymer (from LG Chemicals, Korea, PW-100DP, styrene/acrylonitrile ratio = 75/25, polybutadiene content = 40%) were used as received.

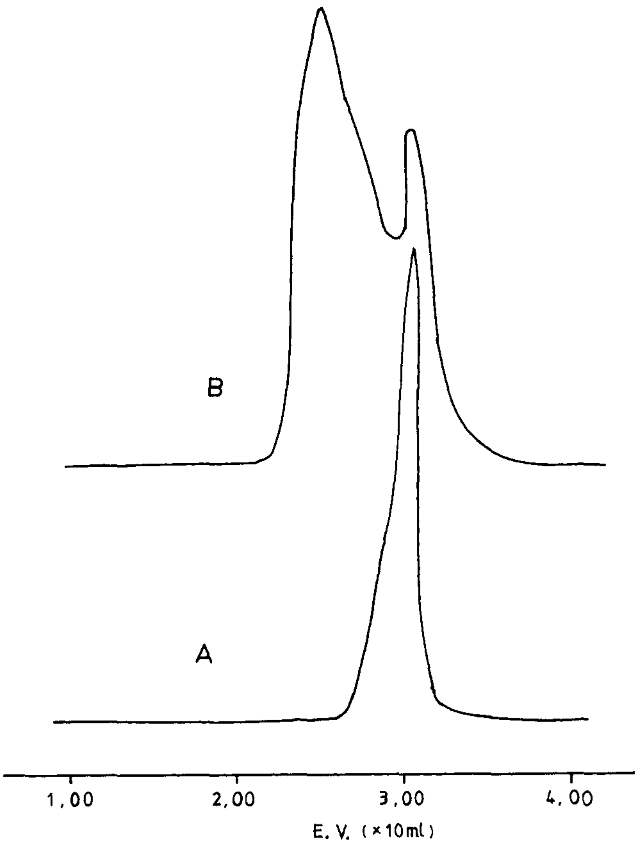
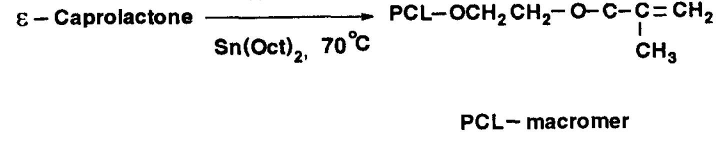


Figure 1 G.p.c. traces of (A) PCL macromer and (B) PEtAcr-g-PCL graft copolymer



Scheme 2 Synthesis of PCL-macromer

Graft copolymer synthesis

For the preparation of methacryloyl terminated polycaprolactone macromer, ϵ-caprolactone was polymerized with HEMA and tin octoate initiation as in *Scheme 2*.

After polymerization (for 15 h) the reaction mixture was precipitated into an excess amount of methanol, washed, and dried under vacuum at 50°C (yield 85%). Its molecular weight and distribution were determined by g.p.c. using THF as the elution solvent. Determined molecular weight was 12 000, and M_w/M_n was 1.21 based on the polystyrene standard.

End group functionality was determined by using proton n.m.r. spectroscopy (300 MHz) and found to contain 0.91 double bonds per chain. For the determination, n.m.r. peaks of terminal $C\underline{H}_2=$ and $-O-C\underline{H}_2-(CH_2)_4-C(=O)-$ in repeating units were integrated[9], and the ratio was compared to that calculated from g.p.c. molecular weight.

The macromer obtained was copolymerized with alkyl acrylate in the presence of 2,2′-azobisisobutyronitrile (AIBN) at 70°C for 2 days in ethyl acetate. The resultant poly(alkyl acrylate)-g-PCL graft copolymer was precipitated into methanol, and dried under vacuum at 60°C. The g.p.c. trace of the product (PEtAcr-g-PCL in *Figure 1*) shows that it contains homopolymer (mostly unreacted PCL macromer), and this was removed by fractionation with MeOH/ethyl acetate (*ca.* 75/25 by volume) mixture. A g.p.c. trace of the fractionated graft copolymer showed only a small bump corresponding to the unreacted macromer.

Blend sample preparation

Mixtures of PC, ABS, and the graft copolymers were extruded in a corotating twin screw extruder (Leistritz T/W) at 240°C and made into pellets. Average residence time was 120 s. Pellets were dried at 120°C for 5 h and injection moulded to standard tensile and impact specimens by using a Battenfeld-75 ton injection moulding machine. Melt mixing time was 52 s at 260°C and cooling time was 15 s. All specimens were prepared under the same conditions in order to prevent any undesirable interference.

Mechanical testing and characterization

Stress–strain properties were tested at room temperature with an Instron Tensile Tester (Model 4204). A crosshead speed of 50 mm min^{-1} was used for tensile strength measurement (ASTM D638). Grip distance was 100 mm for all cases. Flexural strength of 6 mm test bars was measured by a 3-point bending test on a Zwick 1425 with a head speed of 5.8 mm min^{-1} (ASTM D790). Notched Izod impact strengths were measured according to ASTM D256 for specimens with 6 mm thickness and 3 mm thickness. Dynamic mechanical spectra (DMS) were obtained by Rheometrics' RMS 605 and RMS 800 with 6 mm injection sample or disc of 6 cm × 2 mm.

