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Siloxane modification of polycarbonate for superior flow and impact toughness

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ABSTRACT

Reactive modification of polycarbonate (PC) with a small amount of ultra-high molecular weight polydimethylsiloxane (PDMS) provides an effective route to a novel blend polymer with superior flow and excellent impact toughness. Low temperature impact toughness for such a blend was found to be comparable to polycarbonate copolymers made by interfacial copolymerization of bisphenol A and specialty silicones with phosgene. Interestingly, the blend also showed strong shear thinning behavior and a viscosity that is almost an order of magnitude lower than the starting PC resin. Analysis of the blend composition and blend morphology revealed the presence of both PC–PDMS copolymer and ungrafted siloxane as a dispersed phase in the polycarbonate matrix. The PC–PDMS copolymer provides a compatibilization effect for the stable sub-micron blend morphology in an otherwise immiscible PC–PDMS blend system. Improvement of low temperature ductility (e.g., at −40 °C) by PDMS was thus made possible. The lubricating effect from siloxane and the possibility of fibrillation flow at high shear stress are suspected to be the main reasons for high flow characteristics of these blends.

1. Introduction

Polycarbonate (PC) and its blends are a unique class of engineering plastics. They have been widely used for consumer electronics molding applications such as cell phones, laptop computers, etc. The desire for more slim and sleek design of these consumer electronics demands a polycarbonate with both high flow and good impact toughness. Such a requirement is becoming increasingly difficult to meet by a regular polycarbonate as the high flow characteristics are only possible at relatively low molecular weight (e.g., <20,000 g/mol). At those molecular weights, polycarbonate does not possess adequate impact toughness at low temperature. As the current polymer producers become increasingly conservative towards developing and commercializing new polymers, modification of the existing polymers becomes an effective and perhaps the only economical route for achieving performance properties to meet ever demanding commercial application requirements.

Copolymers and blends of polycarbonate have been extensively studied in the last four decades. An excellent review for the progress of polycarbonate can be found in a recent monograph edited by LeGrand and Bendler [1]. One area that has drawn considerable amount of interest is the preparation and use of polycarbonate–polydimethylsiloxane block copolymers (PC-*co*-PDMS) [2–10]. Such a block copolymer is typically made by copolymerizing bisphenol A and specialty silicone of oligomers type with phosgene. They attempt to take advantage of the intrinsic properties of polydimethylsiloxane (PDMS) and polycarbonate polymers. Depending on the siloxane commoner content and block lengths [11,12], the properties of a PC-*co*-PDMS copolymer can be varied from a gum to an elastomer to a rigid thermoplastic resin. The general structure–property relationship of PC-*co*-PDMS copolymers has been studied in great details since late 1960s [11–25]. The strong microphase separation between siloxane blocks and polycarbonate blocks plays a governing role in the processing and properties of these copolymers. Examples of physical property improvement of polycarbonate through siloxane copolymerization include better low temperature impact, good weatherability, improved ignition resistance, better hydrolytic stability, and slowed aging, etc. In these copolymers, optical clarity of polycarbonate can generally be retained after siloxane copolymerization despite of the vastly different refractive indices between PC and PDMS.

Reactive modification of polycarbonate with a functionalized siloxane in the melt state provides another route to improve properties of polycarbonate. This approach attempts to make a PC-*co*-PDMS block copolymer in the melt state rather than through an interfacial copolymerization process. The first melt process chemistry of making PC-*co*-PDMS block copolymers dates back to the early 1990s. Carboxylic acid functionalized polydimethylsiloxane fluids were allowed to react with polycarbonate in the melt for production of a block copolymer [26]. Other specialty siloxanes that have been used to modify polycarbonate include alkyl amino

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terminated silicones [27], lactone–siloxane–lactone block copolymers [28,29], and hydroxyaryloxy terminated polydimethylsiloxane [30].

Similarly, there has also been work on exploiting the advantageous property of PDMS for processing by blending a polycarbonate with polyorganosiloxane [31], PC-*co*-PDMS block copolymer [32], Polysulphone (PSN)-*co*-PDMS block copolymers [33], or polycaprolactone (PCL)–PDMS–PCL triblock copolymer [34]. If the right catalyst is present in some of these blend systems, a melt transesterification reaction may occur between polycarbonate and PDMS block copolymers during the melt blending stage. However, these blends are fundamentally different from homogeneous PC-*co*-PDMS copolymers synthesized by either interfacial copolymerization or melt polymerization methods.

Despite a significant amount of progress made on the development of polycarbonate copolymers and blends, there remains a need to further understand and improve their structure–property balance, in particularly with respect to their rheological properties. In this paper, we present a simple approach of modifying bisphenol A polycarbonate by reactive blending a small amount of polydimethylsiloxane in the melt state. This work was inspired by an earlier study conducted by Beach and coworkers [31] and a polycarbonate blending study [34]. By promoting a transesterification reaction between polycarbonate and hydroxyl terminated polydimethylsiloxane, a resinous mixture of polycarbonate homopolymer, PC-*co*-PDMS block copolymer, and un-grafted PDMS homopolymer was produced. Such a blend material is much more complex than conventional PC-*co*-PDMS copolymers made through interfacial polymerization or melt polymerization. But interestingly, such PC–PDMS blends showed remarkably good low temperature impact toughness and excellent flow characteristics. They exhibit a strong shear thinning behavior that has not been observed in conventional PC-*co*-PDMS copolymers. The unique structure, processing, and properties behavior of a reactive PC–PDMS blend are the main subjects of the present study.

