

Compatibility, Adhesional Interaction of Components, Impact Strength, and Rheological Behavior of Polycarbonate/Polycarbonate-Siloxane Block Copolymer

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ABSTRACT: Polycarbonate (PC) blended with a polymer-modifier polycarbonate-polydimethylsiloxane (PC-PDMS) of polyblock structure having equal molar ratios of soft (PDMS) and hard (PC) blocks have been investigated. The kinetics of adhesional interaction in blends and the analysis of interphase interaction conducted by using the relaxation spectrometry showed that intensive interactions between phases can occur. At a concentration of the modifier ≤ 5 wt %, these effects can lead to a partial compatibility of the components. The phase separation comes to completion when PC-PDMS content reaches 7 to 10 wt %. Here the impact strength of the blends improves compared with homopolycarbonate; this factor becomes less sensitive to the notch pattern or surface defects. The micro-heterogeneous blends would fail by the multiple crazing mechanism. The mode of temperature vs impact strength relationship depends on the concentration of the modifier. Low shearing rates applied to the PC blends containing 3 to 7 wt % of PC-PDMS results in a lower melt flow index compared with that for a neat PC. The blends were more sensitive to shearing stresses than the homopolycarbonate. Therefore, they have lower viscosity at a high shearing rate than PC. Introduction of PC-PDMS into PC did not change its thermal stability significantly. The modifier inhibited the chemical crosslinking of PC chains if the melt had been kept for a long period. The optimal mechanical properties combined with improved processability were found in blends containing 7 to 10 wt % of PC-PDMS. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 858–869, 2000

Key words: polycarbonate; polycarbonate-poly(dimethyl siloxane); block copolymer; impact strength; interphase adhesion; rheological behavior; thermal stability; scanning electron microscopy; relaxation spectrometry; reactive processing

INTRODUCTION

Block copolymers containing hard polycarbonate (PC), or polysulphonic, and soft organosiloxane

fragments in the macromolecule possess a wide spectrum of useful properties.¹ One of the most attractive of them is selectivity of gas permeability owing fabrication of the gas-separating membranes. In medicinal practice they find application in blood oxygenators (“artificial lungs”) for treating wounds, etc.^{2–5} In view of this, the siloxane block copolymers are investigated by many researchers.^{4–9}

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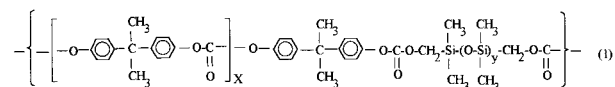
Blending of small amounts (≤ 4 wt %) of the polycarbonate-siloxane block copolymer (PC-PDMS) with PC allows changes to some of its properties.¹ The blends characterize both the reduced wettability and friction coefficient, which effect is understood to result from the fact that the modifier concentrates on the blend specimen's surface owing to low surface energy of the siloxane component. Macromolecular fragments with varying degrees of compatibility with respect to PC that are present in the modifier can influence the processes of microphase separation in the blends and their mechanical properties, particularly the toughness.

The influence of chemical structure of polysulphone-poly(dimethyl siloxane) block copolymers on their compatibility with PC, impact strength, and mechanism of impact failure of the blends was investigated.^{6,7} Impact strength of the PC/PC-PDMS blends can be controlled by varying the PC-PDMS content.⁸ However, the mechanism of impact failure, the relationship of the failure process, and impact characteristics of these blends with the interphase adhesion and the components' compatibility have not been thoroughly investigated. Also, problems related to their rheological behavior and thermal stability, which are factors determining processing behavior, have not been understood. Because of this, the aim of this study was to deal with the mentioned matters.

EXPERIMENTAL

Materials

The experiments were conducted using PC trade name Diflon prepared through reaction of phosgene with 2,2-bis(*p*-hydroxyphenyl)propane and polyblock PC-PDMS of the following structure: where $x = 10$ and $y = 43$.



Scheme 1

Both materials are produced by "AO Zarya" (Volgograd, Russia). Table I lists their characteristics.

Compounding and Specimen Preparation

Polymer blends, the same as in another work,⁷ were prepared by mixing granulated PC and the modifier with subsequent processing of the mixture on a single-screw extruder-granulator line based on Extruder SX-65 (L/D = 32; Klockner Windsor, Germany). The temperature in the outlet zone was 270°C. The modifier content in the blends varied between 1 and 30 wt %. The dried granulate of the PC/PC-PDMS blend was used to make test specimens by injection molding at $265 \pm 5^\circ\text{C}$.

Characterization

The tensile tests were performed on the Instron 1115 testing machine (Instron Limited Corp., England) using dog-bone specimens with the neck 45×3 mm in size. The Charpy impact strength (Pendulum Hammer PSW1.5, Werkstoffprüfm-aschinen, Germany) was measured using bars $60 \times 10 \times 4$ mm in size having sharp and right-angle notches.

The plot of temperature vs impact test results were constructed using specimens which, before testing, had been kept at a preset temperature in a cryogenic chamber, the structure and operating principle of which is described elsewhere.⁷ The test bars were placed onto a bed and kept at a certain temperature with $\pm 1^\circ\text{C}$ accuracy during 1 h. Then they were removed and the impact

Table I Characteristics of Blend Components^a

Polymer	Degree of Polycondensation	$M_w \times 10^{-3}$	Solubility Parameter (MJ/m ³) ^{0.5}	T_g (°C)
PC	140	35	20.4	149
PC-PDMS	$\bar{X} = 10^b$ $\bar{Y} = 43^c$	50.1	20.4 ^b 15.3 ^c	87 ^b 110 ^c

^a Values of \bar{X} and \bar{Y} were chosen according to formula (1).

^b PC block of PC-PDMS.

^c PDMS block of PC-PDMS.

strength was measured. The melt viscosities of the materials were described by the melt flow index (MFI) determined at 280°C and a 2.16-kg load, and also by the plot of the content-shearing rate obtained using the capillary viscometer of Instron 1115 Tester (capillary diameter $D = 1.22$ mm and width $L = 50$ mm) at 280°C.