An SEM picture was taken on a Jeol JSM 840A. For the picture, impact test bars were cut and their cross-section (or longitudinal section) was smoothed by a microtome. The smoothed surface was then etched with an aqueous solution of NaOH (30% w/v, 65°C, 15 min) for the hydrolysis of the PC phase[10].

RESULTS AND DISCUSSION

Graft copolymer synthesis

Table 1 shows the molecular characteristics of graft copolymers from the polymerization of acrylates and PCL macromer. The weight ratios of acrylate main chains and PCL grafts were determined by n.m.r. method. Determined ratios were very similar to the corresponding feed ratio. The number average molecular weight decreased as the alkyl group of acrylate changed from Et- to t-butyl. Because a real molecular weight of a graft copolymer is larger than the one determined by g.p.c. (linear PS standard), the average number of grafts per main chain is probably more than 1.5 for poly(*t*-butyl acrylate) main chain, and 1.6 for poly (*n*-butyl acrylate) main chain. Also, for poly(ethyl acrylate) main chain more than 2.7 grafts and 1.8 grafts are expected per main chain for 60/40 and 70/30 weight ratios, respectively.

Mechanical properties

Tables 2 and *3* show mechanical properties of PC/ABS, 65/35 blends. As in the tables, the used main chain segments of graft polymers were different. Different acrylates were used as the main chain segments in this table, because the glass transition temperatures (T_g) of poly(*n*-butyl acrylate), poly(ethyl acrylate), and poly(*t*-butyl acrylate) are known to be −55, −24, and 43°C, respectively, and solubility parameters are different[11]. In its notched Izod impact strength, blends with P(tBu)Acr-g-PCL, PetAcr-g-PCL copolymers showed increased values as in *Table 2*. Especially noticeable was that impact strengths of specimens with 3 mm thickness showed a quite dramatic improvement. But an expected

Table 1 Molecular characteristics of graft copolymers obtained

Graft copolymers	Wt ratio	M_n^a	M_w/M_n
P(tBu)Acr-g-PCL	60/40	46 000	3.20
P(nBu)Acr-g-PCL	60/40	49 000	2.68
PEtAcr-g-PCL	60/40	80 000	1.93
PEtAcr-g-PCL	70/30	71 000	1.84

[a] Determined by g.p.c. with PS standards

Table 2 Notched Izod impact strength of PC/ABS blends (J m^{-1})

Sample	3 mm	6 mm
Control	559	715
P(tBu)Acr-g-PCL	559	1166
P(nBu)Acr-g-PCL	559	784
PEtAcr-g-PCL	774	1215

Added compatibilizer was 1 phr each, PC/ABS = 65/35
p(Alkyl)Acr-g-PCL: 60/40
At room temperature

Table 3 Tensile properties of PC/ABS blends

	Yield		Break	
Sample	σ (MPa)	ϵ (%)	σ (MPa)	ϵ (%)
Control	52.4	10	55.6	156
P(tBu)Acr-g-PCL	50.7	10	56.4	175
P(nBu)Acr-g-PCL	52.1	10	56.4	165
PEtAcr-g-PCL	53.0	10	55.5	153

Added compatibilizer was 1 phr each, PC/ABS = 65/35
p(Alkyl)Acr-g-PCL: 60/40

effect (or trend) of T_g of copolymer on properties was not observed. This absence of trend, on the other hand, may be attributed to the small amount of copolymer added, and different architecture of the used graft copolymers in terms of number of grafts or molecular weights of main chain segments. Contrary to the impact properties, tensile properties of the blend with 1 part copolymer added did not show any significant differences (*Table 3*).

From the results of impact properties it was obvious that added copolymer at the 1 phr level changed some morphological feature of the obtained blend specimen, and that the added compatibilizer had a higher chance of being located at the PC/ABS interfaces because it was hard to expect that a small amount of graft copolymer could change the property dramatically if it was enclosed in the bulk phase of PC or ABS. As the weight fraction of polyacrylate main chain segment increases, it is expected that used graft copolymer tend to exist at the interface due to the incompatibility of polyacrylate toward PC or ABS, but the interfacial adhesion will be lower due to the less number of grafts per given length of main chain segment.

