

Toughening of Polycarbonate through Reactive Melt Blending: Effect of Hydroxyl Content and Viscosity of Hydroxyl-terminated Polydimethylsiloxane*

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Abstract In this study, four hydroxyl-terminated polydimethylsiloxanes (PDMSOH) with different viscosities and hydroxyl contents were used to improve the toughness of polycarbonate (PC) through reactive melt blending. A largely improved toughness of PC has been achieved, and the low temperature toughness of PC/PDMSOH blends could overtake that of PC homopolymer in much higher temperatures (*e.g.* $-10\text{ }^{\circ}\text{C}$ versus $23\text{ }^{\circ}\text{C}$). Moreover, it was found that the more the hydroxyl content, the less the PDMSOH was needed to reach the highest toughness, suggesting that equivalent molar ratio between the carbonyl group content of PC and the hydroxyl group content of PDMSOH was required for the toughening of PC. Ultraviolet spectrophotometry was used to analyze the possible reaction between PC and PDMSOH. Contact angle was measured to assess the change of interfacial interaction between PC and PDMSOH as change of viscosity and hydroxyl content. The formation of PC-*co*-PDMSOH copolymer was believed to be the key for the toughening effect. This work gives a profound recommendation of the optimum kind and dosage of PDMSOH which should be used to improve the toughness of PC and will find immediate industrial applications.

Keywords: Blends; Low temperature toughness; Polycarbonate; Polydimethylsiloxane.

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INTRODUCTION

Bisphenol A polycarbonate (PC) is one of the largest consumed engineering plastics with a wide range of applications^[1–4]. It is a transparent polymer with outstanding thermal and mechanical properties, including high impact strength, good dimensional stability, high gloss, high thermal stability and heat distortion temperature. However, its utilization still faces challenges, since new designs tend to emphasize more on key application areas where thin-wall parts, complex geometries and high-impact products that can withstand very low temperatures with no compromise on flow and process-ability are required.

Modification of polycarbonate with other components through copolymerization and melt blending has been extensively studied in the last four decades. Toughening of PC by using polydimethylsiloxane (PDMS) has drawn much attention^[5–7]. PDMS has low glass transition temperature resulting in low temperature ductility, high thermal stability and versatile functionality^[8–11], which makes it an ideal modifier for PC. The compatibility

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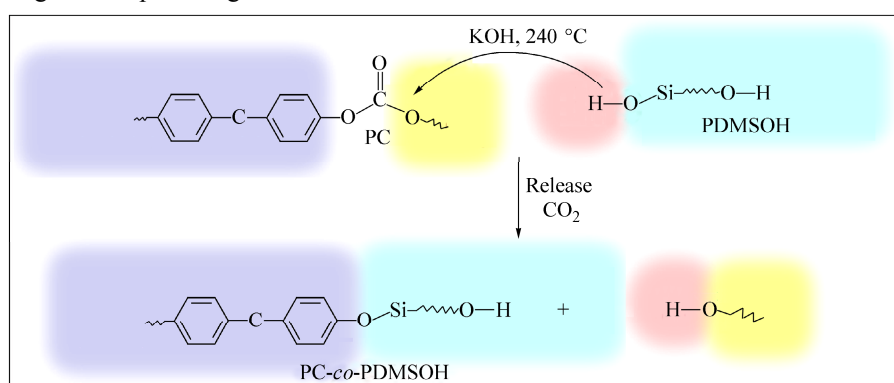
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between PC and PDMS is the key for the performance. Both the preparation and use of (PC-*co*-PDMS) block copolymers have drawn considerable amount of interest^[12–18]. However, side-reactions usually occur in the preparation of (PC-*co*-PDMS) block copolymers *via* copolymerization which results in chain extension of the siloxane blocks or chain cleavage of the polycarbonate blocks, leading to polydisperse block lengths and extensive phase separation between the hard (PC) and the flexible (PDMS) segments^[19].

Compared with the traditional copolymerization, reactive modification of polycarbonate with a functionalized siloxane in the melt state provides a more efficient and friendly route for industrial production without the concern for the side reactions and extremely toxic phosgene used for interfacial polymerization. Many attempts have been made to utilize versatile functionalized PDMS as PC's modifier in order to acquire desired properties of the materials. Hawkins *et al.* reported an approach to functionalize polycarbonate with carboxylic acid decorated polydimethylsiloxane fluids in the melt for production of a block copolymer^[20]. Peters described an invention of modifying polycarbonate with several alkyl amino terminated silicones using the melting mixing process as well^[21]. Other specialized siloxanes that have been used to modify polycarbonate include lactone siloxane-lactone block copolymers^[22], hydroxyaryloxy terminated polydimethylsiloxane^[23], *etc.* Wu *et al.*^[5] reported a PC/PDMS blend with remarkably good low temperature impact toughness and excellent flow characteristics based on modifying bisphenol A polycarbonate with ultra-high molecular weight hydroxyl-terminated polydimethylsiloxane (PDMSOH) in the form of gum (*i.e.*, high viscosity) through reactive blending. The structure-property relationship in particularly with respect to rheological properties of this polycarbonate blend was investigated and discussed. Comparison between the reactive and non-reactive PC-PDMS blends was made, and the differences in morphology were demonstrated to be the main reason for the disparate physical properties. The work highlights the importance and necessity of reactive compatibilization that has long been recognized for immiscible blends.