The light transmission factor of the materials was determined using film specimens 100- μm thick as prepared by compression molding of PC and the blends, and also methylene chloride solutions of these materials (concentration 10 wt %). The measurements were performed using the photoelectric colorimeter KFK-2 (Optical Engineering Factory, Russia).

The dynamic thermogravimetric analysis was done by using the derivatograph Q 1500 (MOM, Hungary) at a 5°C/min heating rate.

The topography of the impact-fractured specimens was observed using the scanning electron microscope JSM-50A (Jeol, Japan).

The reverse torque pendulum tester operated at 1-Hz frequency was used to study the relaxation properties of the materials. The specimens were rectangular in cross-section and $60 \times 5 \times 1$ mm in size.

Changes in the blend properties can be expressed as an additive relationship⁹:

$$P = P_1\Phi_1 + P_2\Phi_2 + k\Phi_1\Phi_2 \quad (2)$$

where P_1 and P_2 are the properties of the blend and the components; Φ_1 and Φ_2 are portions of the components in the blend; k is the interaction factor as applied to the relaxation spectrometry data. The interphase interaction in blends was characterized using the zG_3 criterion¹⁰:

$$zG_3 = G_{bl} - \Phi_1G_1 - \Phi_2G_2 \quad (3)$$

where G_1 , G_2 , and G_{bl} are the dynamic shear moduli for the components (1) and (2), and the blends, respectively; z is some function dependent on the components' ratio in the blend; G_3 is the parameter that takes into account interaction between the components. For immiscible systems having weak interactions $zG_3 < 0$ and for high negative values of this criterion, the system tends to separate. If $zG_3 > 0$, the interaction between component phases in the blend is supposed to become more intensive.¹⁰

The experiments on adhesional interactions in the PC/PC-PDMS blends were conducted on

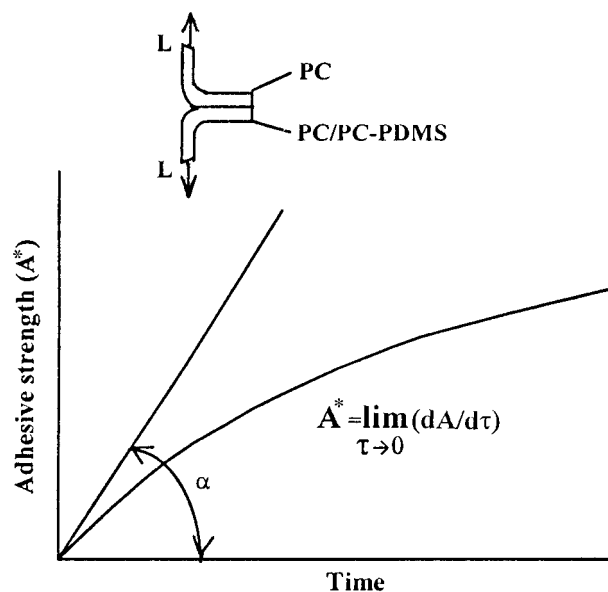


Figure 1 A scheme to determine the relative rate of increasing adhesional strength (A^*) by separating film specimens at 180°.

model specimens as films 300 μm in thickness; these were prepared by pellet compression molding. Adhesional contact between the film specimens was done by compression at 250°C and 5 MPa during varied periods. Both the adhesional strength (A^*) of the systems (measured by separating PC/PC-PDMS film from pure PC films) and a tentative rate of increasing the A^* were estimated.¹¹ Figure 1 scheme shows how to estimate A^* . It is evident that the approach is based on constructing the kinetics of adhesional strength for the systems made from PC and its blends, and finding the tangent of the curve in a point of coordinate origin. The values of A^* were found using the following expression:

$$A^* = \lim_{\tau \rightarrow 0} \left(\frac{dA}{d\tau} \right) \quad (4)$$

where τ is the time necessary to form an adhesional joint.

It should be noted that A^* value depends not only on the chemical nature of the materials involved, but also on the conditions at which adhesional contact is formed, i.e., temperature, pressure, environment, presence of impurities, etc. With strictly constant processing factors, A^* value depends only on the nature of the contacting materials. As the A^* value is experimentally

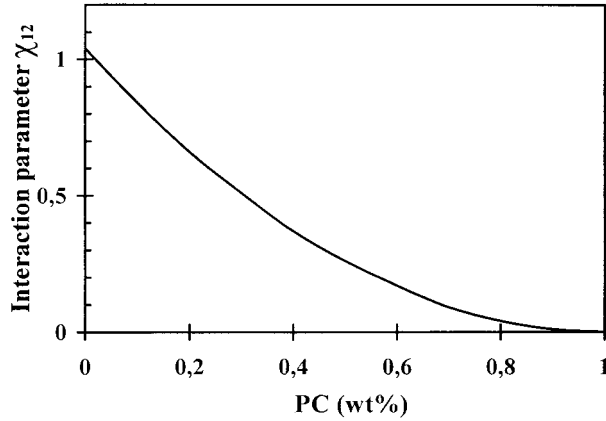


Figure 2 Calculated values of interaction parameter for PC/PC-PDMS blends vs the hard PC-block content.

found in the course of an ultimately short (momentary) contacting of the materials ($\tau \rightarrow 0$), the effects of diffusion processes on adhesional interaction of the materials are not considered. It means that A^* values, like the thermodynamic parameter of interaction χ_{12} ,¹² considers only the interaction energy within the zones of the interphase contact. But of importance is the fact that experimental estimation of A^* values is based on the analysis of the polymeric specimens of real content and not on some idealized objects, which are used to calculate the χ_{12} parameter.

RESULTS AND DISCUSSION

Analysis of Compatibility and Interphase Adhesion

The PC blocks, identical in the chemical structure to the homopolycarbonate, being present in the block copolymer structure, should favor the components' compatibility in the PC/PC-PDMS blends. One should assume, however,¹² that the degree of compatibility of the components depends on the PC-block content in the modifier; this is determined by the ratio of molecular weight of PC and PDMS blocks. Considering the great difference in solubility parameters of PC and PDMS block in the modifier (Table I), the compatibility must be analyzed in view of the mean field theory^{13,14} while taking into account the repulsive forces between PC and PDMS blocks. In a general case, the structural formulation of the considered blends can be written as follows: B/B_xC_{1-x} , where B is homopolycarbonate; C is a PDMS block in the modifier; and x is the mol fraction of the PC block in the PC-PDMS.