Comparison has also been made between reactive and non-reactive PC–PDMS blend systems. In the case of reactive modification, the blend forms a stable dispersion morphology with PDMS domains approximately 0.2–0.9 μm in size. On the contrary, macroscopic phase separation with the size of PDMS domains as large as 10 μm was observed for the non-reactive PC–PDMS blends. This is a direct result of immiscibility between PC and PDMS homopolymers, and not surprisingly, improvement in physical properties was not observed in the non-reactive PC–PDMS blends, highlighting the importance and necessity of reactive compatibilization that has long been recognized for immiscible blends [35].

2. Experimental

2.1. Materials

Raw materials used in this study and their basic characteristics are listed in Table 1. Bisphenol A polycarbonate (PC) resins were obtained from The Dow Chemical Company. Three general purpose polycarbonate grades CALIBRE[1] 200-3, 200-14 and 200-80 were used as received. They have a nominal melt flow rate (MFR) of 3, 14 and 80 g/10 min, respectively. In addition, one commercially available siloxane–bisphenol A polycarbonate copolymer LEXAN[2] EXL 1433 was also used in this study. The latter polycarbonate copolymer was manufactured by Sabic. It has a nominal melt flow rate of 10 g/10 min. These four materials will be denoted as PC-1, PC-2, PC-3 and PC-*co*-PDMS, respectively. In all cases, the melt flow rate refers to the mass flow rate (g/10 min) under the condition of 300 °C melt temperature and 1.2 kg of weight in accordance with American Standard and Testing Method (ASTM) D-1238.

Polydimethylsiloxane (PDMS) was obtained from Dow Corning (Midland, MI). Three PDMS materials (SGM-36, 4-7034 INT, and DC 200-A) were used in this study. Both SGM-36 and 4-7034 INT have ultra-high molecular weight and are in the form of a gum. Their viscosity at room temperature is around 15,000,000 cSt. DC 200-A is a silicone fluid of much lower viscosity at about 60,000 cSt. According to the product information from Dow Corning, SGM-36 and 4-7034 INT are identical except for a different end capping. The former is terminated with a hydroxyl group (–OH), whereas the latter material is end capped with $-Si(CH_3)_3$. The –OH content in SGM-36 was measured to be about 90–120 ppm level. The variability comes from the manufacturing lot-to-lot difference. It should also be mentioned that both types of silicone materials contain a detectable amount of potassium at the ppm level. The approximate amount of potassium in the form of KOH was measured to be about 50 ppm for both SGM-36 and 4-7034 INT. As will be shown in the later section, the combination of –OH group and potassium hydroxide in SGM-36 has a profound impact for morphology and properties when it is blended with polycarbonate.

2.2. PC–PDMS blends and preparation

PC–PDMS blends were prepared in two different ways. One blending method used a 50 mL Haake bowl mixer. The mixer was pre-heated to 280 °C and then polycarbonate and PDMS were added at a desirable weight ratio. The melt temperature of the PC and PDMS reached 280 °C after about of 2 ~ 3 min of mixing. This was typically followed by another 5–10 min of mixing. Small chunks of the blend were taken out the Haake bowl after 5 min and 10 min of mixing at 280 °C for analysis. Haake blending was used when only a small quantity of sample was needed or when there was no easy way of making PC–PDMS blends by other means.

PC–PDMS blends were also prepared by compounding varying amounts of PDMS into PC-1 or PC-2 materials using a 30 mm co-rotating twin-screw extruder. This approach allows sufficient quantity of blends to be made for injection molding parts needed for a detailed structure–property study. An experimental protocol was developed to directly compound siloxane gum (i.e., SGM-36 and 4-7034 INT) into polycarbonate. Silicone gums were first manually rolled into small balls of approximately 3–5 mm diameter and then dusted with finely ground polycarbonate powder. The amount of silicone used to make silicone balls and the final weight of silicone balls coated with polycarbonate powder were carefully weighed and then mixed with a proper amount of polycarbonate base resin before feeding into the twin-screw extruder. PC–PDMS blends coming out of the twin-screw extruder were pelletized and then re-extruded with a second pass to ensure homogeneous mixing of the blend and proper dispersion of PDMS into the polycarbonate matrix. This handling protocol provides an easy and accurate amount of silicone incorporation into polycarbonate resins for feeding and extrusion compounding.

A screw speed of approximately 350–400 rpm and feed rate of approximately 30–35 lb/h resulting in a torque level of about 70% of maximum was used for the preparation of twin-screw compounded blends. The temperature profile of the four processing zones is the following: Zone 1 (Feed) at 250 °C; Zones 2–5 (Die) at 290 °C. The melt temperature at the die exit was not measured, but it was noted that the melt zone temperature did not rise up during the preparation of PC–PDMS blends. A four-hole die was used with an open vent in Zone 4.

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[1] Trademark of The Dow Chemical Company.

[2] Trademark of General Electric.