Given that the reaction between PC and PDMSOH will largely depend on the content of hydroxyl and mobility of PDMSOH, in this work, four PDMSOHs with different viscosities and hydroxyl contents are chosen for reactively melt blending with PC. The PDMSOH used are all with low molecular weight in the form of fluid to promote the interaction between these two components. The prepared PC/PDMSOH blends exhibit much improved toughness and this has not been investigated in PC-*co*-PDMS copolymers mentioned before. Comparison has also been made between reactive and non-reactive PC/PDMS blend systems to further investigate the role of PC-*co*-PDMSOH copolymer in the toughening effect.

Given that the datasheet of PDMSOH used in this study revealed the presence of KOH at ppm level, a probable reaction scheme between PC and PDMS can be proposed in Scheme 1, showing that the —OH terminal group on siloxane initiates a transesterification reaction on the carbonyl groups of bisphenol A polycarbonate, which results in the formation of a PC-PDMS block copolymer with the siloxane chain directly bonded to the polycarbonate backbone. The by-product for the proposed reaction is the formation of CO₂, which is released into the air during the compounding.



Scheme 1 The proposed reaction scheme between PC and PDMSOH during melt blending

EXPERIMENTAL

Materials

Bisphenol A polycarbonate (PC, Lexan 131R, $M_w = 47$ kg/mol, $M_w/M_n = 2.10$) from Sabic Innovative Plastics was used as matrix in this study. Hydroxyl-terminated polydimethylsiloxane and normal polydimethylsiloxane were obtained from Dow Corning (Midland, MI). All the PDMSOH and PDMS used in this study are all fluid. The viscosity of PDMSOH and its corresponding molecular weight and hydroxyl content are listed in Table 1. It should be mentioned that all the four kinds of PDMSOH contain a detectable amount of potassium at 10^{-6} g/L level which works as the catalyst for the reaction between PC and PDMSOH. As a reference, PDMS with a viscosity of 500 mm²/s was used to study the toughening mechanism in PC/PDMSOH system. It should be noticed that physical properties of this PDMS are close to those of the PDMSOH with a viscosity of 750 mm²/s.

Table 1. Basic parameters of the siloxanes investigated in this study

Viscosity (mm ² /s)	Molar mass (kg/mol)	$W(\text{OH})\%$
750	7.8	0.2
5000	50.8	0.07
20000	77	0.04
80000	130	0.025

Sample Preparation

The PC pellets were dried in a vacuum oven at 100 °C for 12 h before blending. After that, PC and PDMSOH were mixed at a desirable weight ratio in an internal mixer (HaakeRC-90, Germany) at 240 °C, 60 r/min for 5 min. Considering its good flow-ability, PDMSOH was added slowly into the chamber after PC had been poured in. Then, compression molding was used to prepare specimens for Izod impact test. It should be mentioned that all counterparts of the PC/PDMS blends were prepared under the same procedure.

In this paper, blends are denoted as PC/PDMSOH- x - y , where x and y represent the viscosity and content of PDMSOH in this blend, respectively. For example, PC/PDMSOH-750-1% represents the sample containing 1 wt% PDMSOH and its corresponding viscosity is 750 mm²/s.

Characterization

Impact toughness of the blends under different temperatures

The samples were prepared by a compression molding device (KT-0701, Kangte Technology Co. Ltd, Beijing, China) at 280 °C with a pressure of 10 MPa for 3 min. Dimension of the specimen was 50 mm × 10 mm × 4 mm (length × wide × thickness). Notched Izod impact toughness of the specimens was measured with a VJ-40 Izod machine according to ASTM D256-04. Before measurements, a 45° V-shaped notch was made (depth 2 mm, thickness 4 mm), and the notch was 3 cm away from one end of the specimen. Before the test, the specimens were kept in a constant temperature container at −40 °C, −10 °C and 23 °C respectively for 2 h, and then immediately subjected to impact. Five specimens of each blend were tested.

Determination of the formation of PC-co-PDMSOH copolymer

Ultraviolet spectrophotometric (UV) analysis was performed on a UV-1800PC spectrophotometer (Shanghai Mapada Instrument Co. Ltd., China) to detect the reaction between PC and PDMSOH during melt blending. PC homopolymer, PDMSOH-750 homopolymer and the PC/PDMSOH-750-20% blend were dissolved in methylene dichloride at 23 °C for testing. In addition, a mixture of 80 wt% PC and 20 wt% PDMSOH-750 homopolymer was prepared through solution mixing using methylene dichloride as the solvent at 23 °C for reference. The samples were tested under the wavelengths of 200–350 nm in a quartz container at 23 °C.