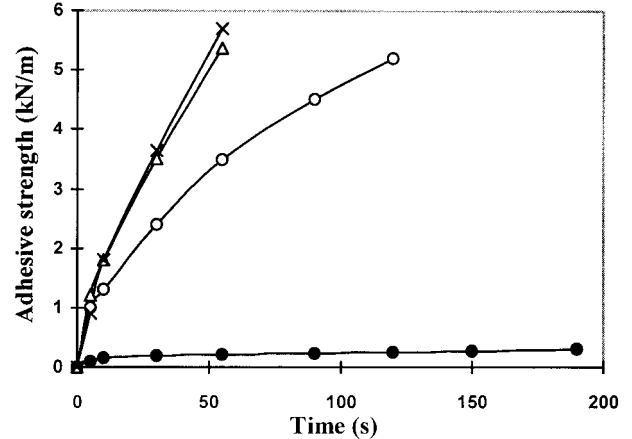


Figure 3 Adhesional strength of PC-PC joints (x) and PC-PC/PC-PDMS joints when block copolymer was added in the following amounts (wt %): 3 (Δ); 7 (\circ), and 15 (\bullet) vs time of adhesional contact formation.

Then, in accordance with,¹³⁻¹⁵ the expression for the thermodynamic parameter of interaction in the blends χ_{bl} will be as follows:

$$\chi_{bl} = (1 - x)^2 \chi_{BC} \quad (5)$$

Assuming that PC/PC-PDMS blends belong to the systems with relatively weak interphase interactions, it can be anticipated that compatibility occurs at critical values of interaction parameter $\chi_{bl,cr} \geq 0.1$. From Eq. (5) follows that the plot of χ_{bl} vs blend content for a studied case is a parabolic curve approaching asymptotically zero if PC concentration in the modifier is equal to one. Figure 2 shows that compatibility occurs with

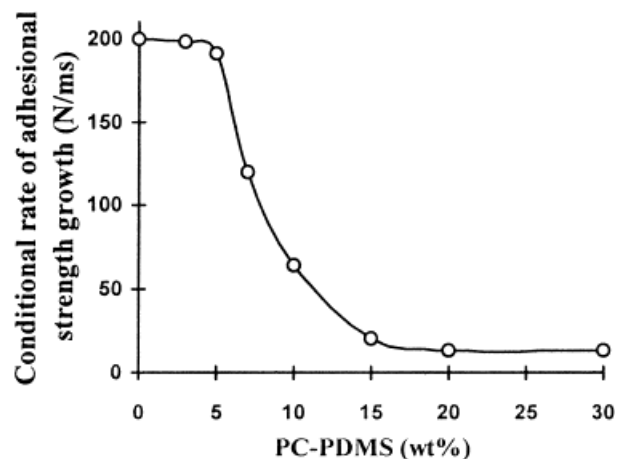


Figure 4 Relative rate of increasing adhesional strength vs PC-PDMS blended with PC.

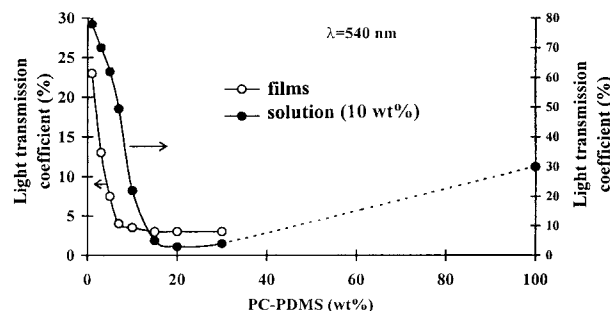


Figure 5 Light transmission coefficient for films (○) and solutions in methylene chloride (●) of blends vs PC-PDMS content (solution concentration was 10 wt %).

0.75 to 1.0 molar parts of PC hard block. As the present work was performed using the 1:1 ratio of soft blocks to hard blocks in PC-PDMS, the given copolymer cannot form miscible blends with PC with reference to Figure 2. Considering the strong effects of component concentrations in the blend on their compatibility,¹² the compatibility can be anticipated to occur within a certain range of component concentrations. To prove this suggestion, the experiments were conducted to investigate interphase adhesion and light transmission.

Figures 3 and 4 show data on adhesional interaction in PC/PC-PDMS blends. This interaction evidently depends on the modifier concentration. At 5–7 wt % contents there was observed a sharp drop in the relative rate of increasing the adhesional strength. Probably, within this range of concentrations, PC-PDMS migrates to the region of the interphase contact owing to phase separation and weakens adhesion between the phases.

The degree of the phase separation depends on the components' ratio (Fig. 5). Photometry of the

film specimens of the blends indicated that this process was completed at 7–10 wt % of PC-PDMS. This conclusion correlates with that obtained based on data shown in Figure 4.

In methylene chloride solutions the phase separation was completed at higher concentration of the modifier in the blends than in film specimens; this is, probably, because of particulars of interaction in the polymer (1)–solvent–the polymer (2) systems.¹² Thus, the PC-PDMS used in this work create immiscible systems with PC. At low concentrations, however (≤ 5 wt %), partial compatibility can be achieved; the degree of microphase separation depends on the block copolymer content in the blend. A complete microphase separation is typical of the blends containing ≥ 7 wt % of PC-PDMS.

Mechanical Characteristics of PC/PC-PDMS Blends

It can be seen in Table II that the addition of PC-PDMS to PC changes markedly its mechanical properties. Of particular interest is the influence of the modifier on the toughness of the blend. PC homopolymer is highly sensitive to the notch shape (type of surface defects) and has relatively low impact strength at low temperatures.^{12,16–18} Introduction of PC-PDMS modifier lessens differences between the impact strength determined for the specimens with sharp and right-angle notches and allows up to a six-fold increase in it at -40°C . The optimal modifier content in the blend, considering the set of all mechanical properties, is 7 to 10 wt %.