Table 4 Effect of PEtAcr/PCL ratio on mechanical properties of blends

	Control	60/40	70/30
Izod impact strength ($\mathrm{J\,m^{-1}}$)	510	617	578
Tensile strength (MPa)	51.7	52.9	52.9
% Elongation at yield	10	10	10

PC/ABS = 70/30
6 mm test specimens for Izod impact at room temperature

Table 5 Effect of compatibilizer concentration on mechanical properties of blends

		Compatibilizer conc. (phr)			
		Control	1	2	3
Izod impact strength ($\mathrm{J\,m^{-1}}$)	6mm	441	441	382	392
	3 mm	539	1176	882	882
Tensile strength (MPa)		45.9	46.4	46.3	46.1
Elongation at yield (%)		9.4	9.3	9.3	9.6
Flexural modulus (GPa)		1.69	1.66	1.65	1.63
Flexural strength (MPa)		66.0	65.7	65.0	64.5

PC/ABS: 60/40
PEtAcr/PCL ratio: 60/40
At room temperature

Table 4 shows some mechanical properties of the test specimens with 6 mm thickness at two different weight ratios of PCL/PEtAcr in graft copolymers. Tensile strengths and percentage elongation at yield were the same for both graft copolymers and this may be interpreted as one of either two reasons. One is that interfacial adhesion is not a controlling factor for tensile strength or percentage elongation at the compatibilizer level of 1 phr. The other is that interfacial adhesion between PC and ABS itself is stronger than that between compatibilizer and PC or ABS. If one considers the tensile values in *Table 5* the latter case is more likely.

Notched Izod impact strength of 6 mm specimens, on the other hand, showed slight decrease as the weight fraction of PCL decreased. But the reason is not clear in this case as to whether the number of grafts per chain is important, or a certain weight fraction is needed regardless of the main chain length. As mentioned previously, a number of PEtAcr-g-PCL 60/40 has at least 2.7 grafts per chain, and 70/30 has at least 1.8 grafts per chain.

Table 5 shows mechanical properties of PC/ABS, 60/40 blends. As shown in the table, tensile strength and elongation at yield stayed almost the same, though the compatibilizer concentration increased up to 3%. On the

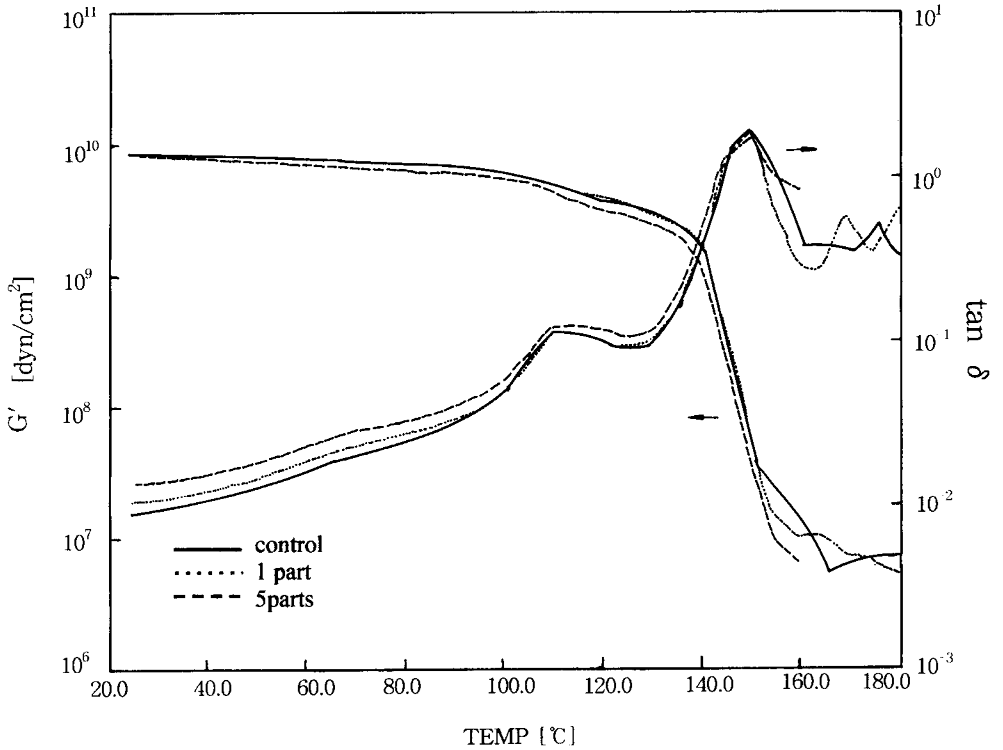


Figure 2 DMS curves of blends with different compatibilizer level; —, control; ......, 1 part; - - - 5 parts

other hand, the flexural modulus and strength tapered down slightly.

