Blends of Polycarbonate and Polysulphone–Polydimethyl– Siloxane Block Copolymers: Analysis of Compatibility and Impact Strength

S. S. PESETSKII,¹ B. JURKOWSKI,² I. P. STOROZCUK,³ V. N. KOVAL¹

¹ V. Bely Metal-Polymer Research Institute, National Academy of Sciences, 32A, Kirov Street, 246 652 Gomel, Republic of Belarus

² Division of Plastic and Rubber Processing, Institute of Materials Technology, Poznan University of Technology, Piotrowo 3, 60-965 Poznan, Poland

³ State Research Center for Composite Materials, 9, Miusskaya Square, 125 047 Moscow, Russia

Received 3 February 1998; accepted 28 September 1998

ABSTRACT: The possibility of modifying polycarbonates by using dian (Bisphenol A) polysulphone–polydimethyl siloxane block copolymers having multiblock structure and triblocks with end polydimethyl siloxane or a polysulphone block structure was shown. In triblock copolymers the polydimethyl siloxane blocks have a constant molecular weight equal to 2500, while in polyblocks it was assumed to be 2500 and 10,000. The molecular weight of polysulphone blocks varied between 700 and 9000 in triblocks or between 500 and 4500 in polyblocks. It was found that block copolymers of both multiand triblock structure with polydimethyl siloxane end blocks of concentration 45–68 wt % are created with PC microheterogenous blends. These blends, in a wide temperature interval (from cryogenic to the glass transition temperature of PC), have high impact strength when multiple crazes are created independently on testing temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1823–1834, 1999

Key words: polycarbonate; polysulphone–polydimethyl–siloxane; triblock copolymer; compatibility; impact strength; light transmission; failure pattern; scanning electron microscopy; relaxation spectrometry

INTRODUCTION

Polycarbonate (PC) belongs to the class of amorphous thermoplastic polymers that can quite readily undergo polymer-polymer modification. Many PC blends differ favorably in some of the characteristics from the values of the homopolymer included into their composition. Blends of PC

Contract grant sponsor: State Committee of Scientific Research of Poland; contract grant number: 7 TO8 E 01411. with ABS,^{1–3} polyalkylene terephthalates,^{4–6} modified polyamides,^{7,8} elastomers,^{9,10} etc., have been studied extensively, and can be produced commercially.

Of a certain theoretical and applied interest are blends of PC with polysulphone–polydimethyl–siloxane block copolymers (PSN–PDMS). Block copolymers of polysulphone and polydimethylsiloxane have been studied in detail by now, mainly as materials for making gas-separating membranes, medical catheters, blood oxygenators, optical elements with protective coatings, etc.^{11–13} Application of PSN–PDMS block copolymers to modify polysulphones (PSN) to increase their impact strength has been described in the

Correspondence to: B. Jurkowski.

Contract grant sponsor: Found of Fundamental Research Republic of Belarus; contract grant number: M-96- 077.

Journal of Applied Polymer Science, Vol. 73, 1823–1834 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/101823-12

Nos.	Polymer and Molecular Weight of PSN and PDMS Blocks	$\mathrm{MW}\cdot 10^3$	Content of PDMS Block (wt %)	η, (dL/g)	MFI, (g/10 min)	$T_{5\%}$ (°C)	
1	PC	35	0	0.65	6.6	414	
-	PDMS-PSN-PDMS	00	Ū	0.00	0.0		
2	2500-700-2500	5.7	88	0.13	85.0*	350	
3	2500-1500-2500	6.5	77	0.12	17.4^{*}	355	
4	2500-3000-2500	8.0	63	0.20	6.2^{*}	360	
5	2500 - 4500 - 2500	9.5	53	0.23	3.4	378	
6	2500-9000-2500	14.0	36	0.26	10.2	360	
	PSN-PDMS-PSN						
7	700-2500-700	3.9	64	0.11	78.0	345	
8	1500-2500-1500	5.5	45	0.24	1.6^{*}	357	
9	3000-2500-3000	8.5	29	0.30	9.8	370	
10	4500-2500-4500	11.5	22	0.29	8.7	380	
11	9000-2500-9000	20.5	12	0.30	2.9	403	
	PSN-PDMS						
12	1500-2500	4.0	62	0.27	2.3^{*}	360	
13	3000-2500	5.5	45	0.25	6.5	385	
14	4500-10000	14.5	68	0.29	14.5	360	