It was of interest to analyze the mechanism of how PC-PDMS affects the impact strength. Introduction of this modifier causes variations in the character of impact failure (Fig. 6). For the neat

Table II Effect of PC-PDMS Content on Mechanical Properties of Blends

Factor	Content of PC-PDMS (wt %)								
	0	1	3	7	10	15	20	30	100
σ_F (MPa)	56	58	54	54	50	42	37	30	12 ^a
ε_E (%)	25	35	46	89	78	74	18	12	480
$\alpha_{r.a.n}$ (kJ/m ²)	50	51	50	48	46	45	43	40	^b
$\alpha_{sh.n}$ (kJ/m ²)	20	22	23	43	40	52	51	59	^b
$\alpha_{sh.n}$ at -40°C (kJ/m ²)	13	14	18	23	25	42	57	78	^b

^a Ultimate tensile stress.

^b Did not fail by impact loading.

σ_F and ε_E are flow limit and relative elongation at rupture, respectively; $\alpha_{r.a.n}$, $\alpha_{sh.n}$, $\alpha_{sh.n}$ at -40°C stand for toughness of specimens with sharp and right-angle notches tested at 23°C , and also for specimens having sharp notch and tested at -40°C .

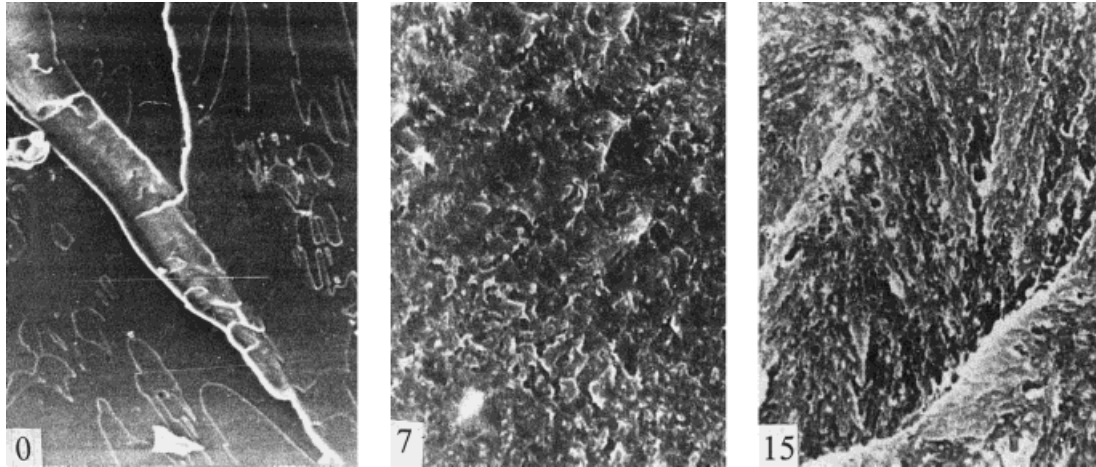


Figure 6 Scanning electron micrographs of failed surfaces of PC and its blends with PC-PDMS cooled in liquid nitrogen. Digits stand for block copolymer content (wt %). Original magnification, $\times 1000$.

PC the specimens failed by shear flow⁷ accompanied by generation of smooth surfaces in split sites. Introduction of PC-PDMS initiated crazing. On the scanning electron halftone photomicrographs of the blend's splits (7 and 15 wt % of PC-PDMS) crazes look like a multitude of tiny ($0.1\text{--}0.3\ \mu\text{m}$ in diameter) pores formed in the impact failure regions. If tests were carried out at the room temperature, the "bleached" zone spread over the whole impact-failed surface, thus indicating that multiple crazes promote energy absorption during the whole failure process and not only on its initial stage.^{12,18}

One of the conditions to strengthen the blend material against impact failure is controlled phase separation of the components. The dispersed phase must have a lower shear modulus than that of the matrix material, as well as adequate adhesion to the matrix, low glass-transition temperature, etc.^{7,12} Evidently, these conditions are quite fully achieved in PC/PC-PDMS blends containing 7 to 10 wt % of the modifier.

Results of Relaxation Spectrometry

Blocks of PC and PDMS in the modifier have greatly differing values of solubility parameters; this fact predetermines their immiscibility and formation of a micro-heterogeneous structure in the PC-PDMS itself. As revealed by the relaxation spectrometry technique, the glass transition temperature (T_g) of poly(dimethyl siloxane) soft blocks in the neat PC-PDMS copolymer is -110°C whereas of hard PC blocks it is 48°C (Fig. 7).

For the blends containing 3 wt % of PC-PDMS the temperature of β -relaxation peak of PC shifts from -75 to -83°C . The PC glass transition temperature ($T_{g\text{PC}}$) was decreased by $1\text{--}2^\circ\text{C}$. For the blends containing 15 wt % of the copolymer the β -transition temperature would shift along with shoulder formation having the temperature of transition related to glass transition of the soft PDMS block at -110°C ; this suggests precipitating the copolymer into an individual phase. The $T_{g\text{PC}}$ in the blend also decreases by $1\text{--}2^\circ\text{C}$. Besides, the low-temperature branch of glass-transition peaks for PC in the blends containing 3 and 15 wt % of PC-PDMS has kinks or weak loss maxima. They are probably due to glass transi-

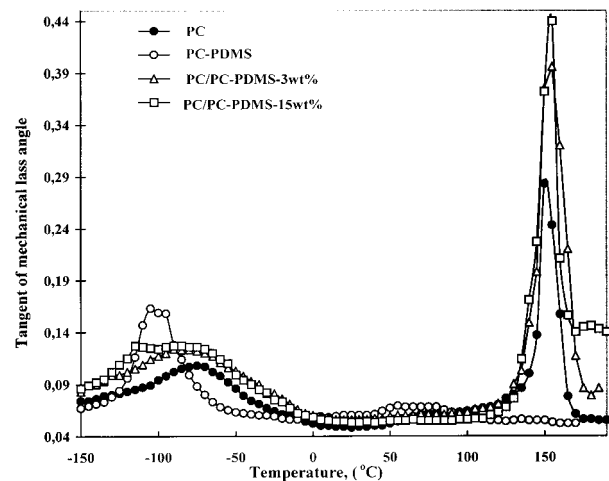


Figure 7 Temperature vs mechanical loss tangent for PC, PC-PDMS, and their blends.