This behaviour is clearly seen in DMS in *Figure 2*, where storage modulus, loss modulus, and tan δ were almost the same to those of control when 1 phr of graft copolymer was added. On the other hand, as the graft copolymer concentration increased from 1 phr to 5 phr, storage modulus decreased, and shapes of loss modulus, and tan δ curves were changed. This phenomenon may suggest that graft copolymers start to dissolve into bulk phase as isolated chains or micelles[12,13], and interfacial area per graft copolymer decreases as the concentration increases[14]. T_g changes were not significant from the curves. Notched Izod impact strength were also changed as the graft copolymer content increased from 1 phr to 2 phr as in *Table 5*. In this case a decrease was observed and stayed almost the same when the concentration level increased to 3 phr. On the other hand, this table clearly shows that optimum graft concentration is *ca.* 1 phr. This may imply that interfacial coverage is adequate with this

Table 6 PC content vs. tensile strength and elongation

		Yield		Break	
PC content (%)	Compatibilizer	σ (MPa)	ϵ (%)	σ (MPa)	ϵ (%)
30	×	41.7	8	35.1	103
	O	40.0	8	36.7	183
50	×	47.3	9	46.3	156
	O	46.3	9	48.9	187
60	×	51.1	10	53.6	155
	O	51.8	10	58.6	186
65	×	50.9	10	56.6	190
	O	51.1	10	56.5	186
70	×	51.3	10	61.3	206
	O	51.7	10	57.5	182

×: No compatibilizer
O: 1 phr compatibilizer added

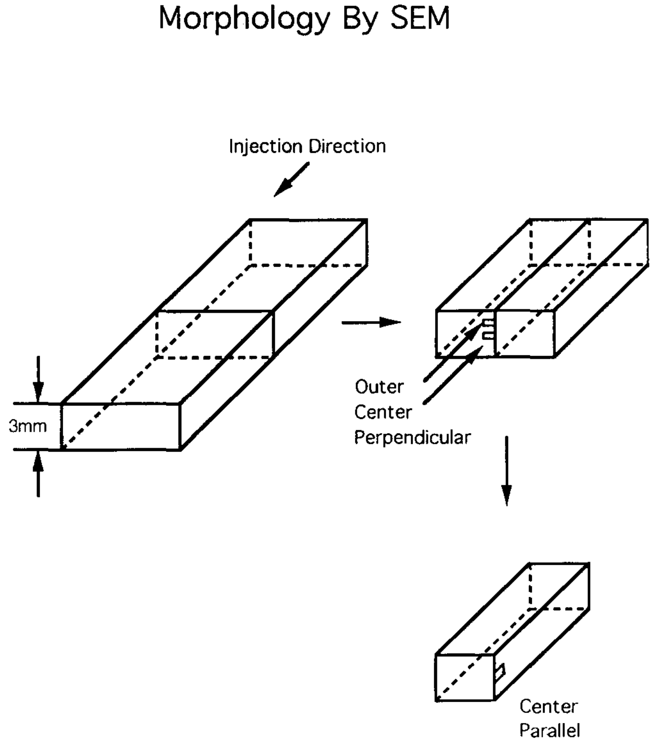


Figure 4 Schematic representation of sample preparation for SEM

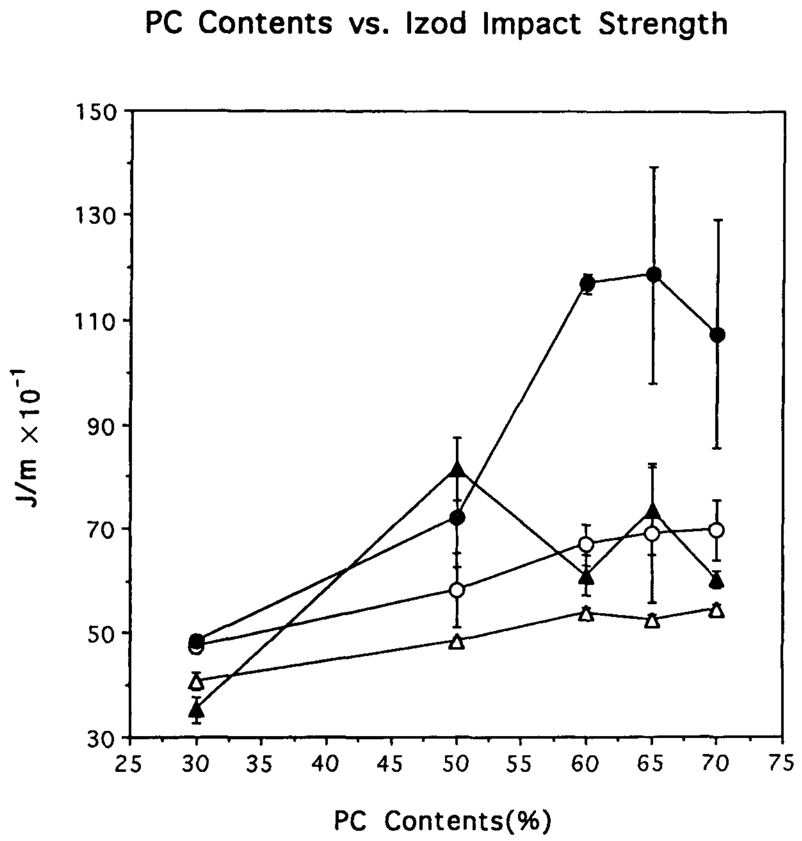


Figure 3 PC contents vs. Izod impact strengths of blends: ●, 3 mm sample with compatibilizer; ○, 3 mm sample, control; ▲, 6 mm sample with compatibilizer; △, 6 mm sample, control