Table 1
Composition and basic characteristics of materials investigated in this study.

Material code	Type of material	Melt flow rate (g/10 min)	M_w (g/mol)	M_w/M_n	Source
PC-1	Polycarbonate	3	36,950	2.81	Dow
PC-2	Polycarbonate	14	26,840	2.54	Dow
PC-3	Polycarbonate	80	17,800	2.6	Dow
PC-*co*-PDMS	Siloxane–PC copolymer (Lexan EXL 1433)	10	25,284	2.7	Sabic
SGM-36	PDMS (–OH terminated)	n/a	15 M cSt[a]	–	Dow Corning
4-7034 INT	PDMS (end capped)	n/a	15 M cSt[a]	–	Dow Corning
DC 200-A	PDMS (end capped)	n/a	60,000 cSt[a]	–	Dow Corning
PC–PDMS-1	PC-1/SGM-36 blend (95/5 by weight)	10	28,926	3	–
PC–PDMS-2	PC-2/4-7034 INT blend (95/5 by weight)	12	26,272	2.5	–

[a] Note: The kinematic viscosity of silicone at room temperature in the unit of centistokes (cSt) was reported by the manufacturer. Here, we use those viscosity values to indicated the relative molecular weight of three silicone materials used in this study. All the materials were used as received with no further purification or modification.

In addition to preparing various blends for structure–property study, two blends (PC–PDMS-1 and PC–PDMS-2) were studied in detail. The basic characteristics of these two blends were listed in Table 1. Both were made by twin-screw extrusion using the protocol described in the preceding paragraphs. PC–PDMS-1 was made by compounding 5 wt% of SGM-36 into a 3 MFR polycarbonate (PC-1), and PC–PDMS-2 was prepared by compounding 5 wt% of 4-7034 INT into a 14 MFR polycarbonate (PC-2). There two materials were chosen for the study because they have roughly the same melt flow rate.

2.3. Characterization methods

Molecular weight of polycarbonates and PC–PDMS blends was characterized by gel permeation chromatography (GPC) using a Agilent Model 1100 Liquid Chromatograph System equipped with a UV diode array detector. The detection wavelength is set at 264 nm. Solid samples were first dissolved in methylene chloride at an approximate concentration of 0.1 g/mL. The injection volume was 10 μL. The carrier solvent for the GPC system is tetrahydrofuran (THF) and the elution rate was 0.5 mL/min. GPC calibration was based on polystyrene equivalent standards of known molecular weight.

^{29}Si NMR spectra were collected using a Bruker 400 MHz spectrometer operating at approximately 100 MHz. Deuterated chloroform solvent (CDCl$_3$) was used to dissolve all polycarbonate samples for NMR analysis.

The flow properties of PC and PC–PDMS blends were measured using a parallel plate rheometer (ARES, TA Instrument) and a capillary rheometer (Keynes). In the parallel plate rheometer study, materials were first compression molded into 25 mm diameter disks of approximately 2 mm thickness before loading into the parallel plate rheometer. The gap thickness was kept constant at approximately 1.8 mm. Oscillatory shear viscosity curves were measured across a frequency range of 0.1–100 rad/s using a constant strain amplitude of 10% at 280 °C melt temperature. High shear rate viscosity curves of PCs and PC–PDMS blends were measured using a capillary rheometer equipped with a 1 mm diameter capillary die with $L/D = 20$. Data were collected for all materials in the shear rate range of $30-2 \times 10^4$ 1/s at 300 °C. All the rheological data obtained were Bagley corrected using a well known protocol [36].

Injection molded specimens fabricated on a Toyo 90 press were used for blend morphology and physical property characterizations. Pellets were dried for at least 4 h at 250 °F before injection molding. Melt temperature and mold temperature were held constant at about 550 °F and 180 °F, respectively. The back pressure was kept low between 50 and 100 psi and the screw speed was held at 20–100 rpm.

Transmission electron micrograph (TEM) specimens were taken from 4″ injection molded disks that were cryogenically sectioned with a diamond knife on a Leica UCT ultra microtome at −60 °C. The sections approximately 100 nm in thickness were placed on 400 mesh virgin copper grids and post-stained with the vapor phase of an aqueous 0.5% ruthenium tetraoxide solution for approximately 10 min. TEM images were collected on a JEOL JEM-1230 operated at 100 kV accelerating voltage and collected on Gatan-791 and 794 digital cameras. The images were post-processed using Adobe Photoshop 7.0.

Impact toughness was characterized using the notched Izod testing method in accordance to ASTM D-256 Method. Test specimens were cut out from the middle section of an injection molded tensile bars. These specimens were then notched using a 10 mil radius notcher, followed by a sample equilibration time of at least 48 h prior to testing. Notched Izod toughness values were obtained at both room temperature and sub-ambient conditions.

