

Effect of polycarbonate molecular weight and processing conditions on mechanical behaviour of blends with a core-shell impact modifier

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Morphology, tensile properties and impact strength behaviour of blends of three different molecular weight (or viscosity) grades of polycarbonate (PC) and a core-shell type impact modifier (3–18 wt%) were prepared in a single screw extruder with an intensive mixing head and in a co-rotating, fully intermeshing twin screw extruder at different conditions. The morphology of these blends were quantitatively analysed from transmission electron photomicrographs. Tensile properties and Izod impact strength, as a function of temperature for 3.13 mm specimens, were also measured. All mechanical properties were found to be very sensitive to the degree of dispersion of the impact modifier in the PC matrix. Blends made in the twin screw extruder consistently showed better dispersion and mechanical properties: higher tensile modulus, yield strength and elongation at break; higher notched Izod impact strength and lower ductile–brittle temperature. Blends with higher molecular PC show better impact properties reflecting the matrix properties. A subsequent paper explores a more complete analysis of the fracture toughness of such blends and the modes of deformation they undergo during fracture. Copyright © 1996 Elsevier Science Ltd.

(Keywords: blends; polycarbonate; core-shell modifier)

INTRODUCTION

Bisphenol A polycarbonate (PC) is widely used as an engineering material^{1,2} because of such desirable properties as optical clarity, toughness and high heat distortion temperature. However, PC has some characteristics that limit its use in many applications; for instance, its exceptional toughness is not retained in thick moulded sections or in the presence of sharp notches^{3–5} or at low temperatures. In addition, physical ageing below its glass transition temperature (T_g) causes severe embrittlement^{6–8}.

In 1978 Yee and Kambour reported that PC can be made tough in thick sections or at high testing speeds by the incorporation of a small amount of another polymer such as polyethylene³. They suggested that the dispersed polyethylene particles cause a transition from a plane strain state to one of plane stress. Blends of PC with core-shell impact modifiers provide an alternative approach to this problem and are of great commercial interest. The concentration of the core-shell impact modifier may vary from a minimum of 4% to about 20%⁹. In accord with the initial report by Yee and Kambour³, addition of small amounts of these particles gives rise to many desirable improvements in PC, including reduced notch

sensitivity, toughness of thick sections and good low temperature toughness etc., with only small sacrifices in other important properties^{10–20}.

This paper gives a detailed report on the problem of dispersing a particular core-shell impact modifier into a PC matrix. It is shown that the intensity of mixing or extruder type, process conditions and PC molecular weight all have profound effects on the degree of dispersion of the core-shell rubber particles into the PC matrix which in turn greatly affects the impact properties achieved by the blend. A subsequent paper explores a more detailed analysis of the fracture toughness of such blends and the modes of deformation they undergo during fracture.

EXPERIMENTAL

Table 1 describes the polycarbonates and the core-shell modifier used in this study. The three commercial grades of PC which vary in molecular weight were obtained from Mitsubishi Engineering-Plastics Corp. The core-shell impact modifier was obtained from Kureha Chemical Industry Co. Ltd. It is a complex chemical product that basically consists of a butadiene-based rubber core and a hard grafted methyl methacrylate copolymer shell. Further chemical details of this proprietary product have not been published; however, the experimental characterization done as part of this

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Table 1 Materials used in this study

| Designation used here | Commercial designation | Form | PC ^a | Brabender torque after 10 min (N.m) | | Source |
|----------------------------|--|-----------------|--------------------------------|-------------------------------------|-------|---------------------------------------|
| | | | | 260°C | 290°C | |
| L-PC | Polycarbonate (Iupilon H3000) | Pellet | $M_n = 7400$ $M_w = 20100$ | 7.0 | 2.7 | Mitsubishi Engineering-Plastics Corp. |
| M-PC | Polycarbonate (Iupilon S3000) (Iupilon S3000F) | Pellet Flake | $M_n = 8500$ $M_w = 23700$ | 9.7 | 4.7 | Mitsubishi Engineering-Plastics Corp. |
| H-PC | Polycarbonate (Iupilon E2000) (Iupilon E2000F) | Pellet Flake | $M_n = 10800$ $M_w = 32000$ | 19.3 | 10.6 | Mitsubishi Engineering-Plastics Corp. |
| Core-shell impact modifier | HIA-28 | Powder | - | 14.5 | 16.5 | Kureha Chemical Industry Co., Ltd. |

^a Determined by g.p.c. using polystyrene standards

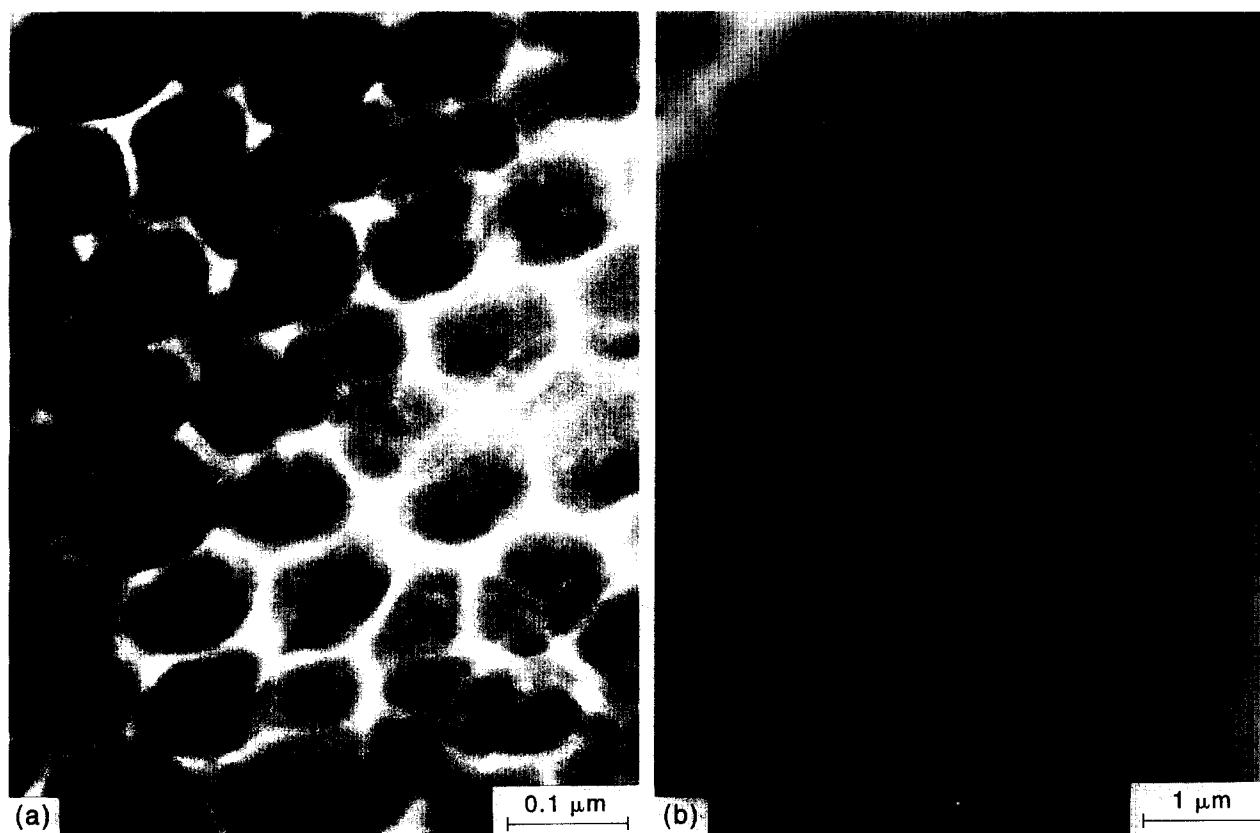


Figure 1 TEMs for (a) neat core-shell impact modifier after extrusion via a single screw extruder at 220°C and (b) H-PC/modifier (99/1) blend prepared in a twin screw extruder at 260°C, stained with osmium tetroxide (OsO_4)

work provide a useful insight for what follows. The rheological behaviour of these materials was characterized by Brabender Plasticorder torque measurements. A 50-ml mixing bowl and standard rotors were used for measurements at 260 and 290°C and 60 rpm⁻¹. To avoid trapping air during torque measurements the core-shell rubber was first extruded at 220°C and chopped into pellets. The core-shell impact modifier was characterized by a Polymer Laboratories dynamic mechanical thermal analyser (DMTA) at a frequency of

1 Hz and a heating rate of 3°C min⁻¹ in a single-cantilever bending mode.

All the materials were predried for 16 h at 80°C in a vacuum oven before melt processing. A Killion single screw extruder (SS, $L/D = 30$, $D = 2.54$ cm) outfitted with an intensive mixing screw and a Baker-Perkins co-rotating, fully intermeshing twin screw extruder (TS, $D = 15$ mm) were used for melt blending. For twin screw extrusion, the polycarbonate had to be fed in flake form which was prepared by cryogrinding of pellets. Blends

were extruded at 290°C and 40 rpm in the SS and at 260 and 290°C at 160 rpm in the TS. Some blends were prepared by a master batch approach involving two extrusions; first a 50/50 PC/modifier blend was formed which was then diluted with PC to the desired composition.