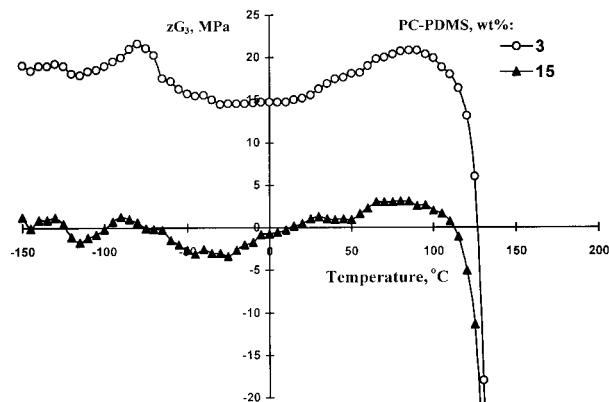


Figure 8 Temperature vs zG_3 criterion for blends of PC with PC-PDMS 3 wt % (○) and 15 wt % (▲).

tion of PC fragments present in the interfaces.⁷ The given results point to intensive interphase interaction of PC blocks in the polymer-modifier with the polymer-matrix, and that interfaces are formed in the blend.

For the blends with concentration of PC-PDMS equal to 3 and 15 wt %, positive values of the zG_3 criterion are present in the temperature interval between 20 and 100°C (Fig. 8). However, according to Eq. (3), values of the shear moduli for the blend should be higher than that for the virgin PC. Because of this, introduction of the block copolymer PC-PDMS with lower shear modulus than PC into the latter resulting in an increase of the shear moduli for the blend, implies the intensive interaction of components in the blend. It means that now a low-molecular weight component increases stiffness of the blend. Based on this, it is concluded that influence of PC-PDMS modifier acts as antiplasticizer at temperatures below the T_{gPC} . Above the T_{gPC} PC-PDMS acts as plasticizer, because now $zG_3 < 0$. The temperature vs zG_3 plot shows that this criterion decreases over the temperature range where the PC segmental mobility unfreezes in the interfaces. The main cause of weaker components' interaction is high mobility of the copolymer chains at the liquid-liquid temperature evaluated from expression¹⁹ $T_{11} = T_g + 76^\circ\text{C}$ is $\approx 120^\circ\text{C}$. This temperature corresponds with polymer transition into the true liquid state and related molecular mobility, which reflects in respective changes in zG_3 values. This is the highest temperature limit when is pronounced the cooperative segmental motion. Over this temperature the chain segments behave quasi independently. It leads to disrapture of the physical junctions and noncoin-

cidence of isopropyl-carbonyl groups between PC and modifier chains.⁷ The criterion begins to decrease, however, at a lower temperature (90°C). The reason is defrosting of the segmental mobility in the temperature range of α -relaxation process in the interfaces of the PC/PC-PDMS system.

High positive values of zG_3 for PC-PDMS—3 wt % blends observed over a wide temperature range indicate strong interactions between phases despite PDMS blocks preventing compatibility. This proves formation of interfaces in studied blends having a molecular structure differing from that of the initial components. For high concentrations of PDMS blocks (15 wt % of the polymer-modifier) the zG_3 value decreases significantly; this proves that interphase adhesion weakens in the blends under the effect of poly(dimethyl siloxane) blocks (Figs. 3 and 4).

Effect of Test Temperature

Figures 9 and 10 show effects of test temperature and PC-PDMS contents on the impact strength of the blends. These data reveal direct analogies between PC blends and polysulphone poly(dimethyl siloxane) block copolymers (PSN-PDMS). Similar to PC/PSN-PDMS, the PC/PC-PDMS blends have higher resistance to impact failure over a wide test temperature range. The temperature vs impact strength relationship depends on the blends' composition, and their character can be explained in view of the relaxation transitions

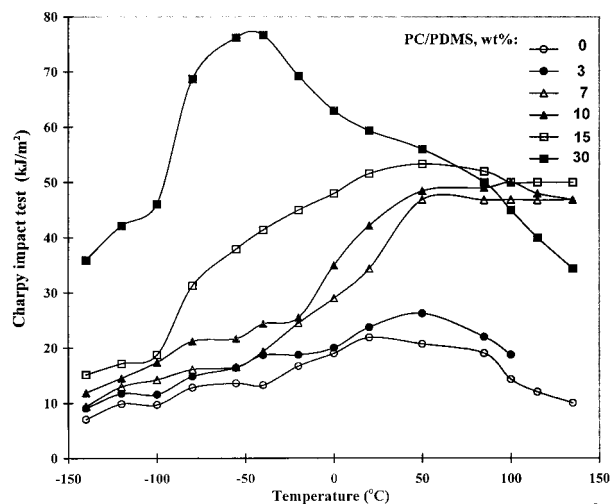


Figure 9 Effect of test temperature on impact strength for sharp-notched specimens made from PC (○) and PC/PC-PDMS containing PC-PDMS: 3 (●), 7 (△), 10 (▲), 15 (□), and 30 (■) wt %, respectively.