3. Results and discussion

3.1. Evidence for reaction between PDMS and polycarbonate

The possibility of a reaction between polydimethylsiloxane and polycarbonate was discovered by accident in an attempt to find an economical route to make high flow and good impact resistant polycarbonates. Fig. 1 compares the oscillatory shear viscosity curve of the PC–PDMS-1 blend with those of its blend components. The blend viscosity is significantly lower than the base polycarbonate resin (PC-1) with this drop in viscosity being larger than would be expected from classical rheology of immiscible blends [37]. Further study revealed that the molecular weight of polycarbonate in the

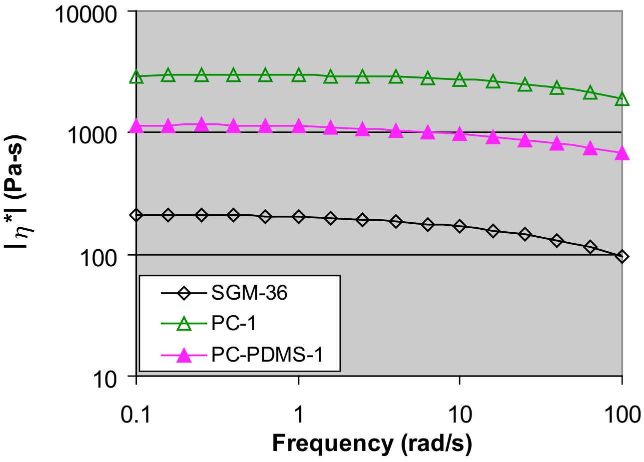

Fig. 1. Oscillatory shear viscosity of PC–PDMS-1, PC-1 and SGM-36 silicone as a function of oscillatory shear frequency at 280 °C.

PC–PDMS-1 blend was lower than the base resin PC-1. A lower molecular weight is believed to account for part of the overall viscosity reduction observed in our experiments.

A further study was conducted to investigate the effect of SGM-36 silicone on the molecular weight reduction of polycarbonate after extrusion compounding. By simply mixing a small amount of SGM-36 into PC-1 resin, a systematic reduction in both M_w and M_n of polycarbonate was observed. Detailed results are shown in Fig. 2. At 10 wt% of silicone (the highest concentration explored in this study) the weight average molecular weight (M_w) reduced from ca. 37,000 g/mol to 20,000 g/mol. Similarly, the number average molecular weight (M_n) dropped from 13,200 g/mol to about 7400 g/mol. Both observations indicate the possibility of a chain scission reaction occurring on polycarbonate with the addition of SGM-36 in the melt state.

To better understand the mechanism for the molecular weight degradation of polycarbonate in the presence of SGM-36, another set of experiments was conducted by adding a different silicone material 4-7034 INT. This silicone material is almost identical to SGM-36 but is end capped with a trimethylsilyl group instead of a hydroxyl group. Measures of M_w and M_n for a series of PC-1/4-7034 INT blends are shown in Fig. 3. Interestingly, no measurable change in either M_w or M_n for the entire series of blends was detected. In yet another set of blends, an additional amount of potassium hydroxide (KOH) at about 100 ppm was added into the blends of PC/4-7034 INT. KOH can function as a transesterification catalyst for polycarbonate, but again no considerable change in molecular weight of polycarbonate was observed. These results suggest that no transesterification reaction occurs between polycarbonate and $-Si(CH_3)_3$ terminated polydimethylsiloxane.

The drastically different behavior exhibited by these two PC–PDMS blend systems suggests the molecular weight degradation of polycarbonate in the PC-1/SGM-36 blend was not caused by trace chemistry in the silicone materials. Instead, the hydroxyl end group of SGM-36 must have played a role in reacting with polycarbonate molecules, whereas the trimethylsilyl group of 4-7034 INT was inert and non-reactive. Analysis of both silicones revealed the presence of KOH at about 50 ppm. It is well known that the combination of base and –OH group can lead to transesterification reactions in a polycarbonate melt. A probable reaction scheme between PC and PDMS is proposed in Fig. 4, showing that the –OH terminal group on SGM-36 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. As common to other transesterification processes, the reaction between PC and PDMS would also result in chain scission and molecular weight reduction of polycarbonate backbone. This mechanism would explain the observed molecular weight degradation shown in Fig. 2. One by-product for the proposed reaction is the formation of CO_2. Indeed, gaseous CO_2 was detected during the extrusion compounding of PC-1 and SGM-36 at the extruder vent (i.e., Zone 4). This provides indirect evidence for the proposed reaction scheme.

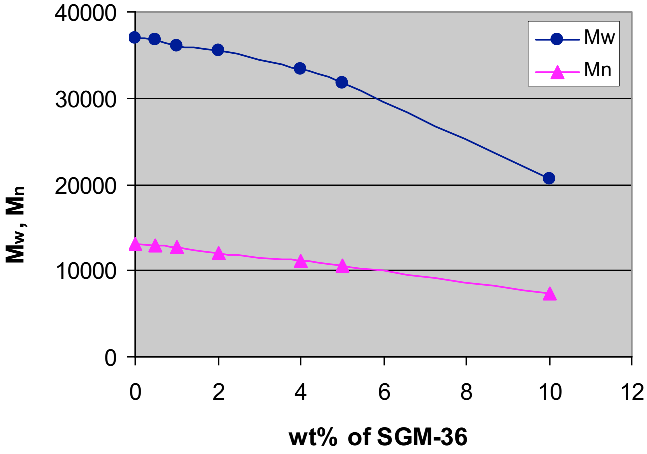

Fig. 2. Molecular weight of polycarbonate (M_w and M_n) versus the amount of SGM-36 silicone in a series of PC-1/SGM-36 blends. This set of materials was prepared by one extrusion pass in a twin-screw extruder at about 290 °C.