Table I Properties of Tested Materials

MW is molecular weight calculated as a sum of molecular weights of blocks; η is reduced viscosity of 0.5 wt % solution of the materials in chloroform at 23°C; MFI is a melt-flow index determined at 220°C (*) in all other cases at 280°C; $T_{5\%}$ is the temperature of 5% weight loss as determined by the dynamic thermogravimetry.

monograph.¹⁴ Introduction of only 5–7 wt % PSN– PDMS resulted in a 20-fold increase in the impact strength, as was measured using notched specimens. This effect is believed to be due to the presence—in the block copolymer—of polysulphone rigid blocks possessing good compatibility with the homopolymer, which leads to effective dispersion of the additive along with a high interphase adhesion.

As PSN forms compatible blends with PC^{14} [solubility parameters of PC and PSN being 20.4 and 21.0 (MJ/m³)^{0.5}, respectively], one can anticipate that efficient modifying action of PSN–PDMS will show when it is blended with PC. This work was undertaken to find how the chemical structure of PSN–PDMS block copolymers influences the compatibility with PC, impact strength, and other mechanical characteristics of their blends.

EXPERIMENTAL

Material

PC used in the experiments was obtained by interaction of phosgene and 2,2-bis(*p*- hydroxyphenylo)propan (Diflon) at the Zarya Joint-Stock Company (Volgograd, Russia). PSN–PDMS block copolymers were synthesized by polycondensation, making use of aromatic oligosulphone based on dian (Bisphenol A) and 4,4'-dichlorodiphenyl sulphone. The greater number of experiments was carried out with triblock copolymers of ABA and BAB types, where A is the PSN rigid block, and B is the PDMS elastic block. These blocks are connected with segments of diphenylolpropan (DFP). Polyblocks $(AB)_n$ were used in some experiments. Molecular weight (MW) of PSN block was varied between 700 and 9000; for PDMS blocks it was constant (2500). Data on the structure and properties of the starting materials for blends are given in Table I. The chemical structure of the block copolymers used is of the following configuration:



where x = 1-13 (MW between 700 and 9000), y = 30 (MW 2500)







Figure 1 Schematic diagram of a cryogenic chamber.

Blending and Preparation of Test Specimens

Compositions for blending were prepared by mixing both solid PC granules with chopped block copolymers (maximum size being 3 mm) and, next, melt mixing by using a single-screw extruder with a granulator system; the extruder was an SX-65 (L/D = 32, Kroener Windsor, Germany). The temperature of the metering zone was 270°C. The quantity of block copolymers in all blends was assumed to be 7 wt %, the exception being blends with PSN-PDMS (1500-2500). where it was up to 30 wt %. This value was chosen in view of the pilot experiments, in which dependence of a blend's mechanical properties on block copolymers concentration had been estimated.¹⁵ The dried granulate produced from a PC/block copolymer blend was used to make test pieces by injection molding at $270 \pm 5^{\circ}$ C.

Characterization

The tensile strength measurements were carried out using an Instron 1115 testing machine (Instron Ltd. Corp., UK). The dumbbell specimen had the neck size of 45×3 mm. The impact strength was determined on bars $60 \times 10 \times 4$ mm in size, and notched at small and right angles.

Charpy technique was used (pendulum hammer PSV-1.5, Werkstoff Prufmaschinen, Germany).