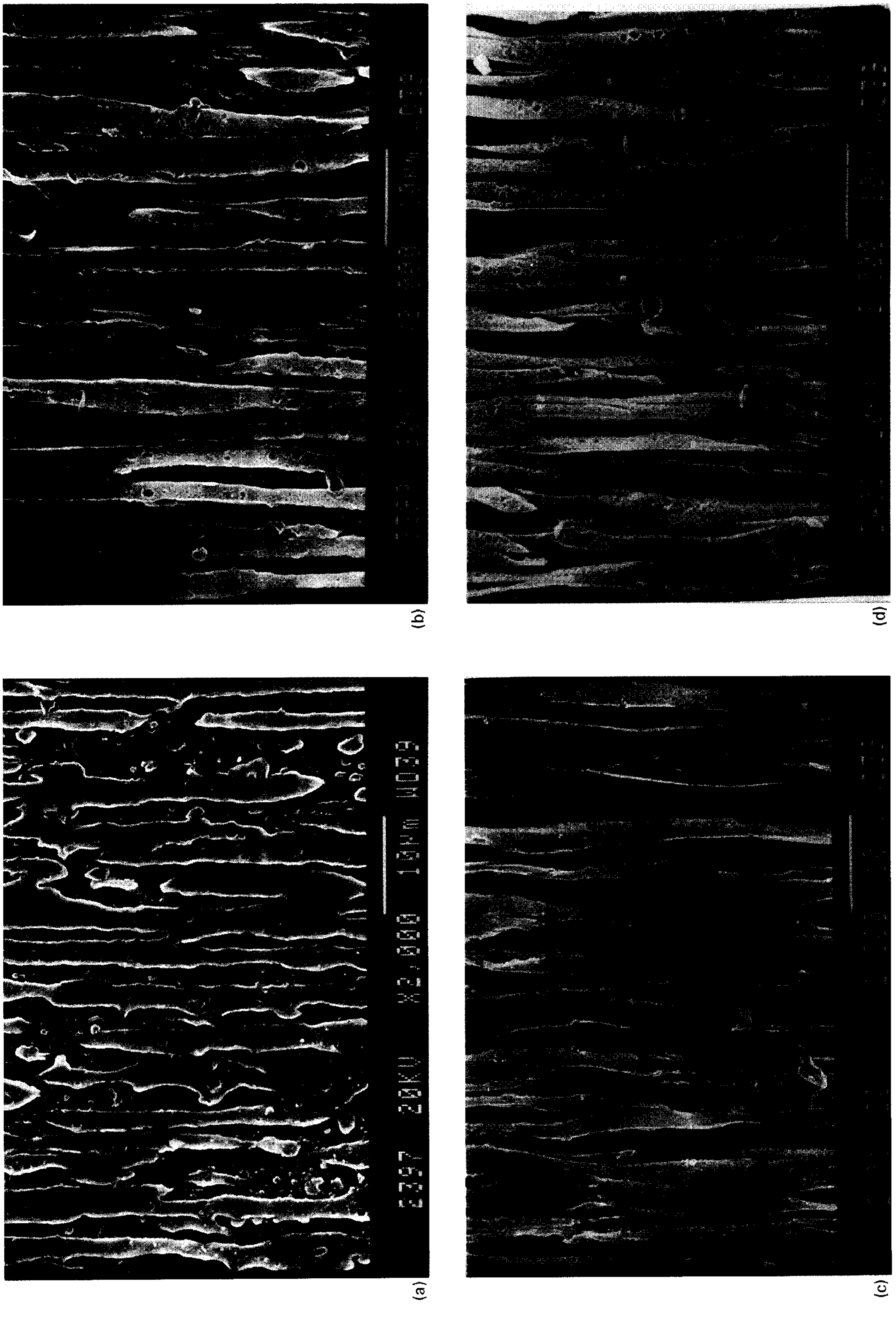


Figure 5 SEMs of centre parallel surface of the injection moulded PC/ABS 60/40 blend added with different amounts of graft copolymer: (a) 0 phr; (b) 1 phr; (c) 2 phr; (d) 3 phr