The blends were injected moulded into standard Izod bars (ASTM D256) and dog-bone shaped tensile specimens (ASTM D638 type I) of 3.13 mm thickness using an Arburg Allrounder injection moulding machine set at a melt temperature of 280°C and a mould temperature of 65°C. Specimens without defects were selected for testing.

Transmission electron microscopy (TEM) was used to observe the morphology of injection moulded blends. Observation planes were chosen both perpendicular and parallel to injection flow at the centre and edge of specimens, usually 6.25 mm in thickness. After a mesa-cut, thin sections (about 20 nm) were obtained by a Reichert-Jung Ultracut E microtome under cryogenic conditions (-45°C) with a diamond knife. Thin sections were stained by osmium tetroxide (OsO₄) vapour through exposure to 2% solution for 18 h at room temperature. The butadiene-based rubber particles appear black in TEM images. A JEOL TEM 200 CX transmission electron microscope was used at an accelerating voltage of 120 kV.

Quantitative analysis of blend morphology from TEMs was carried out with the aid of a semi-automatic digital analysis technique based on Image[®] software

from the National Institutes of Health; the dispersed phase size is reported as the observed area occupied in the TEM by core-shell particle clusters.

CHARACTERIZATION OF IMPACT MODIFIER

A high magnification TEM of core-shell particles, obtained from extruded pellets, is shown in *Figure 1a*. In this form, the particles are severely deformed and do not appear circular in shape as they would when they are individually dispersed in a PC matrix. The effective diameter of these particles, as seen here, ranges from 0.06 to 0.15 μm. The average cross-sectioned area per impact modifier particle computed from *Figure 1a* is 0.0078 μm²; this value will be used in subsequent morphological analyses. It is also estimated that the rubber core comprises about 60 vol% of the core-shell material. *Figure 1b* shows a typical photomicrograph of a blend of 1% modifier in 99% high molecular weight PC, designated as H-PC in *Table 1*. This result indicates that the core-shell particles can be well dispersed in PC under appropriate conditions and few, if any, of the particles appear to be permanently clustered by their manufacturing process.

Figure 2a shows dynamic mechanical properties at 1 Hz for a moulded sample of the core-shell impact modifier as a function of temperature. The storage modulus E' and $\tan \delta$ responses show resolution of at least two phases with glass transition temperatures of -40°C for the core phase and (T_{gC}) and 100°C for a hard

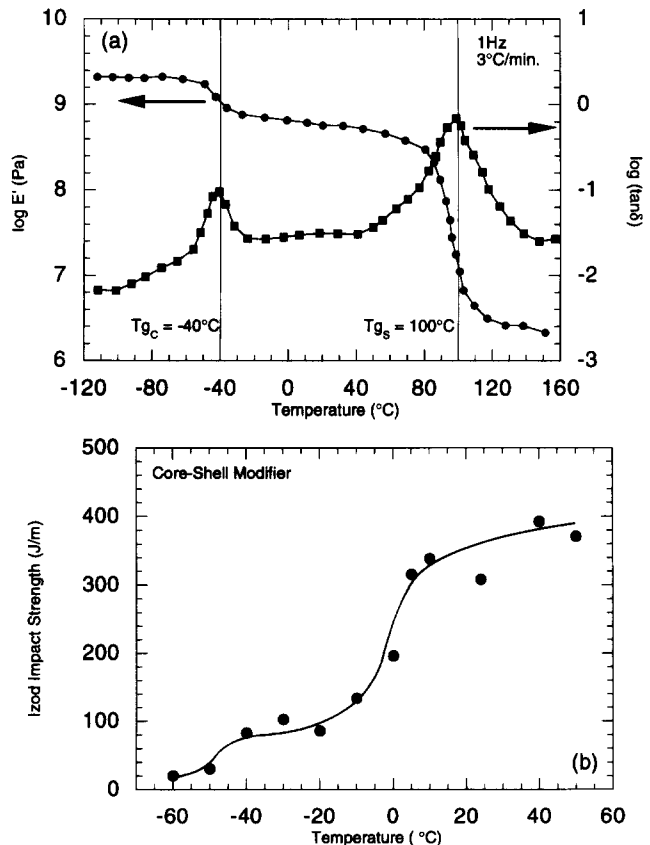


Figure 2 (a) Dynamic mechanical properties of core-shell impact modifier at 1 Hz measured while heating at 3°C min⁻¹. (b) Notched Izod impact strength as a function of temperature for core-shell impact modifier

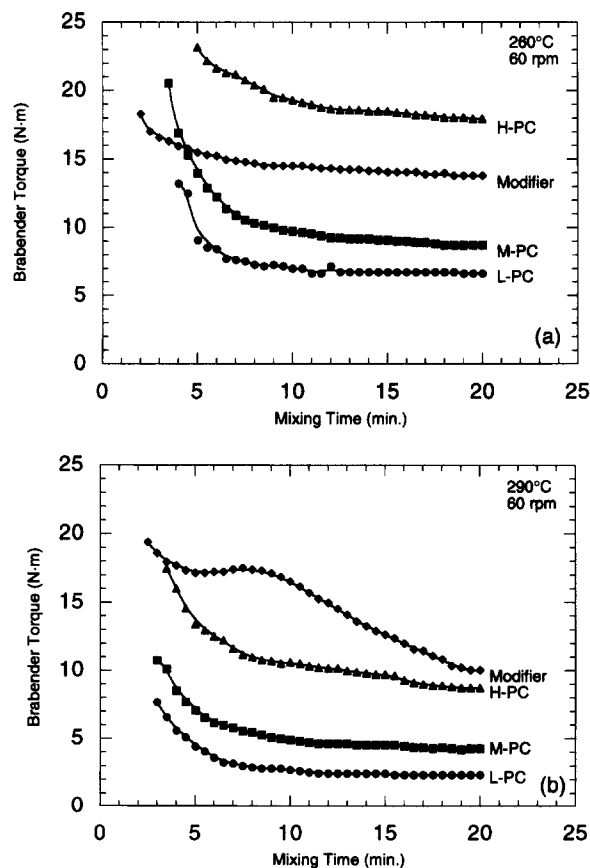


Figure 3 Brabender torque of three molecular weight grades of PC and core-shell impact modifier as a function of time at (a) 260°C and (b) 290°C, at 60 rpm