Morphology of the PC/PDMSOH blends

Cryo-fractured surface of the impact sample was characterized to observe the morphology of the PC/PDMSOH blends by using a scanning electron microscope (SEM, Inspect F, FEI Company, USA) under an acceleration voltage of 20 kV. The samples were coated with a thin layer of gold.

Tensile properties of the PC/PDMSOH blends

The specimens for the mechanical property testing were prepared by mini-injection molding of the internal mixed samples at 240 °C and standard tensile tests were performed using an SANS universal tensile testing machine with a crosshead speed of 50 mm/min. 5 specimens for each blend were tested.

Contact angles of PDMSOH and PC

Contact angles were measured in a sessile drop mold with KRUSS DSA100. PC samples for contact angle measurements were compression molded at 280 °C under 10 MPa pressure for 5 min then cooled to 23 °C, and the PDMSOH samples were made by dropping siloxane liquids evenly on glass slides. Contact angles were measured with 3 mL of wetting solvent at 23 °C, and the results reported were the mean values of 3 replicates. The surface tensions, dispersion and polar components of surface tension of these samples can also be obtained from contact angle measurements.

RESULTS AND DISCUSSION

Impact Toughness of the Blends

In this study, blends containing 0.05–5 wt% PDMSOH are prepared, and in all cases the siloxane is fully incorporated into the blend based on the phenomenon that there is no siloxane oil effused the chamber of the mixer once the mixing process is suspended and the chamber is opened. Figure 1 shows the notched Izod impact toughness of PC/PDMSOH blends with diverse viscosities and contents of PDMSOH at three temperatures,

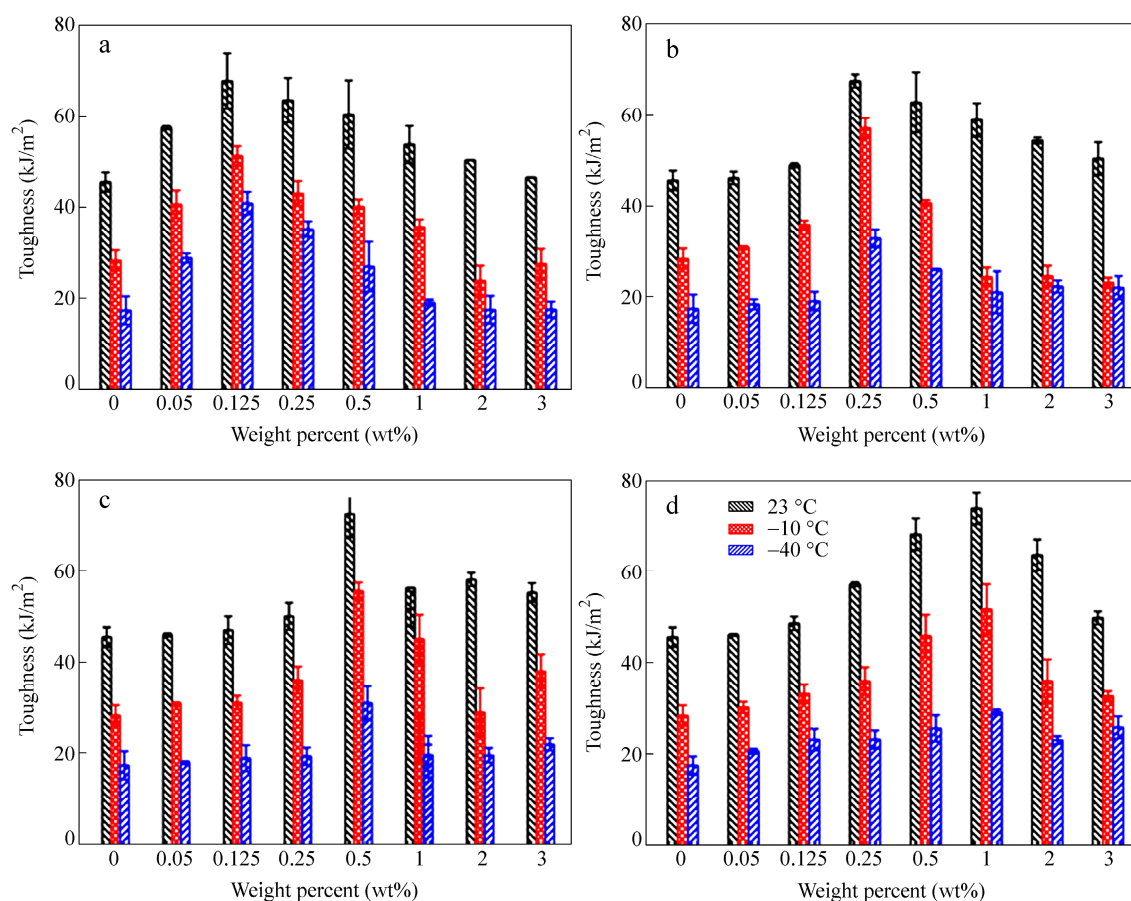


Fig. 1 Notched Izod impact toughness of the PC/PDMSOH blends at three different temperatures, 23 °C, -10 °C and -40 °C. The viscosities of PDMSOH added into the blends are (a) 750 mm²/s, (b) 5000 mm²/s, (c) 20000 mm²/s and (d) 80000 mm²/s