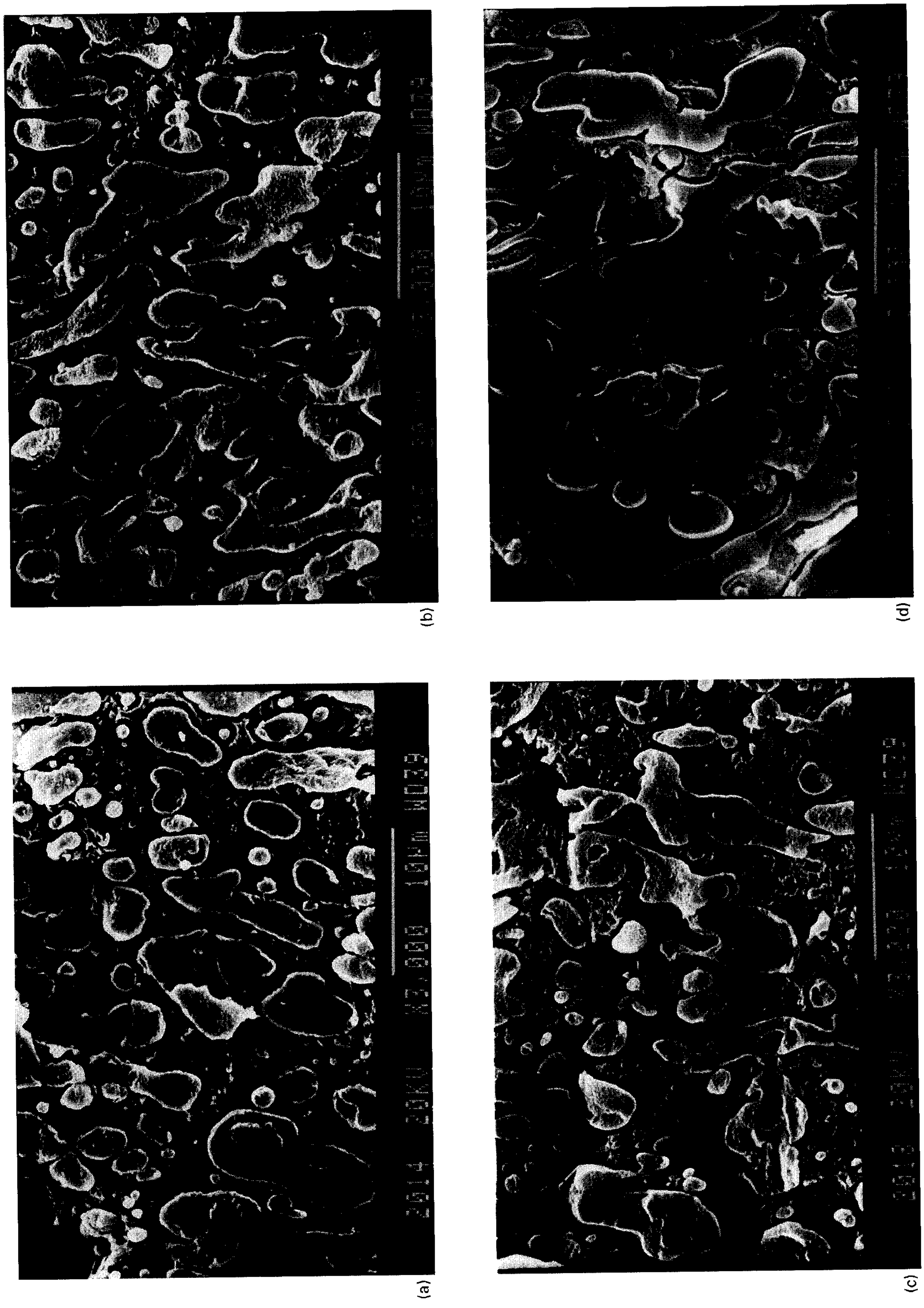


Figure 6 SEMs of centre perpendicular surface of the injection moulded PC/ABS 60/40 blend added with different amounts of graft copolymer: (a) 0 phr; (b) 1 phr; (c) 2 phr; (d) 3 phr