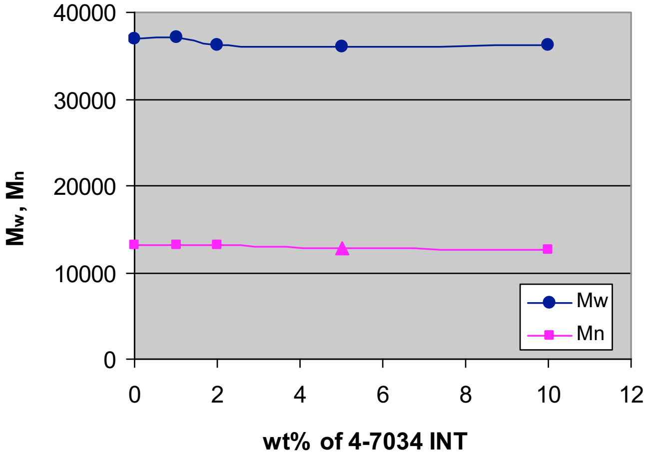

Fig. 3. Molecular weight of polycarbonate (M_w and M_n) versus the amount of 4-7034 INT silicone in a series of PC-1/4-7034 INT blends. This set of materials was prepared by one extrusion pass in a twin-screw extruder at about 290 °C.

^{29}Si NMR experiments were conducted to generate further evidence for the formation of PC–PDMS block copolymer and the bonding between polycarbonate and polydimethylsiloxane. A model blend with 50 wt% of PC-1 and 50 wt% of SGM-36 was prepared on a Haake bowl mixer for this purpose. This blend composition was chosen to maximize the amount of bonding between PC and PDMS since the concentration of reactive groups on SGM-36 is quite low in the PC–PDMS-1 blend material. Fig. 5 compares the NMR spectra of the 50/50 PC-1/SGM-36 blend (a) with SGM-36 itself (b). It is noted that the chemical shift corresponding to silicone atoms in the main backbone of PDMS dominates both NMR spectra. In order to extract the information on the chemical structure of the terminal groups attached to siloxane, the spectra have to be scaled up. Fig. 5a and b was scaled up by a different factor to qualitatively highlight their compositional difference.

Comparing the chemical shifts between the blend and SGM-36, one can see a new chemical shift in the range of −13 to −14 ppm. This can be attributed to the formation of bisphenol A–O–Si bonds [4,24]. In addition, a new chemical shift at approximately −5.3 ppm is observed in the blend, while at the same time a sharp chemical shift at approximately −19 ppm disappeared from the original silicone SGM-36 (Fig. 5a and b). It is unclear whether the occurrence and disappearance of these two chemical shifts, respectively, are related or not. Furthermore, the chemical shift corresponding to the silicone attached to the terminal hydroxyl group ($\delta \approx -11$ ppm) did not completely go away in the blend, suggesting the transesterification between PC and PDMS did not proceed to 100% completion.

3.2. Morphology of PC–PDMS blends

Irrespective of whether there is a reaction between PC and PDMS, both PC/SGM-36 and PC/4-7034 INT blend systems were

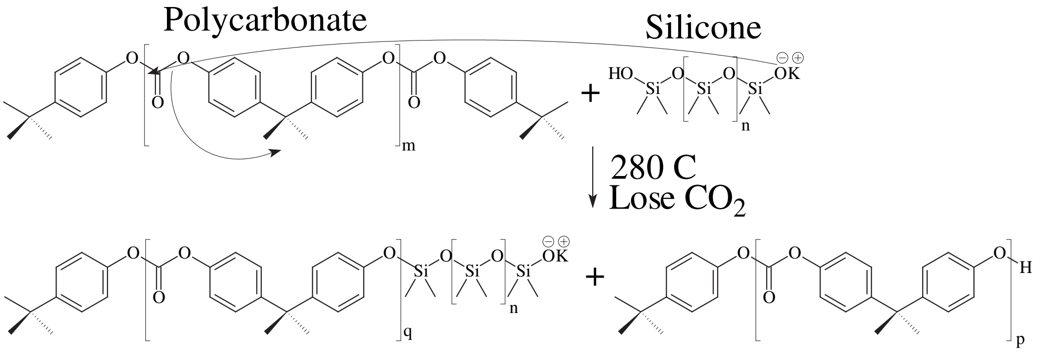

Fig. 4. A proposed reaction scheme between PDMS and Polycarbonate during melt extrusion compounding.

found to be opaque. This is true even at the lowest amount of siloxane loading studied here (i.e., 0.5 wt%). TEM morphology of two PC–PDMS blends prepared by twin-screw extrusion compounding, PC–PDMS-1 and PC–PDMS-2, are presented in Fig. 6a and b, respectively. In the case of PC–PDMS-1, SGM-36 silicone material was found to be well dispersed in the polycarbonate major phase forming small spherical domains with the domain size of about 0.2–0.9 μm (Fig. 6a). In contrast, the PC–PDMS-2 blend which was prepared by adding a non-reactive siloxane 4-7034 INT into a polycarbonate base resin PC-2, showed a much poorer dispersion of siloxane (Fig. 6b) with the silicone domains exhibiting elongated cigar shapes with a length scale of 15–20 μm. Clear evidence of significant siloxane domain pull out during microtome sectioning of this material at the cryogenic condition was given by the observation of a multitude of voids in the specimen. White regions in TEM micrographs correspond to those voids. It should be noted that some degree of siloxane pull out was also observed in PC–PDMS-1 blend, but at a much lesser degree.