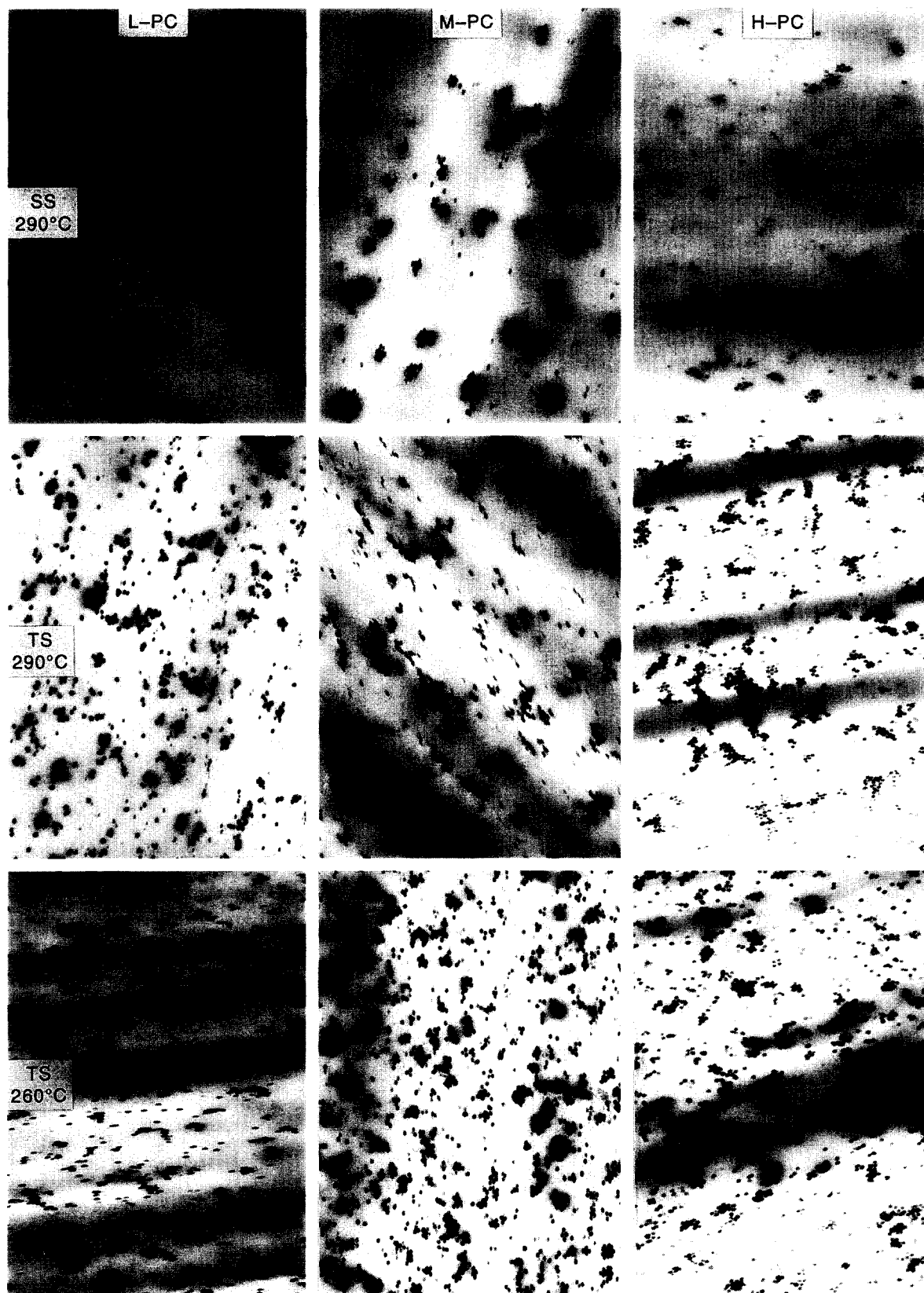


Figure 4 TEMs of PC/core-shell impact modifier blends (94/6) for three molecular weight grades of polycarbonate (L-PC, M-PC, H-PC) prepared by a single pass through a single screw extruder at 290°C (SS/290°C) and a twin screw extruder at 290°C (TS/290°C) at 260°C (TS/260°C)

shell phase (T_{gs}). The storage modulus is constant at about 2 GPa below T_{gc} and ranges from 250 MPa to 630 MPa between T_{gc} and T_{gs} .

Figure 2b shows notched Izod impact strength of the

modifier measured as a function of temperature using test specimens formed by injection moulding at 220°C. There is a significant step increase in toughness at about 0°C, between T_{gc} and T_{gs} , and at -40°C corresponding

to T_{gC} . Above 0°C specimens fail in a ductile manner exhibiting hinged breaks and stress whitening. All fractures below 0°C were brittle; however, between 0°C and -40°C the fracture surfaces were rough while below -40°C the fracture surfaces were very smooth.

RHEOLOGY

Brabender torque rheometry was utilized to characterize the individual blend components. Torque measurements were carried out at both 260 and 290°C as a function of time with the results shown in Figure 3; 10 min torque readings are reported in Table 1. The three PCs exhibit different torque values as seen in Figure 3a, the core-shell modifier has an effective viscosity that is lower than that of H-PC but higher than that of the other two PCs. The torque readings at 290°C (see Figure 3b) present a different picture. Here, the core-shell material exhibits a higher effective viscosity than all three polycarbonates. The modifier shows a rather unusual torque vs time response. Its torque at 290°C is higher than the value of 260°C up to about 12 min, and then decreases rapidly; this unusual behaviour was not explored further and may

be due to consequences of either physical or chemical issues. The polycarbonates are stable for more than 20 min at 290°C.

BLEND MORPHOLOGY

The degree to which these particles can be dispersed in a PC matrix was examined using the two types of extruders described in the Experimental section; three PC molecular weights or melt viscosities; and two melt compounding temperatures. Figure 4 shows the morphology of blends containing 6 wt% of the impact modifier prepared in the SS (at 290°C) and the TS (at 260 and 290°C) extruders. All observations were made on sections cut from the centre of an injection moulded bar in a plane perpendicular to the flow direction. Other observation locations gave similar results. It appears that dispersion of the impact modifier particles is generally improved as the molecular weight or melt viscosity of the PC is increased and by the more intensive mixing provided by the TS.

Blends prepared in the SS at 290°C show rather clearly the effect of PC melt viscosity on dispersion of the

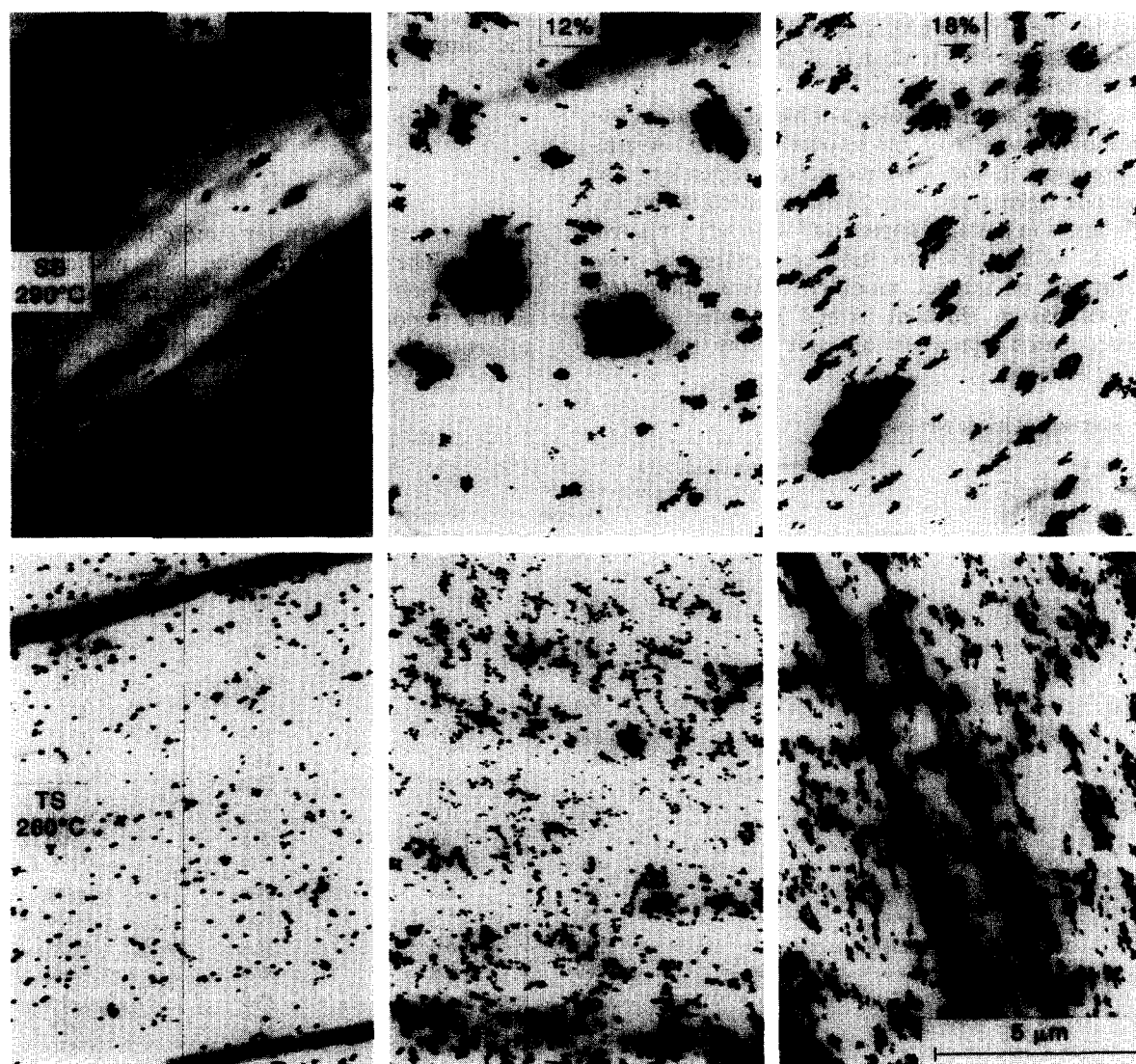


Figure 5 TEMs of blends medium molecular weight grade polycarbonate, M-PC, containing 3%, 12% and 18% of the core-shell impact modifier by a single pass through a screw extruder at 290°C (SS/290°C) and in a twin screw extruder at 260°C (TS/260)

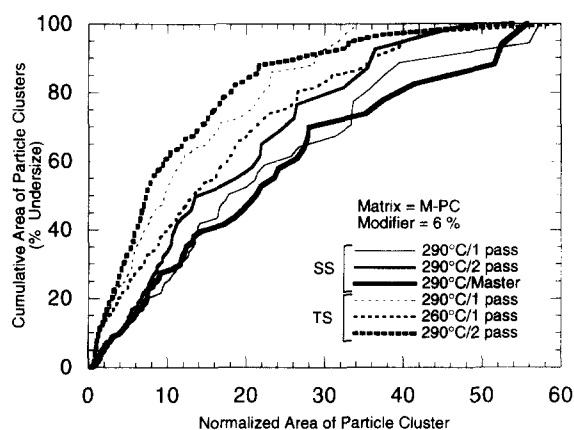


Figure 6 Cumulative area of particle clusters versus normalized area of particle cluster (i.e. actual area observed in TEM divided by that of a single particle which is estimated to be $0.0078 \mu\text{m}^2$) for M-PC/core-shell modifier (94/6) blend prepared by different procedures

impact modifier particles. Blends with L-PC have large aggregates of particles, while blends based on H-PC show distinctly improved particle dispersion. The effect of matrix viscosity on dispersion is less evident in blends prepared by the TS. This suggests that the type of mixing provided by the TS diminishes somewhat the effects of rheological factors on the degree of particle dispersion that can be achieved.