23 °C, -10 °C and -40 °C. It is obvious that the impact toughness behavior of these blends is similar regardless of the variety of the adding PDMSOH, thus PC/PDMSOH-80000 blend is taken as an example to discuss the results. As observed in Fig. 1(d), the addition of PDMSOH-80000 in PC results in enhance toughness, irrespective of the exerted temperature, a peak which represents the highest toughness point of these blends is observed, in this case, adding 1 wt% PDMSOH-80000 in PC leads to the toughest blend in this system. At ambient temperature (23 °C), the impact toughness of PC/PDMSOH-80000-1% is 73.8 kJ/m², which is 62% higher than that of pure PC whose impact toughness is 45.5 kJ/m²; the predominance of this blend is much more distinct when it comes to low temperature toughness, the impact toughness of pure PC is enhanced by 82% and 88% at -10 °C and -40 °C, respectively. The same toughening behavior can also be found in the other three systems according to Figs. 1(a)–1(c).

However, the highest toughness occur when the contents of PDMSOHs are 0.125 wt%, 0.25 wt%, and 0.5 wt% for PC/PDMSOH-750, PC/PDMSOH-5000 and PC/PDMSOH-20000 blends; the required content of PDMSOH in the toughest PC/PDMSOH blend increases with the increment of the viscosity of PDMSOH. The toughening effect is most prominent in PC/PDMSOH-750 blends. At -10 °C, the impact toughness of PC/PDMSOH blend containing 0.125 wt% PDMSOH-750 is 51 kJ/m², which is even 5.7 kJ/m² higher than that of pure PC at 23 °C, not to mention the 82% excess at -10 °C. Even more intriguingly, the toughness of PC/PDMSOH-750-0.125% at -40 °C surpasses that of pure PC by 135% at -40 °C, and it is even 43% tougher at -10 °C and almost equals to that of pure PC at 23 °C. This blend with only 0.125 wt% PDMSOH-750 demonstrates unmatched toughness by PC homopolymer at all the chosen temperatures, and this advantage cannot be reached by any kind of unreacted rubber particles^[24–27], which is surmised to be achieved through reaction between the carbonyl group of PC and the hydroxyl group of PDMSOH in PC/PDMSOH blends.

Identification of Reaction between PC and PDMSOH

In order to explain the toughening effect of PDMSOH in enhancing the impact toughness of PC, UV spectrophotometry was used to verify the reaction between PC and PDMSOH. As the approach of UV spectrophotometry is more sensitive than Fourier transform infrared spectrometry (FTIR) method for detecting organic compounds with conjugated structure in its molecular chain between wavelength of 200 nm and 350 nm^[28–32], a comparative study of such spectra is used to draw conclusions relating to the chemical linkage formed during the blending procedure. A model blend with 80 wt% PC and 20 wt% PDMSOH-750 was prepared at 240 °C for 5 min on the Haake mixer for this purpose. PDMSOH-750 was chosen over the other three PDMSOHs due to the highest concentration of reactive hydroxyl groups in this material. Besides, this blend composition was chosen to maximize the amount of interaction between PC and PDMSOH. In spite of PC homopolymer, PDMSOH-750 homopolymer and the PC/PDMSOH-750-20% blend, a reference sample undergoing no thermal blending process was examined; the sample was referred to as the unreacted PC+PDMSOH-750 mixture containing 80 wt% PC homopolymer and 20 wt% PDMSOH-750 homopolymer. As seen in Fig. 2, the spectrum of PC exhibits two peaks at 235 nm and 269 nm, and these two bands are attributed to the π - π^* transitions of the aromatic fragments^[29, 33]. No sign of reaction is observed, since the spectrum peak of the unreacted mixture of PC and PDMSOH-750 at 235 nm is the same as that of pure PC. However, as seen in Table 2, the fact that all the absorption peaks of PC/PDMSOH-750-20% blend move toward higher wavelengths indicates that the interaction between PC and PDMSOH exists. Thus, despite of the possibility of hydrogen bonding between these two materials, the red-shifts of the peaks illustrate that reaction indeed occurs between PC and PDMSOH-750 during the melt blending process. Therefore, due to the resemblance of the four PDMSOH chains, a conclusion can be made that reaction has taken place in the above mentioned PC/PDMSOH blends, that is, PC-co-PDMSOH copolymer has been produced during the blending procedure.