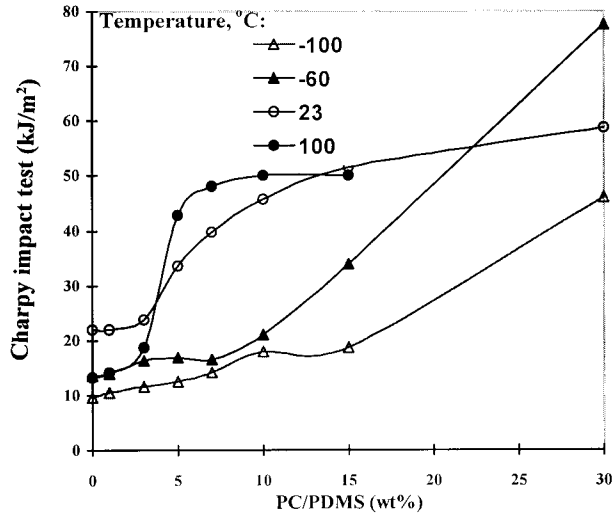


Figure 10 Effect of PC-PDMS content on impact strength of blends at test temperatures, °C: 23 (○), 100 (●), -60 (▲), and -100 (△).

and interphase interactions.⁷ Extremes present on the temperature curves can be explained by relaxation transitions in the blends and by ratios of mechanical energy required to initiate failure (origination of micro cracks) and micro crack propagation through the specimen.^{7,12,18} Figures 9 and 10 show that variations in block copolymer contents change the temperature vs impact strength plot, hence the mechanism by which this additive acts. For PC/PC-PDMS 3 wt % blends, the same as for the neat PC, the impact strength decreases at temperatures above 50°C after passing the maximum (Fig. 9). Higher concentration of PC-PDMS, 7–10 wt %, gives practically constant impact strength 46–50 kJ/m² over the temperature range 50–130°C. It was mentioned earlier that with these copolymer contents in the blends a developed micro-heterogeneous structure is formed. We assume that such a structure leads to high impact strength over a wide temperature range.

Addition of 15 wt % of the modifier causes the impact strength of the material to decrease again at temperatures above 50°C (Fig. 9). As the general level of the material's mechanical properties fall when PC-PDMS content grows (Table II), it becomes evident that the named effect can be explained by lower amount of energy required to start failure. A certain contribution can be made by weaker interphase interactions occurring at the test temperature that approaches T_{gPC} (Fig. 8).

With 30 wt % of PC-PDMS in the blend, it probably forms a dispersed phase; this is proved by sharp lowering of cohesion characteristics of the blends compared with PC (Table II). Therefore, maximum on the temperature vs impact strength plot are observed at much lower temperature (-50°C), when the modifier has high cohesive strength [Fig. 9, curve (■)]. The highest impact strength can reach 88 kJ/m². However, the specimens did not fail completely owing to improved elasticity of the PC-PDMS phase and interfaces. The high impact strength for the PC/PC-PDMS 30 wt % system results from intensive crazing that leads to increased energy required to propagate micro cracks.¹²

Rheological Behavior and Thermal Stability of Blends

Figures 11–15 show the most important relationships describing changes in flow ability and viscosity of the melts with composition, temperature, time of temperature exposure, and shear stresses. At low shear stresses and rates (conditions usually provided for finding an MFI) the concentration plot has a minimum of a flow for PC-PDMS 3–5 wt % (Fig. 11). Such a dependence is unusual, because quite often a minimum viscosity was observed for blends of immiscible or partially miscible polymers.¹² Weak evidence of increased viscosity of the blends in comparison with homopolycarbonate can be additionally explained by the fact that the MFI of the modifier at 280°C is about five times as high as that of PC (Fig. 11). This effect is hard to interpret unambiguously. Probably, even a small quantity of the studied modifier that has the surface active properties¹ affect the flow mechanism of the blends. The laminar na-

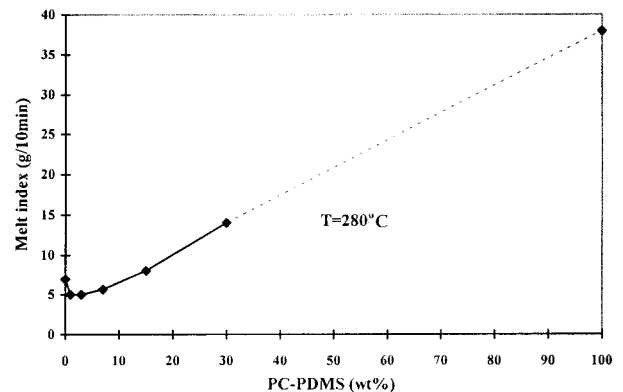


Figure 11 Effect of PC-PDMS content in a blend with PC on MFI values.

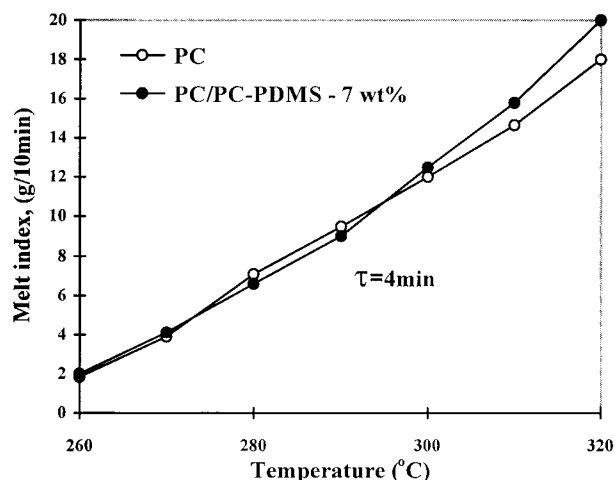


Figure 12 Temperature vs MFI for PC and its blends with PC-PDMS 5 wt %.

ture of the flow is disturbed and is becoming tunnel-like¹⁷ owing to melt slipping along the capillary walls. It should also be considered that due to the partial miscibility, as was mentioned above, some portion of the modifier and PC moves to the interface; the density of the latter can be significantly higher than that of the components of the blend.^{12,20-22}

Great differences in rheology of PC and PC/PC-PDMS blends influence the kinetic relationships of the MFI (Fig. 13). Unlike PC, for which the MFI decreases with increasing the exposure time at 280°C, blends containing 7 and 15 wt % of PC-PDMS usually have steady values of this index. It only slightly increased with the exposure

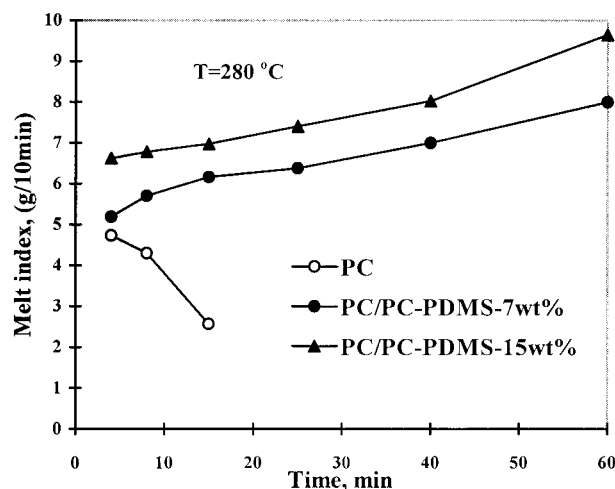


Figure 13 Effect of exposure time at 280°C of PC materials on their MFI.