To obtain temperature-impact strength relationships the specimens, prior to impact tests, had been thermostated at a given temperature for 60 min in a cryogenic chamber shown in Figure 1. This chamber acts as follows: the heater evaporates liquid nitrogen, thus creating pressure inside the closed Dewar flask. The gaseous nitrogen passes along the pipe, cools down in liquid nitrogen, and enters the chamber for preheating, where it gets heated up to a temperature close to the preset one. Then the gas directly enters the thermostating chamber. The temperature in the chamber is measured with a thermoelectric gauge introduced into it through the heat-insulating lid, and is maintained with a device that controls the gas flow to the chamber by switching the power circuit of the heater. To improve heat insulation, the chamber has hollow walls. The space between the inner and outer walls are evacuated. During testing the specimens bars were put on the bottom of the chamber and were thermostated for an hour because of the stabilization of temperature inside this chamber. The time of this stabilization

did not exceed 10 min. Temperature there was maintained within $\pm 1^{\circ}$ C accuracy. Then samples were removed from the thermostatic chamber. and impact strength was determined during ca. 8 s from this time. This ensured that a difference between temperature inside the thermostatic chamber and temperature of the sample during testing was below 7°C. Polymers have low both a thermal conductivity and a rate of relaxation processes at a low temperature. Due to this, it is possible to accept that the real temperature of the sample during impact tests and its relaxation state only differs a little from that inside the thermostating chamber. Every point on the temperature-impact test curve was taken as an average from five to seven parallel measurements.

Melt viscosities of the tested materials were characterized by the Melt Flow Index determined at a load of 2.16 kg and a temperature of 220°C (particular copolymers) or 280°C (PC and blends).

The light transmission coefficients of the materials were determined on film specimens 100 μ m thick using a photoelectric colorimeter KFK-2 (Optical Engineering Factory, Zagorsk, Russia).

The dynamic thermogravimetrical analysis was made on the derivatograph Q-1500 (MOM, Budapest, Hungary) when the temperature rate was 5° C/min.

The failure pattern of the specimens was studied by scanning electron microscopy technique (microscope JSM-50A, JEOL, Japan).

The reverse-torsion pendulum was operated at frequency of 1 Hz to study relaxation properties of the materials.

RESULTS AND DISCUSSION

Compatibility Analysis

The small differences between solubility values of PC and PSN block in a block copolymer must favor, as was mentioned above, blend compatibility. It is obvious, however, that compatibility degree should affect the PSN block concentration in a block copolymer or, in another words, the molecular weight ratio of PSN to PDMS.

Theoretically, the effect of a particular block concentration in a block copolymer on compatibility can be estimated using data of the mean field theory.¹⁶ In a general case, the structural formulation of all tested blends can be represented as A/B_kC_{1-k} , where A is the polycarbonate, B is the PSN block, C is the PDMS block, and k is the



Figure 2 Interaction parameter values depending on content of rigid blocks in the block copolymer.

molar concentration of the PSN block in a block copolymer. Then, in view of other works,^{16–18} the expression of an interaction parameter for a given blend would be as follows:

$$\chi_{bl} = k \chi_{AB} + (1 - k) \chi_{AC} - y(1 - k) \chi_{BC} \quad (1)$$

where χ is an interaction parameter for the blend (*bl*) and individual components of the blend (AB, AC, and BC), respectively. In view of the statement¹⁴ that the solubility parameter for the PDMS block is 15.3 (MJ/m³)^{0.5} and for the PSN block is 21 (MJ/m³)^{0.5}, repulsive intramolecular interaction in a block copolymer can be expected to appear, which can lead to what will be quite a small value; therefore, the blend can be compatible.

When making calculations using eq. (1), one should remember the following assumptions: (1) χ_{ij} is assumed to be independent of composition; (2) χ_{ij} values are found from an expression taken from another work.¹⁷

$$\chi_{ij} = \frac{V_r}{RT} \left(\delta_i - \delta_j\right)^2 \tag{2}$$

where V_r is the relative molar volume ($V_r = 10^{-4}$ m³/mol), δ_{ij} is the solubility parameters of the blend components, R is the universal gas constant, and T is the temperature (T = 300 K).¹⁸ (3) The effect of free volume is discarded. (4) The components of a blend are assumed to mix as monomer units.