The striking difference in blend morphology between PC–PDMS-1 and PC–PDMS-2 indicates a clear benefit of reactive compatibilization via the transesterification between PC and PDMS in an otherwise immiscible blend. The large amount of siloxane pull out in Fig. 6b also suggests a rather weak interfacial adhesion between PC and the non-reactive siloxane 4-7034 INT domains, as expected. On the contrary, the formation of PC–PDMS block copolymer in the PC–PDMS-1 blend not only stabilizes the dispersion morphology, but may have also improved the interfacial adhesion as a result of the covalent bonding between PC and SGM-36.

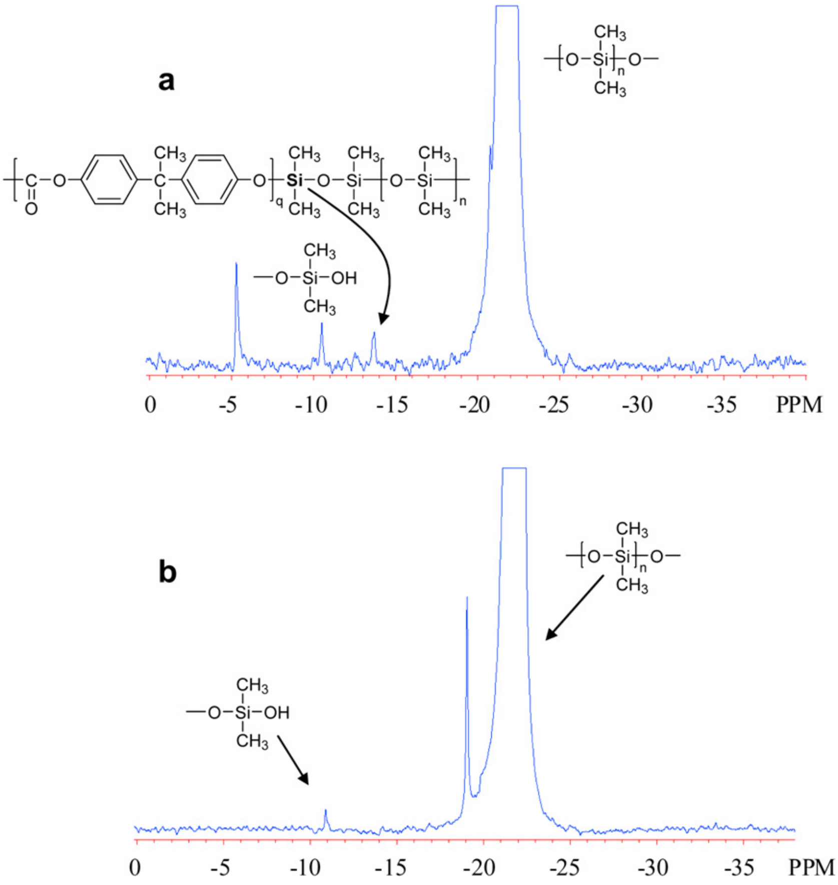

Fig. 5. ^{29}Si NMR spectra showing the evidence of PC–PDMS copolymer formation: (a) the 50/50 blend of PC-1/SGM-36; (b) SGM-36.

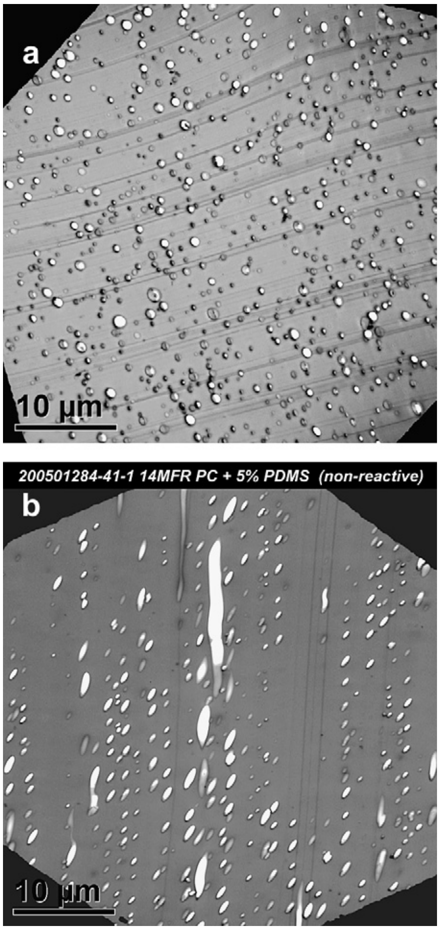

Fig. 6. TEM morphology of PC–PDMS-1 (a) and PC–PDMS-2 (b) showing the dispersion of SGM-36 and 4-7034 INT in polycarbonate: white regions corresponding to the pull out of siloxane materials from the polycarbonate matrix phase during the microtome of sample specimens.