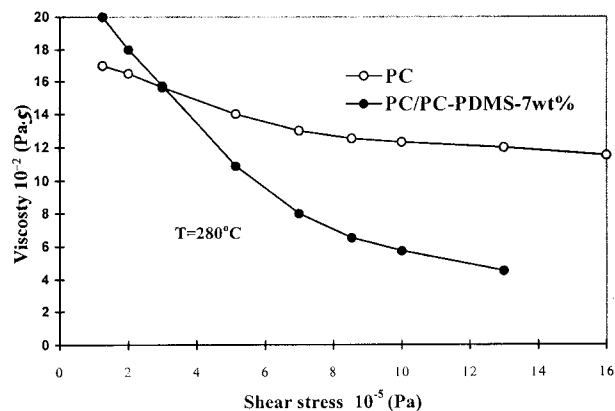


Figure 14 Viscosity of PC and its blends with PC-PDMS 7 wt % vs shearing stresses.

period. Because the most probable cause of the MFI decrease for PC can be chemical crosslinking of its macromolecules, the data in Figure 13 points out that this process can be inhibited by the investigated modifier.

Figures 14 and 15 prove the fact that the blends containing a small amount of the modifier have increased viscosities at low shear rates. Quite an opposite picture is typical of high shear rates (Fig. 14). Evidently, blends are much more sensitive to shearing compared with homopolycarbonate. The microscopy analysis made on stream cross-sections of the extrudate that had passed through the viscometer's capillary at a high shear rate (≥ 1500 s⁻¹) revealed that it consists of a multitude of micro fibrils. The formation of such fibrils can be seen by unarm'd eye for ≥ 15 wt % of PC-PDMS.

In earlier studies, the formation of fiber dispersions having micron and submicron thicknesses, oriented along the extruded stream was described.^{12,23-25} The fibers had a core-shell struc-

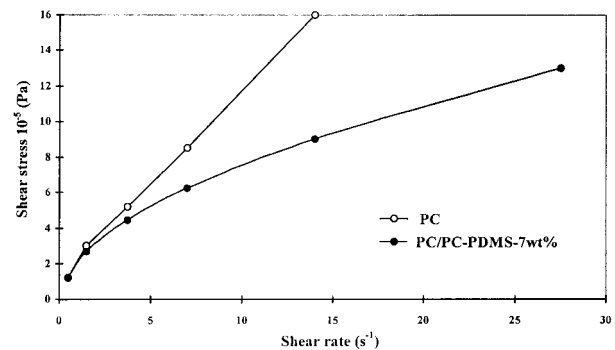


Figure 15 Flow plot of PC and its blends containing PC-PDMS 7 wt %.



Figure 16 Microphotograph of a broken samples neck of PC/PC-PDMS 15 wt % blend. Original magnification, $\times 6$.

ture where the outer shell is of lower viscosity liquid.

The flow curves (Fig. 15) also suggest transformations of the supermolecular structure to occur in the blends with increasing the shearing rate; these transformations are determinants in the rheological behavior. The fibrilla-wise structure is formed during the blend flow owing to interfaces. In addition, shearing causes redistribution of the components in the blend. Migration of the modifier toward the capillary walls and to the microfibril surfaces favor viscosities lowering at high shear rates.

Therefore, blending with PC-PDMS promotes better PC-processability at industrial conditions

due to lower viscosity. It should be taken into consideration, however, that at extremely high shearing rates, the blends must have anisotropic properties determined both in the direction of flow and perpendicular to the flow, which is a typical feature of systems having a tendency to form fibers during flow.^{23,24} It should also be noted that fibrillization is most evident in the polymer blends containing ≥ 5 wt % PC-PDMS. For 7 wt % of this modifier, the viscosity is decreased with increasing shearing stresses, probably due to transition to the "tunnel flow," caused by the modifier migrated to the capillary walls. This could be supported, i.e., by microscopic observations (Fig. 16) of standard specimens after tensile tests, when numerous microfilaments are present on their surface. They are thought to result from delamination in the microfilament structure of the tested material under action of the applied force field.

Introduction of PC-PDMS into PC does not significantly influence the materials' thermal stability (Fig. 17, Table III), thus allowing them to be processed at conditions typical of PC (when processing the blends, the temperature or pressure may be lowered owing to their better flow ability at increased shearing rates compared with homopolycarbonate). The degradation mechanism characterized by two stages on the thermogravimetric curve for PC (Fig. 17) did not change on blending. Table III shows that blending with a modifier promotes some lowering in the material's thermal stability on the first degradation stage; on the second degradation stage, it was somewhat increased. The differences in PC and blends' thermal stabilities were minimal over the processing temperature range (250–290°C) as

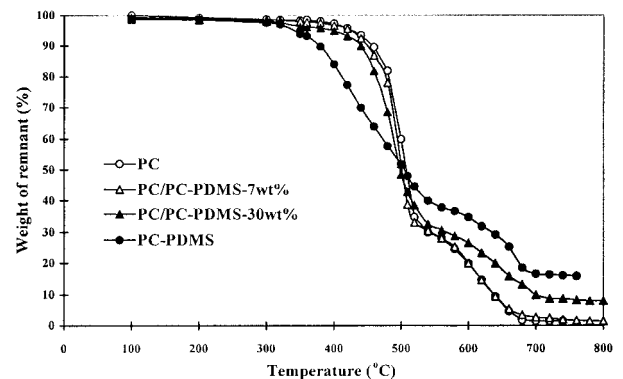


Figure 17 Residual material weight vs temperature when materials were heated in air at the 5°C/min heating rate.