Figure 5 shows the morphology of blends based on M-PC containing 3–18% of the impact modifier. Again, blends prepared in the TS have better dispersion, i.e. fewer particle aggregates, than those prepared in the SS. The differences in particle dispersion for blends prepared in the TS vs the SS are most noticeable at low concentrations of impact modifier. Blends prepared using two passes through either extruder or by the master batch approach did not show improved

particle dispersion, i.e. reduction in particle clusters. No significant differences in blend morphology are noted for extrusion at 260°C vs 290°C.

While the series of photomicrographs shown in Figures 4 and 5 give a visual impression of the degree of particle dispersion, it is useful to analyse these results using more quantitative approaches. Two schemes described below were used to obtain measures of cluster size and their distributions in size and location.

First, Image[®] software was used to define the area of each cluster of impact modifier particles seen in the field of view of the TEMs. The area of a single impact modifier particle was estimated to be $0.0078 \mu\text{m}^2$. Cumulative distribution plots from this approach for selected cases are shown in Figure 6. Here, the ordinate represents the percentage of total area of clusters of impact modifier particles that is at or below the individual cluster area normalized by the area of a single particle, shown on the abscissa. The normalization of the cluster size by that of a single particle aids physical interpretation; this ratio reflects the approximate number of particles in the cluster cross-section seen in the TEM. Table 2 lists two quantitative indications of the impact modifier particle cluster size, normalized by the area of a single particle, for each blend composition and process condition determined by the following methods. One is the simple number average cluster area, defined as follows

$$\bar{A}_n = \frac{\sum_{i=1}^n A_i}{n}$$

where A_i = area of cluster i and n is the total number of clusters. The other is the value of the particle cluster area below which 60% of all clusters are smaller. Both show similar trends, so only the number average will be used subsequently.

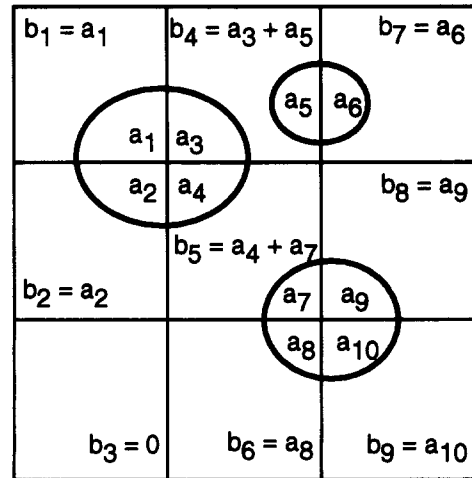
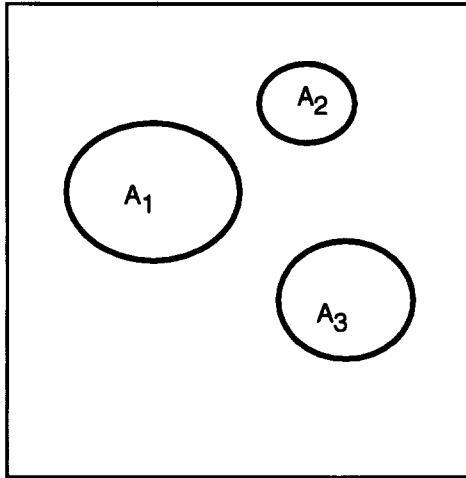
Table 2 Summary of image analysis results

| Matrix PC | Impact modifier content (wt%) | Extrusion conditions | | | Number average cluster area ^a | Cluster area at 60% cumulative area ^a | S | P |
|-----------|-------------------------------|----------------------|------------------|--------------------|--|--|-------|-------|
| | | Extruder type | Number of passes | Process temp. (°C) | | | | |
| L-PC | 6 | Single | 1 | 290 | 12.1 | 36.1 | 0.835 | 0.915 |
| | | Twin | 1 | 290 | 2.2 | 5.9 | 0.900 | 0.988 |
| | | | 1 | 260 | 3.3 | 8.6 | 0.904 | 0.993 |
| M-PC | 3 | Single | 1 | 290 | 4.0 | 16.0 | 0.825 | 0.904 |
| | | Twin | 1 | 260 | 1.5 | 2.9 | 0.913 | 0.990 |
| | | | 1 | 290 | 7.7 | 25.6 | 0.851 | 0.969 |
| | 6 | Single | 2 | 7.9 | 21.8 | 0.877 | 0.892 | |
| | | | 2M ^b | 8.3 | 26.4 | 0.854 | 0.927 | |
| | | | 1 | 290 | 4.2 | 12.1 | 0.886 | 0.986 |
| | 12 | Twin | 2 | 3.8 | 9.5 | 0.900 | 0.987 | |
| | | | 1 | 260 | 4.6 | 17.7 | 0.876 | 0.994 |
| | | | 1 | 290 | 8.6 | 23.8 | 0.849 | 0.935 |
| | 18 | Single | 1 | 290 | 10.6 | 31.8 | 0.874 | 0.974 |
| | | Twin | 1 | 260 | 6.9 | 32.8 | 0.840 | 0.989 |
| | H-PC | 6 | Single | 1 | 290 | 6.2 | 15.9 | 0.883 |
| Twin | | | 1 | 290 | 7.1 | 31.2 | 0.859 | 0.988 |
| | | | 1 | 260 | 4.1 | 15.0 | 0.870 | 0.978 |

^a Normalized by the area of an individual impact modifier particle estimated to be $0.0078 \mu\text{m}^2$

^b 2M = Master batch process

(a)



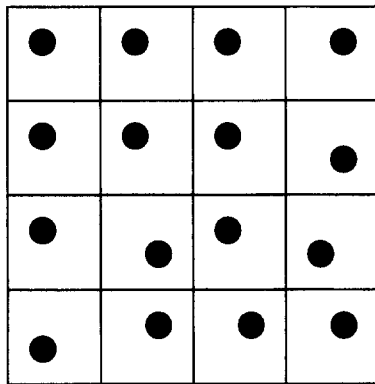
$$S = \frac{\sum_{i=1}^n s_i \ln s_i}{\ln(\frac{1}{n})}$$

$$s_i = \frac{A_i}{\sum_{i=1}^n A_i}$$

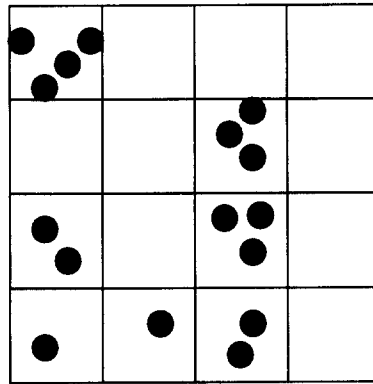
$$P = \frac{\sum_{i=1}^n p_i \ln p_i}{\ln(\frac{1}{n})}$$

$$p_i = \frac{b_i}{\sum_{i=1}^n b_i}$$

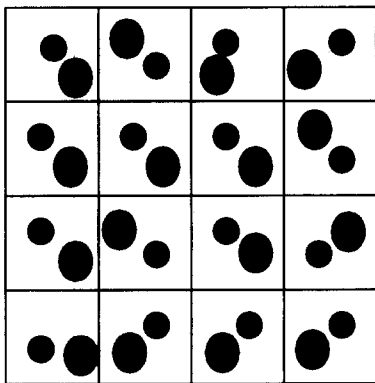
(b)



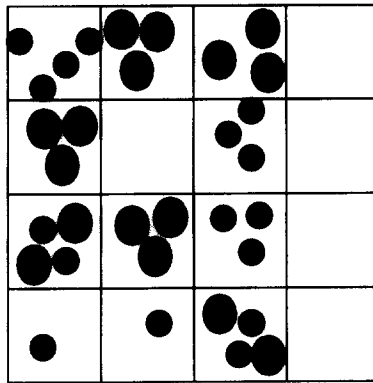
S = 1
P = 1



S = 1
P < 1



S < 1
P = 1



S < 1
P < 1

Figure 7 (a) Definitions of particle size distribution parameter S and position distribution parameter P . (b) Schematic illustrations of S and P for simple models