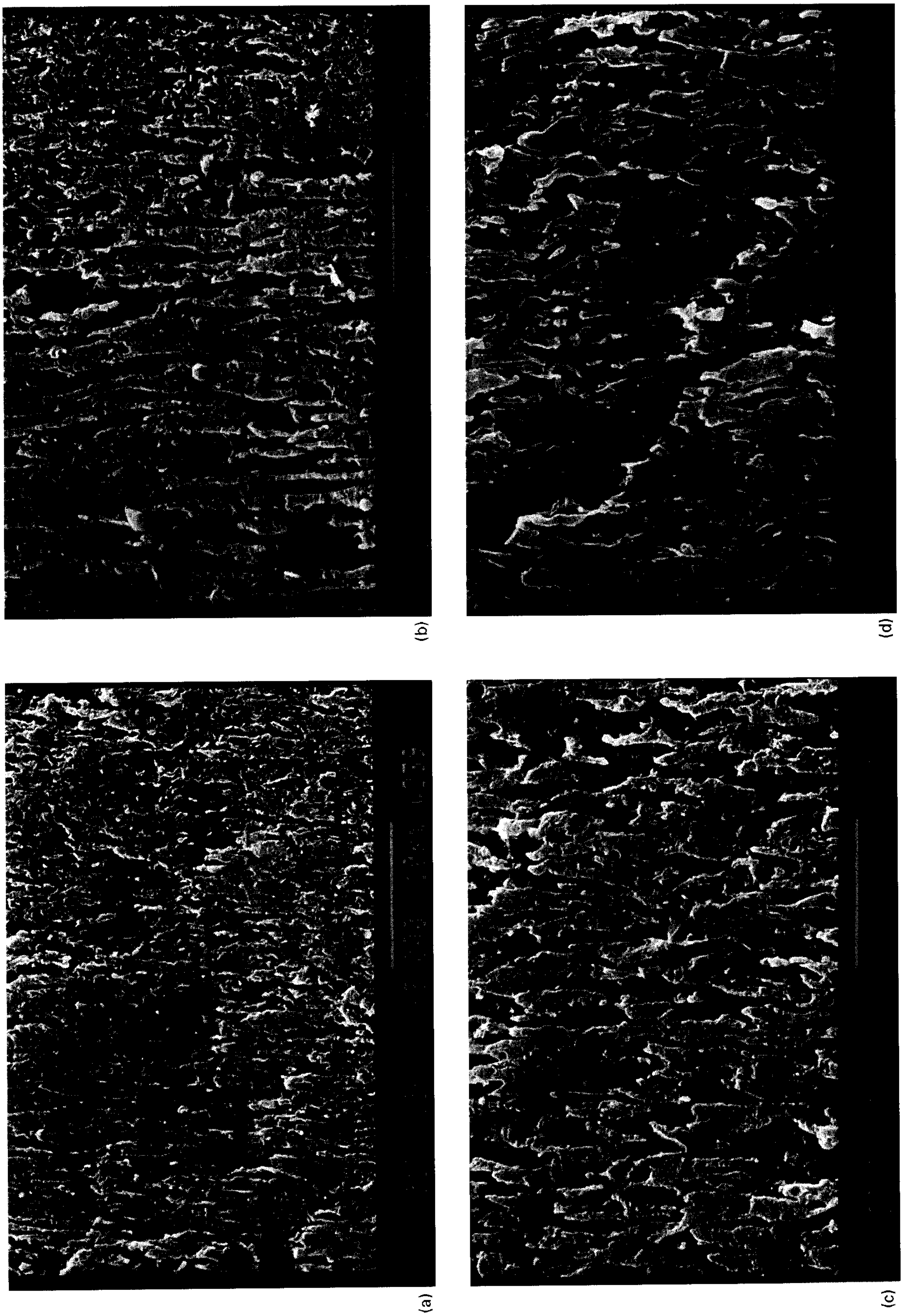


Figure 7 SEMs of perpendicular skin layer of the injection moulded PC/ABS 60/40 blend added with different amounts of graft copolymer: (a) 0 phr; (b) 1 phr; (c) 2 phr; (d) 3 phr

concentration level, and almost all graft copolymer is enriched at the PC/ABS interfaces. When one compares this system with a PC/ABS/PCL blend system, where PCL is used as a compatibilizer, this result is a very meaningful one because it was reported that as much as 20% PCL is needed for some improvement in notched Izod impact strength of a PC/ABS/PCL system[15]. In that system it is known that only a small fraction of used PCL is located at the PC/ABS interfaces due to the solubilization of PCL in PC and ABS bulk phases.

Table 6 shows the summarized results of tensile test values with various PC content in the blend. As in *Table 6* phr compatibilizer did not change values at yield point regardless of PC content. And this tensile yield behaviour is not much different from the one studied by others in the PC/ABS system[16,17]. At break points tensile strength and percentage elongation both showed increased values with PC contents of 30%, 50%, and 60%. With 1% added compatibilizer, elongation at break shows quite an improvement and almost the same value (180%) throughout the PC content tested.

Figure 3 shows impact properties of test specimens with 6 mm and 3 mm thickness. Without any added compatibilizer both specimens of 6 mm and 3 mm thickness showed almost linear increase in impact strength as the PC content increased from 30 to 70%. This figure therefore demonstrates that the PC/ABS blend itself can possibly be included in an additive blend[16] in a range of compositions studied which classifies blends into three categories: additive blend, synergistic blend, and nonsynergistic blend. The test specimens with 3 mm thickness showed higher values compared to that with 6 mm thickness at the same PC content, and this behaviour may be related to characteristics of PC as well as thickness dependent characteristics of injection moulded specimens. It is well known that the impact property of PC is very much dependent on the thickness of a test sample[18]. It is also known that an injection moulded specimen gives higher impact value for a thinner specimen due to higher molecular orientation perpendicular to the impact direction.

One percent addition of compatibilizer, however, made this behaviour different. As seen in *Figure 3*, improvement in impact strength was observed for both 6 mm and 3 mm specimens, and this improved performance can be said to be one of the typical characteristics of the synergistic blend. This behaviour was more prominent in 3 mm test specimens. With the 3 mm test sample, 1% addition of compatibilizer resulted in a dramatic increase in impact strength at PC content of 50–70%. At low PC content impact improvement was marginal. This behaviour clearly implies that addition of compatibilizer at 1 phr level changed morphological features of the blend.

Morphological study

The fractured surface of 3 mm samples was very rugged resembling that of a laminated paper board or plywood. In order to see the morphology, the impact test bar with 3 mm (PC 60%) thickness was first fractured perpendicular to the injection direction as shown in *Figure 4*. A skin layer ($d = 0.5$ mm from the surface) and a centre layer ($d = 1.5$ mm from the surface) were selected for microscopy and then fractured parallel to the injection direction.