It is also worthy to discuss the effect of mixing on the average particle size of PDMS domains in these two blend systems. At a first glance, the difference in the average particle size in PC–PDMS-1 and PC–PDMS-2 may be attributed to the difference in viscosity mismatch between the PC base resin and the PDMS for the two blend systems. However, this turns out not to be the case. The viscosity ratio between PC and PDMS is greater than 1 for both blends. The disparity in the viscosity between the base polycarbonate and the PDMS is actually larger for the PC–PDMS-1 blend components than it is for those of the PC–PDMS-2 but after melt blending, the viscosities of these two blends are quite similar. Thus, the viscosity ratio and mixing seem to be much less important than reactive compatibilization in setting siloxane domain size.

Aside from the obvious difference in morphology between the reactive and non-reactive PC–PDMS blend systems, further insights may be gained from the average particle size and the particle size distribution of the PC–PDMS-1 blend. If we assume all of the reactive PDMS (i.e., SGM-36) is covalently bonded to polycarbonate chains, the microphase separation of the PDMS would result in the formation of discrete spherical PDMS domains with more or less uniform particle size. The domain size would be strictly determined by the chain length of the SGM-36 polymer. However, as shown in Fig. 6a, this was not observed in our experiments. Particle size varied from about 0.2 to 0.9 μm. It is worthy noting here that the PDMS domain size observed in this work is significantly larger than what is typically observed in a microphase separated block copolymer system [38], which is in the range of 15–25 nm except for a few rare cases [39,40].

Based on classical block copolymer thermodynamics theory, the interfacial thickness (i.e., domain spacing) in the strong segregation limit (SSL) [41] is predicted to be given as follows:

$$d \sim \alpha \cdot N^{\frac{2}{3}} \chi^{\frac{1}{6}},$$

where α is the bond length of the repeating units, N is the degree of polymerization, and χ is the interaction parameter between the two blocks. The above equation applies to PC–PDMS block copolymer when $\chi N \rightarrow \infty$. This is readily satisfied for the system studied here where χ is approximately equal to 1 at 300 °K and the degree of polymerization for PDMS is about 5000. Using the SSL relationship, the maximum PDMS domain size is estimated to be only about 50 nm. This is nearly ten times smaller than the average particle size observed in the PC–PDMS-1 blend.

The larger than expected PDMS domain size for the reactive blend of SGM-36 and PC suggests the presence of free siloxane material in the final blend. Free siloxane in the PC–PDMS-1 blend may be phase-separated as a different domain from the PC matrix and PC–PDMS block copolymer. It may also swell into the PDMS domains of microphase separated PC–PDMS block copolymer, resulting in PDMS domains being larger than theoretically predicted. Both situations will lead to a broader size distribution of PDMS domains than the situation where all the PDMS molecules are covalently bonded to PC chains. Un-grafted siloxane in the blend can have an undesirable consequence in that they may migrate and phase coalescence into fewer but larger domains over the time. Several blending design approaches are conceivable to mitigate such an adverse effect, e.g., increase the grafting efficiency and the molecular weight of PDMS. In the particular case of PC–PDMS-1, there was no significant phase coalescence observed during a limited scope aging study. To further examine this possibility, another model material was prepared by melt compounding a non-reactive siloxane of low molecular weight with a polycarbonate resin (PC-2). TEM morphology of this model material is shown in Fig. 7. Indeed, very large PDMS domains were observed due to phase coalescence and macroscopic phase separation. Some of the domains were as large as 10 μm.

The presence of free siloxane in the PC–PDMS-1 blend could be due to several reasons. One source of free siloxane is due to the less than perfect covalent bonding/grafting of the PDMS molecules onto polycarbonate chains during the melt mixing. The other source

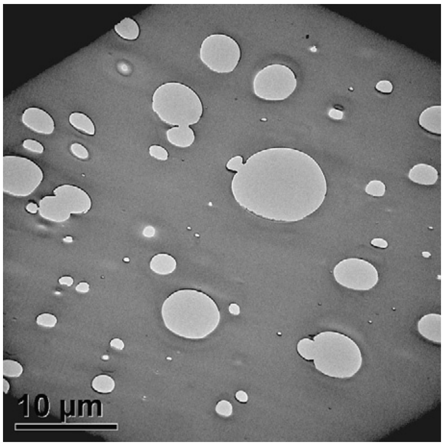

Fig. 7. TEM morphology of a PC–PDMS blend prepared from melt blending the PC-2 base resin with a non-reactive siloxane of low molecular weight at 5 wt%. The grade of siloxane used in this blend is DC 200-A (obtained from Dow Corning).

could be due to the instability of the Si—O—C bond formed between the —OH terminated siloxane and polycarbonate. There is a possibility that the Si—O—C bond might undergo a hydrolysis reaction after the PC—PDMS was reactively blended. Due to the low concentration of Si—O—C bonds in the blend, no attempt was made to quantify the grafting efficiency of PDMS.