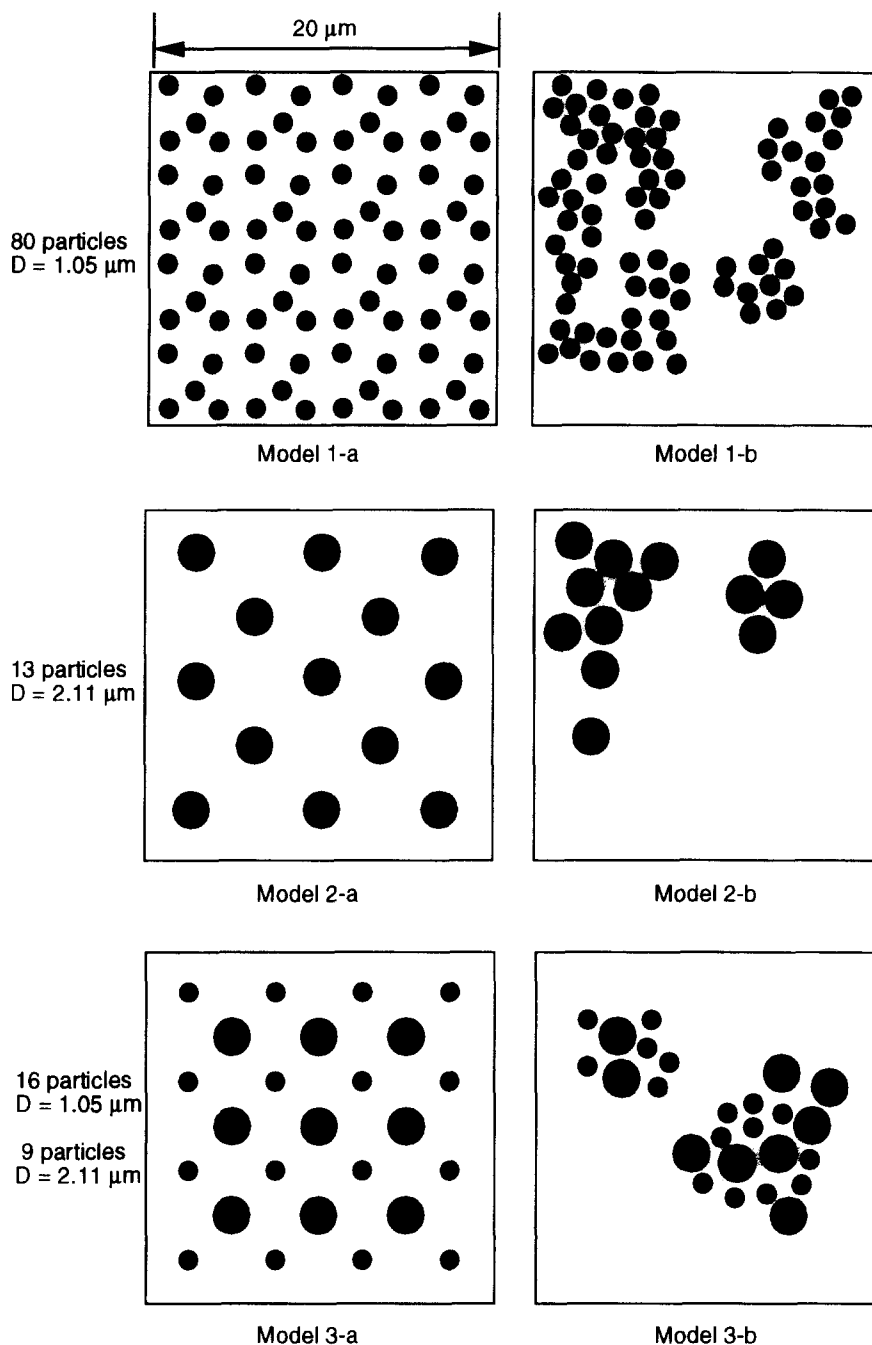


Figure 8 Simple morphology models: Models 1 and 2 employ particles of the same size while Model 3 uses a mixture of two particles of different size. Part a shows a uniform spatial distribution while Part b shows a non-uniform spatial distribution

Table 3 Summary of model calculations

| Model | Dispersion | P | | | Particle size and number | Average particle area (μm^2) | S |
|-----------|------------|-----------------------------|-----------------------------|------------------------------|---|---|-------|
| | | Grid size 2.5 μm | Grid size 5.0 μm | Grid size 10.0 μm | | | |
| Model 1-a | Good | 0.995 | 1.000 | 1.000 | No. of particles = 80 | | |
| Model 1-b | Poor | 0.840 | 0.897 | 0.943 | Diameter = 1 μm | 0.785 | 1.000 |
| Model 2-a | Good | 0.744 | 0.965 | 0.984 | No. of particles = 13 | | |
| Model 2-b | Poor | 0.656 | 0.650 | 0.629 | Diameter = 2 μm | 3.142 | 1.000 |
| Model 3-a | Good | 0.851 | 0.972 | 0.999 | No. of particles = 16 Diameter = 1 μm | | |
| Model 3-b | Poor | 0.667 | 0.762 | 0.934 | No. of particles = 9 Diameter = 2 μm | 1.633 | 0.930 |

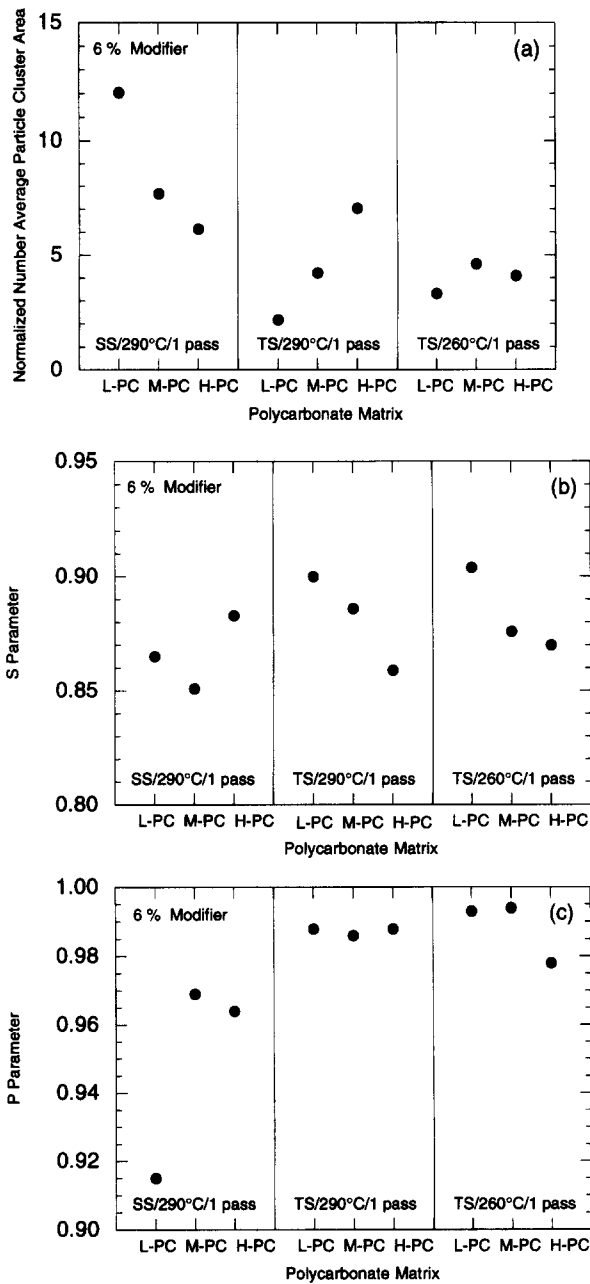


Figure 9 (a) Normalized number average particle cluster area; (b) *S* parameter; and (c) *P* parameter for PC/core-shell impact modifier blends (94/6) as a function of preparation method and PC molecular weight

Second, a method proposed by Nishi and co-workers^{21,22} was used to determine parameters related to particle size distribution, *S*, and position distribution, *P*. These parameters are defined by the equations and schematic illustrations shown in Figure 7a for a field of view containing three particle clusters. The *S* parameter is unambiguously defined; whereas, the *P* parameter depends on the construction of an arbitrary lattice grid. How *P* depends on the choice of the grid size can be illustrated by use of three simple morphology models shown in Figure 8. Models 1 and 2 employ particles of the same size while Model 3 uses a mixture of two particles of different sizes. Part a shows the particles distributed rather uniformly in space whereas Part b shows the same particles distributed in space in a very non-uniform way. Note that the latter distributions lead to large regions of the matrix that contain

no particles. The *P* parameters for each of these model morphologies were computed using the three grid sizes shown in Table 3. As the grid size becomes much larger than the particle size, the values of *P* are compressed to a limited range approaching unity. When the grid size is only a few multiples of the particle size, the values of *P* become smaller and a wider spread in values is achieved. Thus, small grid sizes lead to better discrimination of the position distribution but at the expense of significant increases in the analysis effort required. Obviously, careful thought must be given to the choice of grid size, especially when comparisons are to be made among situations where particle size and size distribution vary. Note that these examples use individual particles while in the text the dispersed phase consists of clusters of small particles; the particle groups shown here are not