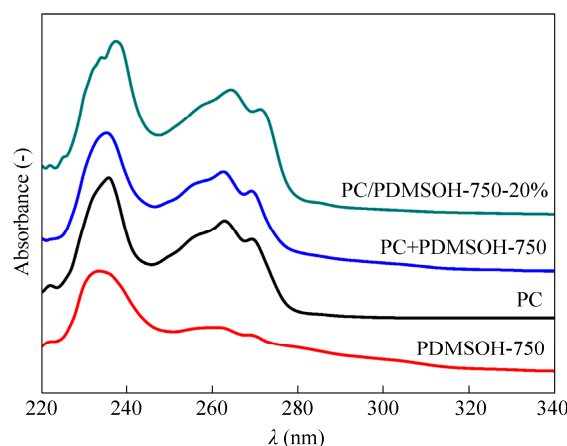


Fig. 2 Evolution of the UV spectra of PC homopolymer, PDMSOH-750 homopolymer, unreacted PC+20% PDMSOH-750 mixture and reacted PC/PDMSOH-750-20% blend

Table 2. Typical absorption peak wavelengths of the samples

Sample	$\lambda_{\max}$ (nm)			
PC	—	235.7	262.5	269.3
PDMSOH-750	233.2	—	262.5	269.3
PC+PDMSOH-750 non-reacted	—	235.7	262.5	269.3
PC/PDMSOH-750-20% reacted	234	237.5	264.3	271.1

Toughening Mechanism in PC/PDMSOH Blends

In order to demonstrate the chemical linkage produced by the reaction dominates the toughening effect of PDMSOH for PC, a non-reactive normal PDMS was used to produce a counterpart for the investigation of the toughening effect. This PDMS cannot react with PC in the blending procedure and there is no copolymer generated in the system, in addition, the interfacial interaction between PC and PDMS can be ignored.

Initially, attention should be paid to the toughness of PC/PDMS blends in Fig. 3. As seen in this figure, PC can be toughened by the addition of PDMS-500 with the content of only 0.125 wt% at 23 °C, all the toughness of PC/PDMS-500 blends at −40 °C and −10 °C, instead of outreaching the initial toughness of PC homopolymer, is much lower than that of PC homopolymer. Based on this result, it is justified to conclude that the PC-*co*-PDMSOH copolymer does play an important role in the toughening of PC at low temperatures.

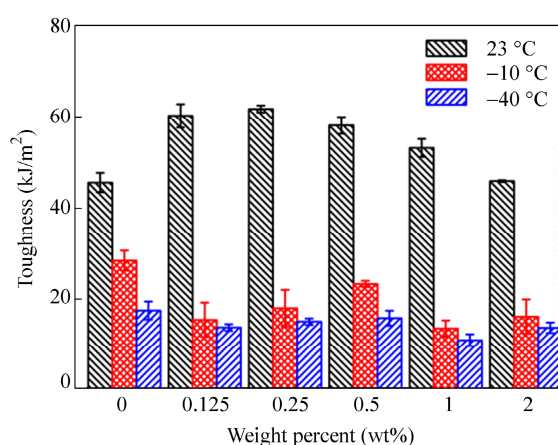


Fig. 3 Notched Izod impact toughness of the PC/PDMS-500 blends at different temperatures as a function of PDMS-500 content

Since the morphology of PC/PDMS-500 and PC/PDMSOH-750 blends shows approximately the same appearance according to Figs. S1 and S2 in Supporting Information, it can be ascertained that the toughening mechanism is dominated by the formation of PC-*co*-PDMSOH copolymer. The copolymer is believed to influence the low temperature toughness in the way that the low glass transition temperature of PDMSOH results in low temperature ductility of the whole PC/PDMSOH blends. Nevertheless, the amount of PDMSOH should be well managed since the redundant PDMSOH will induce phase separation, leading to decrement of toughness.

Comparison of Other Properties of the Four Toughest Blends and the Mechanism

Upon the confirmation of PC-*co*-PDMSOH copolymer produced in these systems, the analyses on the toughness data in Fig. 1 are more valid. Take PC/PDMSOH-750 for example, after incipient increase in toughness up to 0.125 wt% PDMSOH-750, there is no additional gain from adding PDMSOH-750, suggesting that there is a solubility limit for PDMSOH in the matrix. In the samples containing no more than 0.125 wt% PDMSOH-750, the maximum benefit from the generated copolymer is realized, and any additional loading after that point only adds phase-separated PDMSOH domains (see Fig. S1)^[7] which are detrimental to mechanical properties. Therefore, the optimum content of PDMSOH for PC/PDMSOH-750 is 0.125 wt%. It can also be concluded that the optimum concentrations of PDMSOHs are 0.25 wt%, 0.5 wt% and 1 wt% for PC/PDMSOH-5000, PC/PDMSOH-20000 and PC/PDMSOH-80000 blends respectively. According to the information of hydroxyl contents and molecular weights of these PDMSOHs, the molar quantitative relationships between PC and PDMSOHs in the toughest blends are calculated. Figure 4 shows that, no matter in which system, the carbonyl group contents of PC existed in the blends are approximately close to 8×10^{-6} mol, and the molar ratios of the carbonyl group of PC and hydroxyl group of PDMSOH are around 1:1. In that case, the reaction in Scheme 1 can be fully executed; a higher or lower ratio will not reach the perfect point of the toughness curve. Therefore, in future applications, it can be deduced that only one kind of PDMSOH is capable of toughening PC as the toughening result is just relevant to the molar ratio of the carbonyl group content of PC to the hydroxyl group content of PDMSOH. According to the available experimental results, it is speculated that PDMSOH-750 is the best reagent amongst the four chosen materials to toughen PC, since the dosage is the least, the appearance of PC/PDMSOH-750-0.125% is the clearest and the impact toughness of this blend is superb. However, it is essential to assess other properties of the four toughest blends in full scope to make a final recommendation to the industrial application.