The calculated results are given in Figure 2. The χ_{bl} is the concentration relationship parabolic

for blends that forms "compatibility windows."¹⁸ Assuming PC/PSN–PDMS blends to have a relatively weak interphase interaction, one can anticipate¹⁸ compatibility at critical interaction values $\chi_{ijcr} \leq 0.1$. According to Figure 2, its values ≤ 0.1 are typical for blends containing a PSN block in an amount more than 0.7 molar parts.

Compatibility was determined experimentally by analyzing light transmission through film specimens. Block copolymers containing a PSN block between 12 and 36 wt % appeared incompatible with PC, and formed highly separated mixtures. They are characterized by fibrous structure forming and, next, separation on the stage when a blend is cooled and granulated. Film specimens prepared from such blends are cloudy, and have low light transmission coefficients (Fig. 3, Table II). Increased molecular weight in PSN block leads to the fact that a lower content of the PDMS block is used; as a result, the components become more compatible and the blend becomes more transparent (e.g., light transmission coefficient of a blend with a triblock copolymer having a molecular weight of block 9000/2500/9000 approaches that of an original PC).

Data in Figures 3 and 4 support the calculated results (Fig. 2) that blends of PC with a block copolymer can only be compatible at a high content of the PSN block. Besides, the light transmission experiments showed that with identical contents of PDMS blocks, blends of PC with PSN– PDMS–PSN are more transparent compared to those with PDMS–PSN–PDMS. It is thought that in the latter case the flexible PDMS block being immiscible with the PC form a shell–steric barrier for particular intermolecular interactions to take place in the PC/PSN system. As a result, PC/PDMS–PSN–PDMS blends possess a more heterogeneous phase structure than PC/PSN– PDMS–PSN blends.

Influence of Block Copolymer Structure on Blend Properties

Table II shows that block copolymers added to PC markedly change its properties; the extent of change depends on both the elastic block content and arrangement of these blocks within the block copolymer. Triblock copolymers with short PSN blocks containing between 64 and 88% PDMS blocks appeared incompatible with PC, and formed highly separating systems with it (Table II, blends 2, 3, and 7). Such systems tend to form fibrous structures and separate during granula-

tion, and have low transmission coefficients (Fig. 4). Separation leads to severe deterioration in mechanical properties: there is no indication of induced high elasticity on the stress-strain curves.

Increased MW of PSN blocks in the triblock copolymer leads to lower PDMS block contents, and is accompanied by a better component compatibility along with blend transparency (e.g., a light transmission coefficient of the PC blended with the copolymer, where blocks of an MW of 9000–2500–9000 approache that of the PC). These blends are characterized by higher strength and tensile strain values (Table II).

Analysis of blends 4, 5, and 8 that contain triblock copolymers of similar gross composition, but of different structure (PDMS–PSN–PDMS or PSN–PDMS–PSN), showed that block copolymers with end elastic blocks possess a better complex of strength-and-strain characteristics along with higher impact strength values. This can probably be explained by better active surface properties of the block copolymers of the first type¹⁴ and better dispersion in the blend, and also by limitation of PDMS blocks mobility resulting from chemical junctions with PSN.

The PC impact toughness is highly sensitive to the notch pattern and a type of specimen surface defects; it shows lower toughness values at subzero temperatures (Table II).

Addition of a triblock copolymer, especially of the PDMS–PSN–PDMS type, allows one to get rid of these disadvantages. Lower sensitivity to the notch pattern is typical of blends containing block copolymers with low molecular weights in which the degree of phase separation is probably enough for the impact energy to be dissipated independently of the mode the cracks propagate.



Figure 3 Light transmission coefficient for PC films and PC blended with 7 wt % of block copolymers as given in Table I.