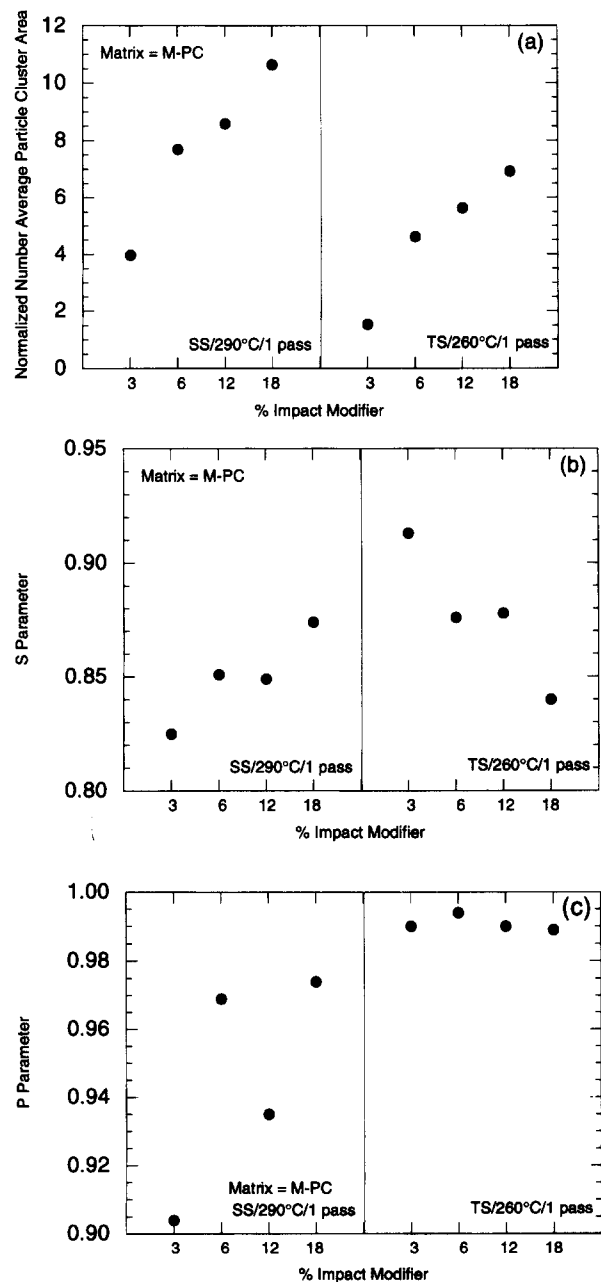


Figure 10 (a) Normalized number average particle cluster area; (b) *S* parameter; and (c) *P* parameter for M-PC/core-shell impact modifier blends prepared under different conditions as a function of modifier concentration

Table 4 Mechanical properties of PC/core-shell modifier blends

| Matrix PC | Impact modifier content (%) | Extrusion conditions | | | Tensile modulus (GPa) | Yield strength ^a (MPa) | Elongation at break (%) | Notched Izod impact strength (J m ⁻¹) | Ductile-brittle transition temperature (°C) |
|-----------|-----------------------------|----------------------|------------------|--------------------|-----------------------|-----------------------------------|-------------------------|---|---|
| | | Extruder type | Number of passes | Process temp. (°C) | | | | | |
| L-PC | 0 | } | N/A | { | 2.3 | 59.9 (62.2) | 183 | 770 | -10 |
| M-PC | | | | | 2.2 | 57.9 (60.7) | 239 | 874 | -35 |
| H-PC | | | | | 2.0 | 56.7 (59.2) | 220 | 991 | -45 |
| L-PC | 6 | Single | 1 | 290 | 2.0 | 54.8 (57.3) | 13 | 138 | +40 |
| | | Twin | 1 | 290 | 2.1 | 57.8 (60.0) | 154 | 680 | -10 |
| M-PC | 3 | Single | 1 | 260 | 2.1 | 54.1 (57.1) | 43 | 650 | -10 |
| | | | 1 | 260 | 2.2 | 57.4 (60.5) | 162 | 834 | -35 |
| | 6 | Single | 1 | 290 | 2.0 | 54.1 (57.5) | 16 | 622 | +10 |
| | | | 2 | 290 | 2.0 | 54.7 (58.6) | 39 | 500 | +15 |
| | 2M ^b | Twin | 1 | 290 | 2.0 | 56.3 (60.0) | 63 | 526 | +10 |
| | | | 1 | 290 | 2.2 | 57.2 (60.2) | 140 | 770 | -30 |
| | | | 2 | 290 | 2.0 | 53.8 (56.7) | 186 | 710 | -30 |
| | | | 1 | 260 | 2.2 | 56.9 (59.9) | 184 | 818 | -35 |
| | 12 | Single | 1 | 290 | 1.9 | 48.5 (52.9) | 20 | 488 | +10 |
| | | Twin | 1 | 260 | 2.1 | 52.3 (54.4) | 175 | 656 | -55 |
| 18 | Single | 1 | 290 | 1.8 | 45.4 (49.5) | 16 | 362 | +10 | |
| | Twin | 1 | 260 | 1.9 | 48.4 (51.6) | 181 | 585 | -40 | |
| H-PC | 6 | Single | 1 | 290 | 1.9 | 54.0 (58.2) | 134 | 683 | -15 |
| | | Twin | 1 | 290 | 2.2 | 53.7 (56.1) | 148 | 831 | -45 |
| | | | | 260 | 2.1 | 53.3 (56.8) | 153 | 881 | -35 |

^a Crosshead speed = 5.1 mm min⁻¹ (Crosshead speed = 51 mm min⁻¹)

^b 2M = Master batch process

analogous to those clusters. Each particle is dealt with separately in *Figure 8* while for the PC/core-shell modifier blends each cluster was dealt with similarly.

In the interest of the time required for analysis, a relatively coarse grid of $2.5 \times 2.5 \mu\text{m}$ was selected for analysing the current blends. A finer division would presumably provide a greater sensitivity of P values but at the expense of a more lengthy process of computation. As illustrated in *Figure 7b*, the S parameter approaches unity as the size of the dispersed particles, or clusters, becomes more uniform. On the other hand, the P parameter approaches unity as the particles or clusters are more uniformly positioned in space. The size of the regions of the PC matrix that are devoid of impact modifier particles or clusters is minimized when the average cluster size is minimized and when P approaches unity. Usually, large regions of matrix without impact modifier are expected to diminish the toughening behaviour of such blends^{16,17}. In general, the size of the clusters of impact modifier particles seen by TEM (quantified by the methods mentioned above) is larger for blends prepared in the SS than the TS, the higher the concentration of impact modifier particles regardless of extruder type, and the lower the molecular weight of the PC matrix for blends made at the same conditions in the SS. The effect of PC molecular weight on the average cluster size generated is not so clear for blends prepared in the TS. The S and P parameters tend to be closer to unity (more uniform size and position distribution) for blends made in the TS vs the SS.

Figure 9 shows results from the image analysis of blends containing 6% impact modifier in each of the three molecular weight grades of PC extruded under several conditions. Blends made by SS vs TS extrusion show rather different responses to molecular weight or viscosity of the PC matrix on the dispersion of the impact modifier. In the SS, better dispersion of the modifier, i.e. smaller average cluster size (*Figure 9a*) and larger S and P parameters (*Figures 9b* and *9c*), is generally achieved the higher the molecular weight or melt viscosity of the PC matrix. On the other hand, blends made by twin screw extrusion tend to show the opposite trend with PC matrix molecular weight. From the Brabender torque of the modifier and the PCs at 290°C shown in *Figure 3b*, the viscosity ratio of the two components becomes closer to unity when using higher molecular weight PC. Blends processed in the TS at 290°C show slightly smaller average particle clusters than at 260°C and nearly the same S and P values. As judged by the Brabender torque data in *Figure 3*, the impact modifier has a higher effective viscosity than all of the PC materials at 290°C. On lowering the temperature to 260°C the viscosity of the PC materials increases more than does the impact modifier. In fact, H-PC has a higher viscosity than the modifier at 260°C. The effect of absolute melt viscosity or the relative viscosity of the components are not so clear from these results for blends made by this TS. Of course, the magnitude and nature of the shear field in the Brabender may not model the situation in the TS as well as in the case of the SS.