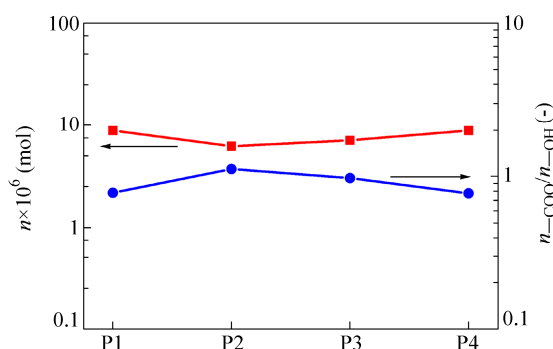


Fig. 4 The molar weights of the carbonyl group of PC (n) and the molar ratios of the carbonyl group of PC and the hydroxyl group of PDMSOH ($n_{\text{-COO}}/n_{\text{-OH}}$) in the toughest PC/PDMSOH blends. The horizontal ordinate represents the four toughest blends of P1 (PC/PDMSOH-750-0.125%), P2 (PC/PDMSOH-5000-0.25%), P3 (PC/PDMSOH-20000-0.5%) and P4 (PC/PDMSOH-80000-1%).

Figure 5 shows the comparison of mechanical properties of the four toughest blends. As seen in Fig. 5(a), the toughness of the four blends is almost the same at both 23 °C and -10 °C, and the equal chemical linkage in the above systems is believed to be the reason and it can also explain the identical thermal stability enhancement shown in Supporting Information (Fig. S3). More importantly, it should be mentioned that the toughness of the

blends at 23 °C were around 70 kJ/m², which were so high that the specimens were not completely fractured during the experiment, thus the data were not accurate. However, the toughness at −40 °C were much lower than those at 23 °C, and the results shown in Fig. 5(a) were more reliable. Therefore, in the discussion of this part, the difference of the toughness at 23 °C was not emphasized, yet it is noticeable that P1 has higher toughness than the other three blends at −40 °C. It is believed that since the molar weight of PDMSOH increases as the viscosity of PDMSOH enhances, the PDMSOH domain size and quantity in the matrix are increased and the phase separation between PDMSOH and PC is fortified. Figure 6 shows the fractured surface of the four toughest blends' impact specimen. The siloxane oil droplets are dispersed in the continuous phase of PC. The degree of phase separation and the number and size of droplets increase as the PDMSOH content is increased. As seen in Fig. 6, the domain size of PDMSOH-750 in P1 is the smallest among all the blends, and the phase separation between PDMSOH-750 and the matrix is the weakest. The influence of the different domain sizes and various phase separation extents are discussed in the following part.

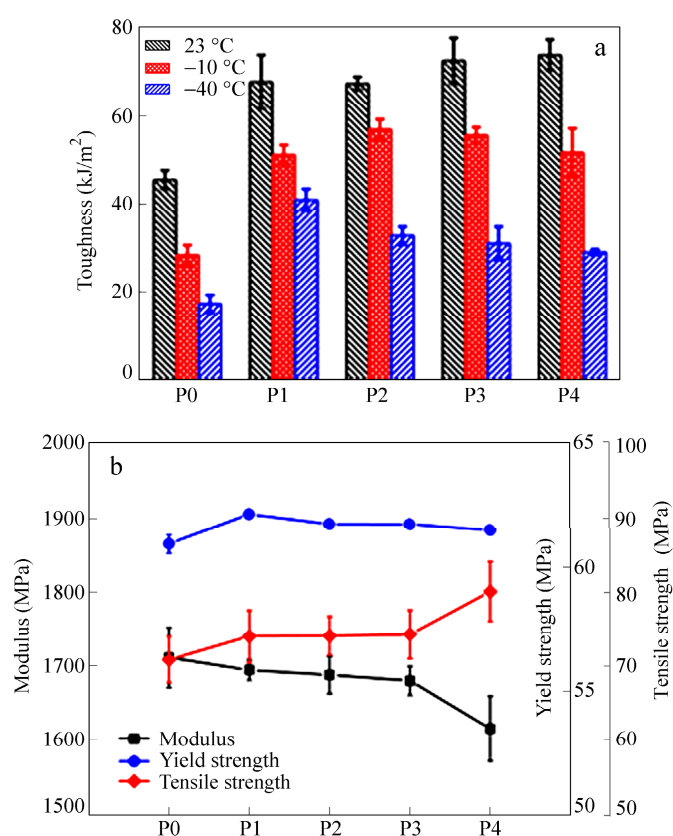


Fig. 5 Comparison of the impact toughness (a) and tensile properties (b) of P0 (PC) and the four toughest blends P1, P2, P3 and P4