Figure 5 shows the SEMs of a centre parallel surface of an injection moulded PC/ABS 60/40 blend. All four micrographs show extended ABS strands parallel to the injection direction. The blend with the 1 phr compatibilizer has slightly thicker ABS strands and is more regularly elongated than the control (and 1 phr has the thickest ABS phase). In the presence of graft copolymer, the PC/ABS interface became smoother, and this can be seen clearly by comparing *Figures 5a* and *5b*. Addition of more graft copolymer made the interface much smoother (*Figure 5c*).

All four micrographs in *Figure 6* show dispersed ABS phases in PC matrix. With the addition of graft copolymer, the ABS phase is being coalesced (*Figure 6b*), and this phenomenon is more clearly seen in the blend with a graft copolymer level of 3 phr (*Figure 6d*). From these micrographs (*Figures 5* and *6*), therefore, it is possible to visualize three-dimensional shapes of ABS phases at the centre part of the test specimens. It seems that the addition of graft copolymer at the 1 phr level made the ABS phase more or less long leaf-like in shape. So, thickness of ABS is only slightly increased (by the addition of graft copolymer), but width of the ABS phase is greatly increased by the addition of graft copolymer through tip to tip coalescence of irregular ABS domains.

With the addition of more graft copolymer, however, this leaf-like shape of the ABS phase changes to a more or less irregular rod-like shape with enlarged lateral size. Micrographs of perpendicular skin layer also support this envisualization (*Figure 7*). Addition of graft copolymer made denser ABS phase and wider leaf-like shape (*Figure 7b*). This leaf-like structure is clearly seen in terms of PC phase. Addition of more graft copolymer, however, disrupted this leaf-like connectivity of PC phase toward denser, and more rounded, ABS domains.

When the mixtures of PC and ABS were extruded, addition of a small amount of graft copolymer gave less screw torque to extrude out a constant volume of the blend. Torque reduction of maximum ~15% was observed for some blend samples. Melt viscosity by a capillary rheometer, however, showed very similar (but slightly reduced) values at 250°C. Because the addition of a small amount of graft copolymer reduced the required screw torque in the extruder, the role of the graft copolymer can be considered as a processing aid or an interfacial lubricant. This fact is certainly related to the observed different microstructures in impact specimens because different flow behaviour of the blend gives different microstructures during injection moulding. In this study, therefore, the principal reason for different microstructure can be attributed to the presence of graft copolymer. Mutual interactions of ABS/PC, ABS/graft, PC/graft, and the relative interaction strengths seem to determine the observed morphology. Depending on the structure of the graft copolymer, it can be enriched at the ABS/PC interface and acts as an interfacial lubricant or adhesion promoter.

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REFERENCES

1. Paul, D. R., *Polymer Blends*. Academic Press, New York, 1978.

2. Utracki, L. A., *Polymer Alloys and Blends.* Hanser Publishers, Munich, 1990.
3. Folkes, M. J. and Hope, P. S., *Polymer Blends and Alloys.* Chapman & Hall, Cambridge, 1993.
4. Leibler, L., *Makromol. Chem., Mackromol. Symp.*, 1988, **16,** 1.
5. Noolandi, J. and Hong, K. M., *Macromolecules*, 1982, **15,** 482.
6. Noolandi, J. and Hong, K. M. *Macromolecules*, 1984, **17,** 1531.
7. Thomas, S. and Prud'homme, R. E., *Polymer*, 1992, **33,** 4260.
8. Auschra, C. and Stadler, R., *Macromolecules*, 1993, **26,** 6364.
9. Dubois, Ph., Jèrôme, R. and Teyssiè, Ph., *Macromolecules*, 1991, **24,** 977.
10. Dong, L., Greco, R. and Orsello, G., *Polymer*, 1993, **34,** 1375.
11. Brandrup, J. and Immergut, E. H., *Polymer Handbook*, 3rd edn. John Wiley & Sons, New York, 1989, Chap. 6.
12. Eastmond, G. C., Ming, J. M. and Malinconico, M., *Brit. Polym. J.*, 1987, **19,** 275.
13. Sakellariou, P., Eastmond, G. C. and Miles, I. S., *Polymer*, 1991, **32,** 2351.
14. Sakellariou, P., Eastmond, G. C. and Miles, I. S., *Polymer*, 1992, **33,** 4493.
15. Suh, K. S., Lee, D. S. and Kang, C. G., *Polymer (Korea)* 1995, **19,** 254.
16. Surez, H., Barlow, J. W. and Paul, D. R., *J. Applied Polymer Sci.*, 1984, **29,** 3253.
17. Chiang, W.-Y. and Hwung, D.-S., *Polymer Eng and Sci.*, 1987, **27,** 632.
18. Mark, H. *Encyclopedia of Polymer Science and Engineering*, Vol. 11, 2nd edn. John Wiley & Sons, New York, 1988, pp. 648–718.