	$T_{5\%}^{5\%}, ^{\circ}{ m C}$	414	395	410	412	399	407	428	400	405	403	380	410	405	392
	MFI g/10 min	6.6	10.8	26.0	10.2	9.3	2.7	12.7	13.3	14.7	9.6	8.7	10.5	9.8	12.9
'm ²	Small-Angle Notch, -40°C	15	38	34	30	23	19	26	21	17	16	16	36	28	32
act Strength, kJ/	Right-Angle Notch	52	32	36	45	57	59	35	41	37	42	38	51	37	35
Imp	Small-Angle Notch	20	35	35	41	37	32	33	24	20	19	19	44	40	42
	εr., %	22	0	14	109	140	102	23	70	106	110	123	82	95	60
	$\sigma_{r,r}$ MPa	57	27^{a}	49^{a}	58	56	59	47^{a}	60	61	61	62	62	61	55
	Specimens Appearance	Transparent	Severe separations	Some	Cloudy	Some	Some	Severe separations	Slight cloudy	Translucent	Some	Transparent	Cloudy	Slight cloudy	Cloudy
	Material and Molecular Weight of Block PSN and PDMS	PC Blend of PC/block copolymer 7 wt %	2500 - 700 - 2500	2500 - 1500 - 2500	2500 - 3000 - 2500	2500-4500-2500	2500-9000-2500	700-2500-700	1500-2500-1500	3000-2500-3000	4500 - 2500 - 4500	9000-2500-9000	1500 - 2500	3000 - 2500	4500 - 10000
	Nos.	1	5	က	4	5 L	9	7	80	6	10	11	12	13	14

Table II Effect of Triblock Copolymer Structure on Blend Properties

^a Tensile strength—these samples cannot reach a yield point; σ_t , ε_R —yield point and ultimate elongation at rupture, respectively.



Figure 4 Light transmission coefficient for PC films and PC blended with 7 wt % of triblock copolymers, depending on PDMS block content in them.

Most favorable mechanical properties can be achieved for PC blended with PDMS–PSN–PDMS (2500-3000-2500). The high toughness of the blends at -40°C probably results from glass transition temperatures of the siloxane blocks, thus providing thermal motion of PC macromolecules participating in the interphase interaction.

It should be noted that addition of block copolymers usually leads to higher MFI, which makes the molten composition processing easier. Herein, the thermal stability of most blends—as evaluated by the 5% weight loss temperature—does not differ significantly from the PC thermal stability (Table II).

As we see, the behavior of PC blends with triblock copolymers of types PDMS–PSN–PDMS and PSN–PDMS–PSN under mechanical action depend on the molecular weight of rigid blocks decisively influencing the components compatibility and extent of phase separation in the blend, and also on the origin of the end blocks in the copolymer.

Blends with increased compatibility (Fig. 2, Table II, blends 10 and 11), as those with poor compatibility (Fig. 2, Table II, blends 2, 7, and 8), have unsatisfactory mechanical properties. The main advantage of the blends in comparison with PC lies in the possibility of increasing toughness, especially at low temperatures; another advantage is lower sensitivity of this value toward a notch pattern.

It can be seen from Table II and Figure 5 that PC mechanical characteristics are much improved by blending it with the polyblock PDMS– PSN. Concerning the set of property values, it appears that the block copolymer $(AB)_n$ can be more effective than triblock copolymers. An optimal set of properties was achieved with 7 wt % of the block copolymer content.

As impact strength could be significantly increased by mixing PC with block copolymers, it was of interest to study this event in great detail. To do this, the effect of the test temperature on impact strength variations and surface failure patterns was considered. In view of the published data,^{19, 20} it could be expected that the pattern of temperature–impact strength relationship would depend on the type of relaxation transition in the blends. Therefore, the materials had been preliminary examined by the relaxation spectrometry technique.