Tensile property is another vital parameter to evaluate a material as it determines whether it could be used in a special application or not, thus, tensile tests of the four toughest blends were conducted. Figure 5(b) shows the tensile properties of these blends and it is revealed that the addition of PDMSOH can, on one hand, improve the tensile strength and yield strength of PC, and on the other hand, deteriorate the modulus of PC. The resultant strong chemical linkage between PDMSOH and PC formed during the reactive blending process is supposed to be responsible to the tensile and yield strengths increment in this system, yet the lessening of the modulus is due to the introduction of the softer molecular chain, PDMSOH, to the rigid PC chain. As for P1, the fact that the yield strength and modulus are the highest compared with others demonstrates that P1 has the best resistance to

deformation. As for P4, although the addition of PDMSOH-80000 can improve the tensile strength of PC, the modulus reduced sharply, meaning that this material is easy to deform, which is fatal to an engineering plastic. Thus, PDMSOH-750 is a better modifier for PC.

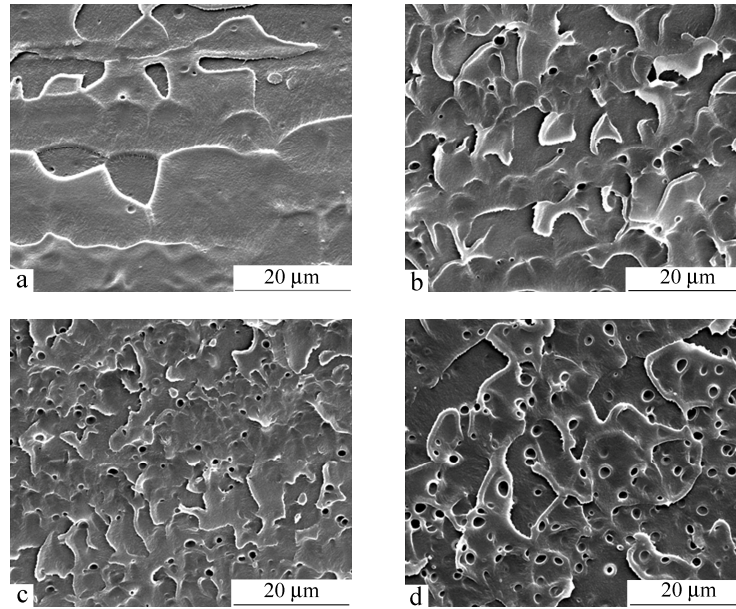


Fig. 6 Cryo-fractured surfaces of the impact specimens: (a) P1, (b) P2, (c) P3 and (d) P4

To investigate the underlying mechanism for the different deformation behaviors of the blends observed above, interfacial interaction between matrix and PDMSOH should be further studied due to its crucial role. The magnitude of the adhesion between matrix and PDMSOH in the blends can be characterized by the thermodynamic work of adhesion (W_{AB}). Contact angle measurements are used as a tool to calculate the thermodynamic work of adhesion between PC and PDMSOH. In fact, the quantity of the formed PC-*co*-PDMSOH copolymer is the same in the four blends (P1, P2, P3 and P4) based on Fig. 4, and the amount is rather little that it is believed that the appearance of this copolymer would not influence most of the interfaces between PC and PDMSOH. Therefore, Eqs. (1) and (2) are used to predict the interaction between PC and different PDMSOHs before the melt blending when the copolymer has not even been generated. The contact angles with water and diiodomethane are listed in Table 3. Then, the surface tension, dispersion and polar components of the materials can be estimated from the contact angle data by using the following equations (Eq. (1) for water and Eq. (2) for diiodomethane) according to Wu^[34]:

$$(1 + \cos \theta_{\text{H}_2\text{O}}) \gamma_{\text{H}_2\text{O}} = 4 \left(\frac{\gamma_{\text{H}_2\text{O}}^{\text{d}} \gamma^{\text{d}}}{\gamma_{\text{H}_2\text{O}}^{\text{d}} + \gamma^{\text{d}}} + \frac{\gamma_{\text{H}_2\text{O}}^{\text{p}} \gamma^{\text{p}}}{\gamma_{\text{H}_2\text{O}}^{\text{p}} + \gamma^{\text{p}}} \right) \quad (1)$$

$$(1 + \cos \theta_{\text{CH}_2\text{I}_2}) \gamma_{\text{CH}_2\text{I}_2} = 4 \left(\frac{\gamma_{\text{CH}_2\text{I}_2}^{\text{d}} \gamma^{\text{d}}}{\gamma_{\text{CH}_2\text{I}_2}^{\text{d}} + \gamma^{\text{d}}} + \frac{\gamma_{\text{CH}_2\text{I}_2}^{\text{p}} \gamma^{\text{p}}}{\gamma_{\text{CH}_2\text{I}_2}^{\text{p}} + \gamma^{\text{p}}} \right) \quad (2)$$