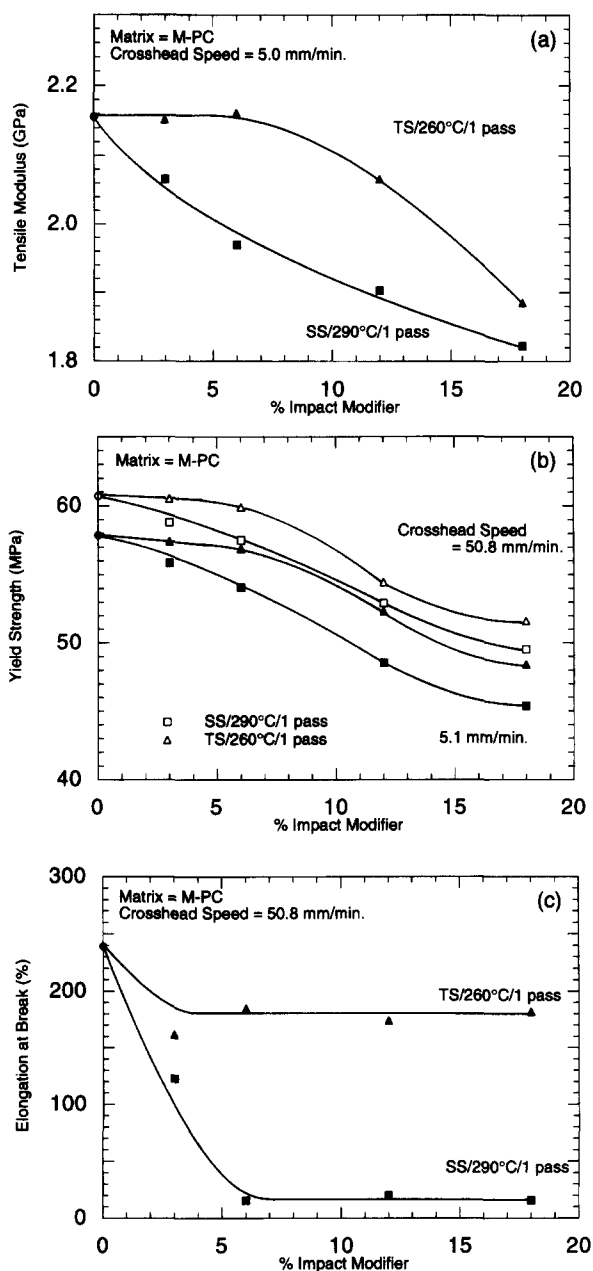


Figure 11 (a) Tensile modulus; (b) yield strength; and (c) elongation at break, as a function of modifier concentration in M-PC/core-shell impact modifier blends prepared by a single screw extruder at 290°C (SS/290°C/1 pass) and by a twin screw extruder at 260°C (TS/260°C/1 pass)

Figure 10 shows the results of image analysis for blends based on the medium molecular weight grade polycarbonate, M-PC, containing different concentrations of the impact modifier. Increasing the modifier concentration leads to larger average cluster sizes in both extruder types as shown in Figure 10a; for any given modifier concentration, the TS leads to smaller clusters. SS and TS extruded blends have quite different S and P parameters. For blends made by SS extrusion, increasing modifier concentration leads to more uniform distribution of cluster size while blends made in the TS extruder become more broad in cluster size as indicated by the S parameter (Figure 10b). The position distribution parameter P for blends made in the SS extruder improves as impact modifier concentration increases while the values for the blends made in the TS extruder are consistently near unity as seen in Figure 10c.

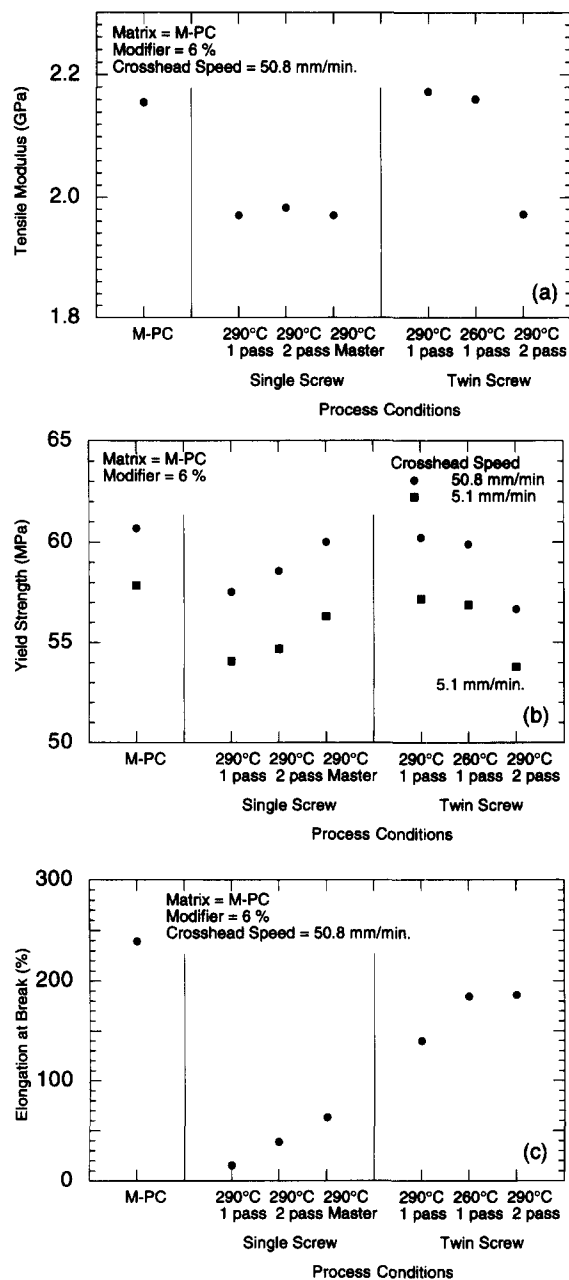


Figure 12 (a) Tensile modulus; (b) yield strength; and (c) elongation at break for PC/core-shell impact modifier blends (94/6) prepared under different conditions for three molecular weight grades of polycarbonate

MECHANICAL PROPERTIES

A summary of room temperature mechanical properties of blends of the core-shell impact modifier with the three PCs prepared in different ways is given in Table 4. Significant differences in elongation at break, notched Izod impact strength, and ductile-brittle transition temperature are seen as the content of modifier, PC molecular weight, intensity of mixing, and extrusion conditions are varied. These effects are more clearly seen by the graphical presentations described below.

Tensile properties

Tensile modulus is reduced by addition of the core-shell impact modifier to PC as illustrated in Figure 11a. In all cases, blends prepared by procedures that are more effective for the dispersion of the core-shell

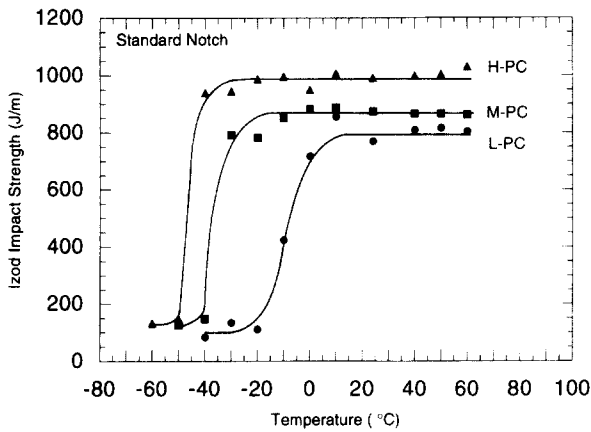


Figure 13 Notched Izod impact strength as a function of temperature for three molecular weight grades of PC

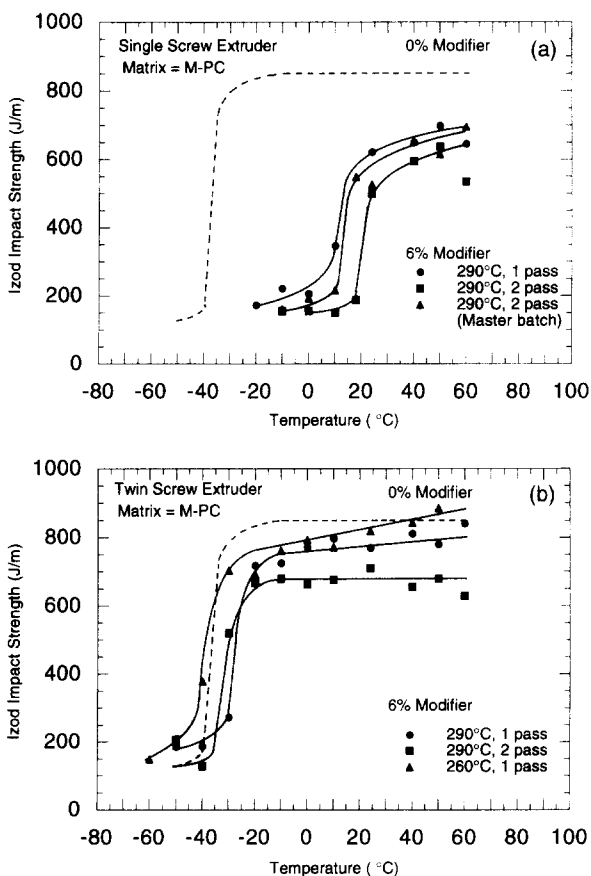


Figure 14 Notched Izod impact strength as a function of temperature for M-PC/core-shell impact modifier blends (94/6) prepared in (a) single screw extruder and (b) a twin screw extruder

particles (e.g. TS extrusion at 260°C) show a smaller reduction in modulus compared to blends made by less effective methods (e.g. SS extrusion at 290°C). For example, Figure 11a shows the modulus is hardly affected by addition of up to 6% impact modifier to M-PC when the TS extruder is used, while addition of as little as 3% by the SS extruder leads to a significant drop in the modulus. A reduction in modulus is to be expected by addition of the impact modifier because of its soft, rubbery core. However, the greater reduction noted when the dispersion is poor is not expected just based on the size of the dispersed phase alone but is

more likely related to the shape of these regions and the position distribution of modifiers in the PC matrix; a tendency towards co-continuity when the modifier is poorly dispersed will lead to a greater loss in stiffness.