Results of Relaxation Spectrometry

Figure 6(a)–(e) shows the analytical results. There are two major peaks on the loss curve for the initial PC related to β - and α -relaxations with transition temperatures $T_{\beta} = -75^{\circ}$ C and $T_{\alpha} = T_{g} = 150^{\circ}$ C²¹ [Fig. 6(a)]. Besides, there is a diffuse peak between 60 and 80°C related to the CH₃—C—CH₃ rotation around the polymer chain axis.²² The low-temperature branch of the β -relaxation peak has a kink caused by the fact that rotations of the methyl groups in isopropyl fragments get frozen (γ -relaxation).²²

Two major transitions are also typical of block copolymers [Fig. 6(a) and (b)]: (a) at the glass transition temperature of the PDMS block $T_{g\rm PDMS} = -100 \div -110^{\circ}\rm{C}$; and (b) at the glass transition temperature of the rigid PSN block



Figure 5 Yield point at elongation and impact strength (after Charpy) vs. content of block copolymer 1500–2500.



Figure 6 Temperature dependence of mechanical loss tangent for PC and PSN–PDMS: 4500-10000 (a), block copolymers: 2500-3000-2500 and 3000-2500-3000 (b), and blends of PC/block copolymer 7 wt % (c-e).

 $T_{\rm gPSN} = 170-180\,^{\circ}$ C, which is equal to that found earlier by Tyagi and co-workers.¹¹ The high-temperature region of PDMS glass transition peaks and the low-temperature region of PSN peaks in block copolymers has shoulders or weak loss maxima. They are probably related to glass transition of the fragments of both blocks PDMS and PSN being present in the interphase layers of the block copolymer. That mixed interphase layers can be formed despite a great difference in the solubility parameters of the block PDMS and PSN, which was stated in another article.¹¹

It should be mentioned that a microphases breakdown of the structure in a block copolymer of a polyblock configuration with a high molecular



Figure 7 Effect of test temperature on impact strength values for small-angle notched specimens.

weight PDMS block proceeds more fully than in a triblock copolymer. This was observed when mechanical loss curves were compared for polyblock PSN–PDMS (4500-10,000) and triblock PDMS–PSN–PDMS (2500-3000-2500), where compositions contain about equal quantities of the PDMS block (68 and 63 wt %, respectively) [Fig. 6(a) and (b)]. The relaxation spectrum of a block copolymer (4500-10,000) has a sharp glass transition peak for PSN blocks at 170° C [Fig. 6(a)]. This peak is diffuse and nonobvious in the spectrum of the triblock copolymer (2500-3000-2500) [Fig. 6(b)].

Relaxation spectra analysis of blends revealed that a block copolymer dispersed in PC did not, in fact, influence the location of the T_{gPDMS} peak [Fig. 6 (c)–(e)]. The PC glass transition peak would shift by 1–3°C to the higher temperature

region, probably, because of intensive interphase interaction with the rigid PSN block of the block copolymer.

Influence of Testing Temperature

It can be seen (Fig. 7) that the chemical structure of block copolymers critically influences the relationship pattern and magnitude of the relationships between temperature and impact strength for PC and blends. Addition to PC of miscible PSN-PDMS-PSN (9000-2500-9000) did not, in fact, change the temperature pattern of the impact strength if compared with the initial polymer [Fig. 7(a) and (c)].

The impact strength values—approaching those of the homopolymer—observed over the

whole temperature range (but excluding the temperature region adjacent T_{gPC})—for blends with PSN–PDMS–PSN: 3000–2500–3000 can probably be explained by increased compatibility with PC and a pseudohomogeneous structure formed [Fig. 7 (a) and (b)].

Triblock copolymers having end-block PDMS and polyblock: 4500–10,000, while being incompatible with PC, formed with it blends with pronounced microphase separation (Table II, Figs. 2 and 3), causes an increase in impact strength over the whole test temperature range along with variations in the temperature relationship pattern (Fig. 7). Probably, a change in the mechanism of impact failure of PC when a block copolymer was added could explain the above differences.