in which $\gamma = \gamma^{\text{d}} + \gamma^{\text{p}}$, $\gamma_{\text{H}_2\text{O}} = \gamma_{\text{H}_2\text{O}}^{\text{d}} + \gamma_{\text{H}_2\text{O}}^{\text{p}}$, $\gamma_{\text{CH}_2\text{I}_2} = \gamma_{\text{CH}_2\text{I}_2}^{\text{d}} + \gamma_{\text{CH}_2\text{I}_2}^{\text{p}}$, γ is surface tension, d is dispersion component and p is polar component, $\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{CH}_2\text{I}_2}$ are contact angles of the polymers with water and diiodomethane, respectively. The numerical values used are $\gamma_{\text{H}_2\text{O}}^{\text{d}} = 22.1$ mN/m, $\gamma_{\text{H}_2\text{O}}^{\text{p}} = 50.7$ mN/m, $\gamma_{\text{CH}_2\text{I}_2}^{\text{d}} = 44.1$ mN/m, $\gamma_{\text{CH}_2\text{I}_2}^{\text{p}} = 6.7$ mN/m. The values of surface tension, dispersion and polar components are also listed in Table 3.

Table 3. Contact angle and surface tension results of PC and PDMSOH

Sample	Contact angle (°)		Surface tension (mN/m)		
	Water	Diiodomethane	Total (γ)	Dispersion component (γ^d)	Polar component (γ^p)
PC	86.0	34.5	45.90	39.92	5.98
PDMSOH-750	51.8	40.5	59.66	36.85	22.82
PDMSOH-5000	63.5	42.4	53.06	36.07	16.99
PDMSOH-20000	82.5	48.3	42.19	33.60	8.60
PDMSOH-80000	92.4	52.9	36.70	31.73	4.97

Then, the thermodynamic work of adhesion (W_{AB}) can be calculated using the following formula^[35]:

$$W_{AB} = 2(\gamma_A^d \gamma_B^d)^{1/2} + 2(\gamma_A^p \gamma_B^p)^{1/2} \quad (3)$$

where γ_A^d , γ_B^d are the dispersive parts of the surface tensions of components A, B; and γ_A^p , γ_B^p are the polar parts of the surface tensions of components A, B; W_{AB} is the work of adhesion between components A and B. Table 3 shows the surface tension coefficients of PC and PDMSOH. The calculated W_{AB} values of PC-PDMSOH-750, PC-PDMSOH-5000, PC-PDMSOH-20000 and PC-PDMSOH-80000 are 100.1 mN/m, 96.1 mN/m, 87.6 mN/m and 82.1 mN/m, respectively. The higher value of W_{AB} indicates the more forceful interaction between two components, thus such interface, as the one in PC/PDMSOH-750, is relatively stronger. The better adhesion between PC and PDMSOH-750, decided by the shorter molecular chain of PDMSOH-750 and relatively more chance of its hydroxyl groups to interact with the carboxyl groups of PC, subsequently realizes more efficient load transfer from PC to PDMSOH. As a result, blend of PC/PDMSOH-750 are hardly deformed under strain. On the contrary, PC/PDMSOH-80000 with weaker interface possesses less efficient load transfers, and thus the lower modulus.

Hereto, the reason for the superior low temperature toughness of P1 is sorted out. Apart from the equal chemical linkage produced by the reaction in the four blends, it is distinguished by the stronger interfacial interaction between PDMSOH-750 and the matrix, thus the impact stress can be efficiently transferred from the matrix to the modifier and higher toughness is obtained.

CONCLUSIONS

PC/PDMSOH blends with outstanding low temperature impact toughness were prepared by reactive blending of polycarbonate and hydroxyl-terminated polydimethylsiloxane. Four different viscous PDMSOHs were chosen to modify PC. Ultraviolet spectrophotometry confirmed the reaction between PC and PDMSOH. It was demonstrated that the PC-co-PDMSOH copolymer obtained during the blending procedure in the matrix resulted in much stronger chemical bonding between PC and PDMSOH, which played a dominant role in the toughening effect. Moreover, it shows that, in whichever system, the carbonyl group contents of PC existed in the blends are approximately the same, and the molar ratios of the carbonyl group of PC and hydroxyl group of PDMSOH are constantly around 1:1. The most intriguing result is that with the addition of only 0.125 wt% of PDMSOH-750 into the PC homopolymer, the impact toughness of the blend at -40°C can approximately meet the level of the PC homopolymer at 23°C . In order to give a comprehensive recommendation to the optimum choice of PDMSOH to toughen PC, comparison of the properties of the four toughest blends (PC/PDMSOH-750-0.125%, PC/PDMSOH-50-0.25%, PC/PDMSOH-20000-0.5% and PC/PDMSOH-80000-1%) was conducted, and it shows that PC/PDMSOH-750-0.125 has the clearest appearance, the highest low temperature toughness and the best resistance to deformation aside from the similar thermal stability as other blends. The underlying mechanism for this phenomenon is the different interfacial interaction between PDMSOH and PC, given that the chemical linkage is equal in the four blends. Therefore, in future applications, only one kind of PDMSOH can be chosen to toughen PC -- the one with the lowest viscosity and highest hydroxyl proportion in its molecular chain.

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