Figures 11b and 11c illustrate the effects of extrusion conditions on yield strength, at two test rates, and elongation at break for blends of M-PC with the core-shell impact modifier; blends with better particle dispersion (see Figure 4) show superior properties. Elongation at break exhibits the most profound difference. All of the blends prepared at 260°C in the TS extruder elongate more than 100% before failure, while those prepared at 290°C in the SS extruder fail just beyond the yield point when the impact modifier content is 6% or more.

Attempts to improve the tensile properties of blends of M-PC with 6% impact modifier made at 290°C in the single screw extruder produced only limited success. Double extrusion or the use of a master batch approach produced no change in modulus, while yield strength and elongation at break were only slightly improved (Table 4).

Figure 12 summarizes the effects of process conditions on the tensile properties using blends of M-PC with 6% impact modifier as an example. The TS extrusion process generally results in superior blend properties. Increasing the number of passes through the SS extruder, or use of a master batch approach, does improve properties. For the TS extruder, higher temperature and longer residence time lead to somewhat mixed results.

Impact strength

Figure 13 shows the notched Izod impact strength of the three different PC materials described in Table 1, without any impact modifier, as a function of temperature. Low temperature toughness is clearly improved as the molecular weight is increased, as expected¹². The ductile–brittle transition temperature is lowered from –10°C to –45°C over the molecular weight range used here. Figure 14 illustrates how the impact strength vs temperature relationship for blends is strongly affected by extrusion conditions using mixtures of M-PC containing 6% of the impact modifier as an example. Blends prepared in the SS extruder at 290°C are significantly less tough than the M-PC control and show ductile–brittle transition temperatures just below room temperature. Poor dispersion of the rubber phase is the primary reason for this. Because blends that were extruded twice show even poorer results, thermal effects may be also a contributing factor. Corresponding blends prepared in the TS have much better impact strength and ductile–brittle transition temperatures; the latter are substantially the same as neat M-PC (–30 to –35°C). Extrusion at 260°C leads to somewhat better results. In all cases, multiple extrusions lead to poorer impact properties. The residence time in the SS (70 s) is substantially longer than that in the TS (20 s). These observations suggest that thermal effects (time and temperature) play some role in establishing toughness of these blends in addition to mixing intensity and rheological issues.

The effect of impact modifier concentration on the impact strength vs temperature relationship is shown in Figure 15. For blends prepared in the SS, Figure 15a, increasing the impact modifier concentration reduces

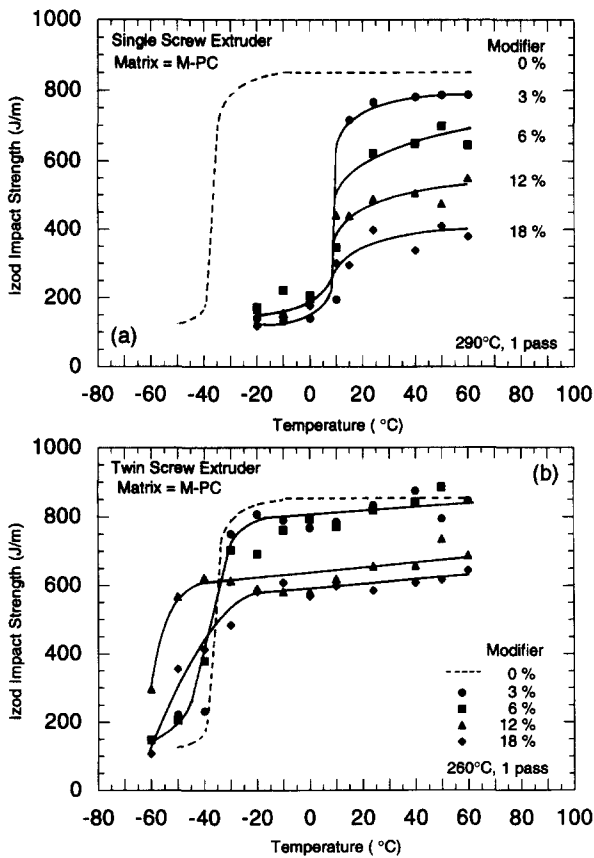


Figure 15 Notched Izod impact strength as a function of temperature for blends of M-PC with various amounts of core-shell impact modifier prepared in (a) a single screw extruder and (b) a twin screw extruder at different conditions

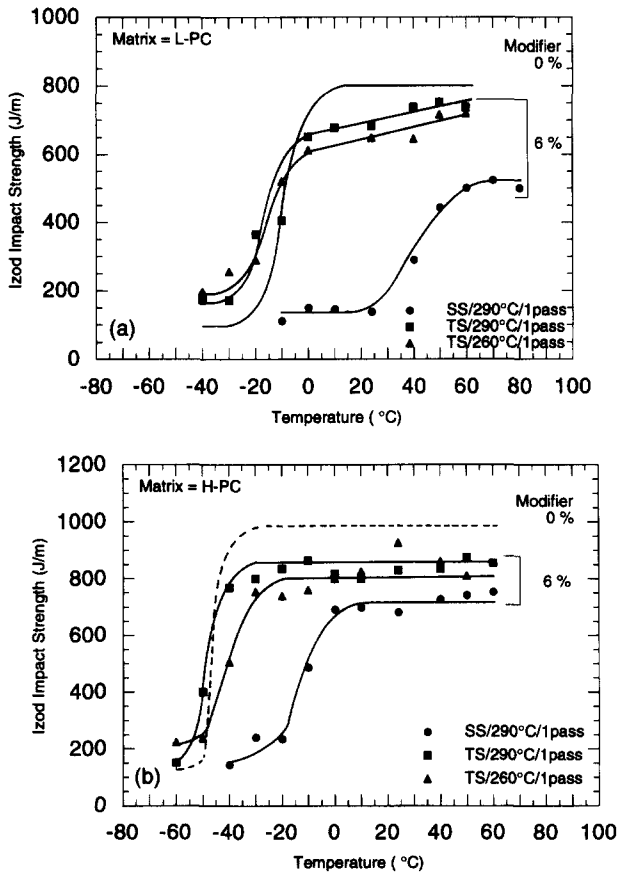


Figure 16 Notched Izod impact strength as a function of temperature for blends of (a) L-PC and (b) H-PC with core-shell impact modifier (94/6) prepared in a single screw extruder and a twin screw extruder

room temperature impact strength while the ductile–brittle transition temperature is about the same (10°C) for all blends and substantially higher than that of neat M-PC. Blends prepared in the TS show much better room temperature roughness and their ductile–brittle transition temperatures are as low or lower than pure M-PC; the blend containing 12% modifier has a ductile–brittle transition temperature of –55°C (Figure 15b).

Blends based on the high and low molecular PC materials show similar trends as those illustrated in Figures 15a and 15b for the medium molecular weight PC. Figure 16a shows that blends based on L-PC containing 6% impact modifier are brittle at room temperature when prepared in the SS; the same blend made in the TS has a room temperature Izod impact strength approaching that of pure L-PC. The latter blend has a slightly lower ductile–brittle transition temperature than the pure matrix PC. Blends based on H-PC containing 6% impact modifier are tough at room temperature regardless of the method of preparation as seen in Figure 16b. However, as the extrusion conditions are made more favourable for dispersion, both room temperature and low temperature toughness are improved. Blends made in the TS can have ductile–brittle transition temperatures as low or lower than pure H-PC.

SUMMARY AND CONCLUSION

The mechanical properties of blends of PC with a core-shell modifier are very sensitive to compounding conditions. This primarily relates to the degree of dispersion of the impact modifier in the PC matrix. A number of quantitative parameters were used to characterize the morphology of these blends. Better dispersion, and therefore properties, are obtained using a TS rather than a SS since the former provides more intensive mixing.

At higher concentrations of the impact modifier, it was not possible to eliminate all clustering of this impact modifier in PC. However, in general, more intensive mixing and higher molecular weight grades of PC lead to smaller clusters of impact modifier particles that are more uniformly distributed in the matrix. This leads to better room temperature tensile properties and toughness as well as lower ductile–brittle transition temperatures. Blends with the best dispersion of the impact modifier have comparable or lower ductile–brittle transition temperatures as the neat PC. Blends based on higher molecular weight grades of PC led to lower ductile–brittle transition temperatures. Future work will address how the nature of the core-shell modifier affects its ability to be dispersed in the polycarbonate matrix.

Notched Izod impact testing using 3.13 mm (1/8 inch) thick specimen provides a limited means for evaluating the toughness of these blends because the neat PC matrix itself has very high impact strength in such thin sections. The addition of modifiers is primarily used to increase the toughness for thicker specimens and ones that have sharp notches. A second paper will characterize the toughness of these blends using fracture mechanics approaches that employ thicker specimens.

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