Amorphous polymers and their blends fail by shearing flow and crazing.^{23, 24} Impact resistant and superhigh impact resistant blended materials fail, as a rule, through crazing, resulting in the bleaching of the failed zone caused by light scattered across many fine pores present in the crazes. Homopolymers being plastic during breaking under action of stress, PC included, fail by shearing flow, and are characterized by high energies at which microcracks are initiated and propagate. Therefore, these materials have the impact-fractured surfaces either smooth or covered with shear streaks.

Comparison of data in Figures 6 and 7 indicate a connection between the impact strength-temperature relationship pattern and relaxation processes taking place in the materials tested. For example, there are weak maxima (shoulders) on the impact strength-temperature curve in the low-temperature regions: between -100 and -120°C and also between -70 and -75°C [Fig. 7(a)]. Data in Figure 6 imply γ - and β -relaxation transitions. Therefore, PC can be said to fail in a semibrittle manner at temperatures between -40and -120° C. It fails in a plastic manner at higher temperatures. Impact strength peaks found between 10 and 50°C can be explained by the fact that above 50°C the motions caused by rotation of the PC isopropyl macromolecular fragments get unfrozen and the material's elastic modulus decreases. As a result, the energy consumed to initiate fracture decreases along with the impact strength values, despite an anticipated increase in the energy of microcrack propagation.²⁴ Simultaneous development and competition of two events: (1) decrease in the microcrack initiating energy, and (2) increase in the propagation energy—could be the main cause of extreme (maxima) observed in the temperature–impact strength relationships for PC and blends failing by shearing flow mechanism [Fig. 7 (a) and (e)]. Surfaces of such materials impact fractured within a wide temperature range are smooth, with folds formed, probably, by shearing in the bulk material [Fig. 8(a)].

For blends with block copolymers: 4500–10,000, 2500-3000-2500, and 2500-9000-2500, which increase the PC impact strength, the fractured surfaces were bleached and contained many small pores, formed due to crazing. The maximum pore size decreases as the test temperature increases. Simultaneously their content in the fracture zone grows. This obviously can be explained by decreasing the craze-initiating energy and increasing the craze-developing energy when the temperature rises. Undoubtedly, at low test temperatures crazing can be caused by low T_{gPDMS} . Because of this and probably involvement of the PC phase in the interphase interactions at the expense of the block PSN compatible with the PC. adequate molecular mobility is provided necessary for craze development.

During impact fracture of the blends, crazing and shear flow processes are usually taking place simultaneously. The crazing region within a polymer blend can become a region of shearing flow as some crack passes across it. In the initial crazing zone crazes can be closed by shearing flow or they can collapse.²⁴ The former or the latter mechanism prevails, and determines the impact strength values, depending on the test temperature and also on the block copolymer composition. For example, for blends containing PSN-PDMS-PSN: 9000-2500-9000 shearing flow prevails over the whole temperature range, whereas for those containing PSN-PDMS-PSN: 3000-2500-3000 shearing flow prevails but only up to 80°C. At higher temperatures crazing intensifies, and the impact strengths increase considerably compared with PC [Fig. 7 (a) and (b)].

An effective dissipation of impact energy owing to crazing and an increase in the impact strength are obviously only possible if block copolymers could form blends with pronounced interphase separation (breakdown). The experimental findings suggest that to increase the impact strength of the PC block, copolymers having polyblok structure or triblocks with PDMS end blocks are recommended.