Table III Characteristic Temperatures of Thermally Degraded PC and PC-PDMS Blends Determined by Dynamic Thermogravimetry at a Heating Rate of 5°C/min

Material	Temperature, ^a (°C)				
	T_{10}	T_{50}	T_c	T_b	T_d
1. PC	460	508	530	576	682
2. PC/PC-PDMS (-7 wt %)	418	502	518	580	678
3. PC/PC-PDMS (-10 wt %)	445	496	522	581	680
4. PC/PC-PDMS (-20 wt %)	443	498	530	582	682
5. PC/PC-PDMS (-30 wt %)	440	500	535	590	712
6. PC-PDMS	380	506	543	593	688

^a T_{10} and T_{50} are loss temperatures of 10 and 50% weight, respectively; T_c and T_b are temperatures of completion of first degradation stage and beginning of second degradation stage, respectively; T_d is temperature of full decomposition.

was established using the dynamic thermogravimetry technique (Fig. 17).

CONCLUSIONS

PC and PC-PDMS containing equal molar ratios of soft (PDMS) and hard (PC) blocks are immiscible. However, the experimental data on the kinetics of adhesional interaction in PC/PC-PDMS blends, and analytical results on interphase interaction obtained using the relaxation spectrometry, show there are intensive interactions that favor partial compatibility of the components at low (≤ 4 wt %) modifier contents. The degree of phase separation depends on the component ratios. The results of photometry, performed on film specimens of the blends, and data on the effect of the blends' composition on the kinetics of adhesional interaction, indicate that the phase separation process is completed with a content of PC-PDMS equal to 7–10 wt %. The impact strength of the blends was much improved compared with homopolycarbonate when tests were conducted on specimens with sharp notches while the sensitivity of this property to the type of notch (type of surface defects) was lower. The micro-heterogeneous PC/PC-PDMS blends failed under impact loading mainly by multiple crazing. The shape of temperature vs impact strength plots depends on the modifier amount in the blend. The effect of PC-PDMS concentration on the temperature vs impact strength relationship is explained both by variations in the cohesion strength of the material that determines the energy level required to initiate failure, and by phase-structural changes

that influence the crazing process as well as the dissipation level of mechanical energy in the material during failure.

At low shearing rates, the PC blends containing 3–7 wt % of PC-PDMS have poorer melt flow ability compared with PC. But they are more sensitive to shearing than homopolycarbonate. In view of this, the blends have lower viscosity than PC at high shear stresses. Introduction of PC-PDMS to PC does not much influence the material's thermal stability. The modifier was found to inhibit chemical crosslinking of PC macromolecules if the melt was kept long in the cylinder of the MFI metering device. PC blends containing 7 to 10 wt % of PC-PDMS appeared to have an optimal set of mechanical properties combined with improved moldability during processing.

REFERENCES

1. Noshey, A.; McGrath, J. E. *Block Copolymers* [Russian translation]; Mir: Moscow, 1980.
2. Manabu, S., Ed.; *Polymers for Medical Applications* [Russian translation]; Mir: Moscow, 1981.
3. Tyagi, D.; Webster, D. C.; Wilkes, G. L.; Mc Grath, J. E.; Hedrick, J. L. *Polymer* 1988, 29, 833.
4. Auman, B. C.; Cantow, H. J.; Percec, V.; Schneider, H. A.; Wu, J. H. *Polymer* 1987, 1, 119.
5. Schneider, H. A.; Auman, B. C.; Cantow, H. J.; Percec, V.; Wu, J. H. *Polymer* 1987, 28, 132.
6. Pesetskii, S. S.; Storozhuk, I. P.; Koval, V. N.; Urbanek, G. O.; Kireev, V. V. *Plast Massy* 1995, 2, 21.
7. Pesetskii, S. S.; Jurkowski, B.; Storozhuk, I. P.; Koval V. N. *J Appl Polym Sci* 1999, 73, 1823.

8. Pesetskii, S. S.; Koval, V. N. Rep Belarussian AS 1992, 36, 34.
9. Utracki, L. A. Polym Eng Sci 1982, 22, 1166.
10. Perepechko, I. I. Rep USSR AS 1986, 291, 147.
11. Pesetskii, S. S. Proc Belarussian AS Chem Sci 1992, 1, 105.
12. Paul, D. R.; Newman, S., Eds. Polymer Blends; Academic Press: New York, San Francisco, London, 1978; Vols. 1 and 2.
13. Ten, G.; Brinke, F. G.; Knight, M. W. Macromolecules 1983, 16, 1827.
14. Kambour, R. P.; Bendler, J. T.; Bopp, R. C. Macromolecules 1983, 16, 753.
15. Coleman, M. M.; Cerman, C. J.; Bhagwager, D. E. Polymer 1990, 31, 1187.
16. Kayano, Y.; Keskkula, H.; Paul, D. R. Polymer 1997, 38, 1885.
17. Kayano, Y.; Keskkula, H.; Paul, D. R. Polymer 1998, 39, 821.
18. Bocknell, K. B. Impact Resistant Plastics [Russian translation]; Khimia: Leningrad, 1981.
19. Baranov, T. G.; Frenkel, S. Y. J Polym Sci Polym Symp 1977, 61, 351.
20. Plochocki, A. P. J Appl Polym Sci 1972, 16, 987.
21. Lipatov, Y. S.; Bezruk, L. I.; Lebedev, E. V. Vysokomol Soedin 1976, 18B, 77.
22. Letz, J. Kolloid-Z 1970, 236, 38.
23. Vinogradov, G. V.; Yarlykov, B. V.; Tsebrenko, M. V.; Yudin, A. V.; Ablazova, T. I. Polymer 1975, 16, 609.
24. Ablazova, T. I.; Tsebrenko, M. V.; Yudin, A. V.; Vinogradov, G. V.; Yarlykov, B. V. J Appl Polym Sci 1975, 19, 1781.
25. Folkes, M. J.; Keller, A.; Scalisi, F. R. Kolloid-Z 1973, 251, 1.