CONCLUSIONS

Block copolymers of PSN and PDMS can be compatible or incompatible with PC, depending on



Figure 8 Scanning electron patterns of impact-fractured surface topography for PC (a) and blend of PC/PDMS– PSN–PDMS: 2500-3000-2500 7 wt % (b) vs. testing temperature.

their chemical structure. The calculations made showed the compatibility to become a fact if the rigid PSN block content in the block copolymer was ≥ 0.7 mol/parts. When the content of the PDMS elastic (flexible) blocks in the block copolymer was increased, a poor component compatibility in the blend was observed; the latter was becoming more heterogeneous. All tested systems were found to possess satisfactory thermal stability in processing. An intensive microphases breakdown in blends with triblock copolymers having high PDMS block contents (64-88 wt %) makes their melt processing more difficult because of macro separation. Polyblock copolymers or triblocks with end PDMS blocks, the content of which being 45–68 wt % formed with a microheterogeneous (opaque) PC blends posses a high impact resistance over a wide temperature range (from cryogenic temperatures up to T_{gPC}). The relaxation behavior of block copolymers shows a presence of interphase layers in them, despite a great difference in the solubility parameters of the PSN and PDMS blocks. In blends with PC a shift of T_{gPC} to a higher temperature region was observed, evidencing an intensive interaction of the PC phase with the PSN blocks. Addition of a block copolymer leads to a transition from shearing flow typical of PC to crazing during impact fracture. Crazing appeared typical only of blends having the microheterogeneous structures. To achieve high mechanical properties of blends it is recommended to use block copolymers of a polyblock structure.

REFERENCES

- 1. Raschilas, W. Plastverarbeiter 1992, 43, 54.
- 2. Utracki, L. A. Polym Eng Sci 1995, 35, 2.
- 3. Joyce, R. P. Des News 1992, 48, 80.
- 4. Hanrahan, B. D.; Angeli, S. R.; Runt, J. Polym Bull 1986, 15, 455.

- Devaux, J.; Godard, P.; Mercier, J. P. Polym Eng Sci 1982, 22, 229.
- Devaux, J.; Godard, P.; Mercier, J. P.; Touillaux, R.; Dereppe, J. M. J Polym Sci Polym Phys 1982, 20, 1881.
- Eguiazabal, J. I.; Nazabal, J. Plast Rubber Proc Appl 1990, 14, 211.
- 8. Gattiglia, E.; Turturro, A.; Pedemonte, E. J Appl Polym Sci 1989, 38, 1807.
- Riew, C. K.; Morris, R. C.; Woods, M. E. Proc Am Soc Compos, 3rd Tech Conf, Seattle, WA; Basel: Lancaster, PA, 1988.
- Starzhynsky, V. E.; Farberov, A. M.; Pesetskii, S. S.; Osipenko, S. A.; Braguinsky, N. A. Precise Plastic Parts and Their Production Techology (in Russian); Nauka i Tekhnika Publ.: Minsk, 1992.
- 11. Tyagi, D.; et al. Polymer 1988, 29, 833.
- 12. Auman, B. C.; et al, Polymer 1987, 28, 119.
- 13. Schneider, H. A.; et al. Polymer 1987, 28, 132.
- Noshey, A.; McGrat, G. Block Copolymers (in Russian); Mir Publ.: Moscow, 1980.
- 15. Pesetskii, S. S.; et al. Plasticzeskije Massy 1995, 2, 21.
- Ten, G.; Brinke, F. E.; Knight, M. W. Macromolecules 1983, 16, 1827.
- Kambour, R. P.; Bendler, J. T.; Bopp, R. C. Macromolecules 1983, 16, 753.
- Coleman, M. M.; Cerman, C. J.; Bhagwager, D. E. Polymer 1990, 31, 1187.
- Narisova, I. Strength of Polymers (in Russian); Mir Publ.: Moscow, 1987.
- Lur'e, E. V.; Lushcheikin, G. A.; Vakhtinskaya, T. N. Vysokomol Soyed. 1991, 33B, 18.
- 21. Varadarajan, K.; Boyer, R. F. J Polym Sci Polym Phys Ed 1982, 20, 141.
- 22. Bartenev, G. M.; Barteneva, A. G. Relaxation of Polymers (in Russian); Khimia: Moscow, 1992.
- Backnell, K. In Polymer Blends; Paul, D. R.; Newman, S., Eds.; Academic Press: New York, 1977, vol. 1.
- 24. Oshima, I.; Sasaki, I. Polymer 1991, 16, 198.