It is important to point out that PC-*co*-PDMS copolymers made by interfacial copolymerization or melt polymerization (unlike the reactive PC—PDMS blends discussed in the preceding paragraphs) should not contain any free siloxane. For this reason the morphological behavior of PC-*co*-PDMS should follow rules governed by classical thermodynamic theory. This is indeed the case as shown from Tang and coworkers' earlier study [11,12] as well as the TEM morphology of a commercial PC-*co*-PDMS copolymer (Fig. 8). In both cases, only microphase separation of the PDMS chains at the nanometer scale occurs. Compared to a well defined lamellar morphology observed by Tang et al., the more or less spherical morphology observed in this commercial PC-*co*-PDMS copolymer (i.e., Sabic Lexan EXL 1433) is probably a result of the asymmetric chain length between PC blocks and PDMS blocks.

3.3. *Impact toughness of PC—PDMS blends*

The reactive blends of PC and PDMS showed interesting impact toughness behavior. Fig. 9 shows the comparison of notched Izod impact toughness for PC—PDMS-1, PC-*co*-PDMS copolymer, and polycarbonate homopolymer PC-2. These three materials have about the same molecular weight as characterized by GPC using a UV detector (Table 1). At both ambient condition and −20 °F, there is relatively little difference in ductility for these three materials. All have very high impact toughness with notched Izod values greater than 10 ft-lbs/in. However, as the temperature lowers to −40 °F, the regular polycarbonate PC-2 becomes brittle, whereas both the PC-*co*-PDMS copolymer and the PC—PDMS-1 blend still showed ductile failure during impact testing. The latter two materials were found to have superior impact toughness at temperature as low as −40 °F (Fig. 9), a significant improvement over regular polycarbonates. PC-*co*-PDMS copolymer exhibits a small gradual drop in notched Izod impact toughness with decreasing temperature. For the PC—PDMS-1 blend, there is hardly any influence of temperature on impact toughness. Compared to the PC-*co*-PDMS copolymer, the PC—PDMS-1 blend showed comparable and even slightly better notched Izod toughness at low temperatures (−20 °F and −40 °F) with the copolymer resin having a slightly higher notched Izod toughness value at room temperature. In both cases, the difference between the two materials is very minor and of little practical relevance in real applications.

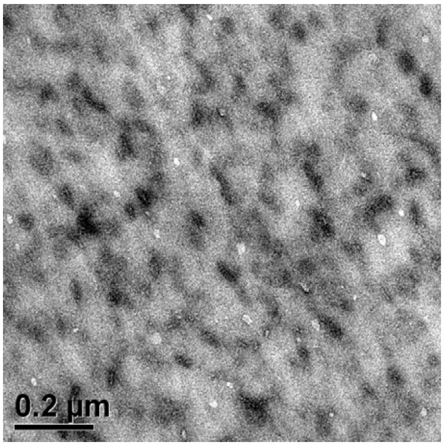

Fig. 8. TEM morphology of a commercial PC-*co*-PDMS copolymer Lexan EXL 1433 made by Sabic.

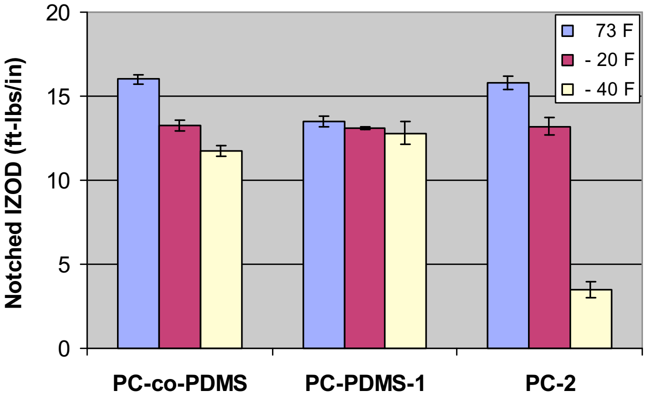

Fig. 9. Notched Izod impact toughness of three materials: PC-*co*-PDMS copolymer (Lexan EXL 1433), PC—PDMS reactive blend PC—PDMS-1, and polycarbonate homopolymer PC-2, at three different temperatures 73 °F, −20 °F and −40 °F. Error bars represent one sigma standard deviation of five independent measurements.

The non-reactive PC—PDMS blend prepared from the siloxane 4-7034 material (PC—PDMS-2) showed quite different impact behavior. The notched Izod impact toughness of PC—PDMS-2 at three temperatures is compared with those obtained from the reactive blend PC—PDMS-1 material in Fig. 10. Although there is not much difference regarding room temperature impact, PC—PDMS-2 exhibited much inferior impact properties than PC—PDMS-1 at sub-ambient conditions. In fact, there was no improvement at all in low temperature impact toughness for the non-reactive blend PC—PDMS-2 compared to the base polycarbonate resin. The poor impact toughness of PC—PDMS-2 is likely due to poor dispersion and weak interfacial adhesion between PC and PDMS phases, which is evident from the TEM morphology shown in Fig. 6b. On the other hand, the superior low temperature impact toughness of the PC—PDMS-1 blend highlights an advantage of reactive blending. The transesterification between PC and the reactive PDMS results in an in situ compatiblized blend that is otherwise immiscible.

The effect of PDMS rubber particle size on the impact property of PC—PDMS blends shown in Fig. 10 is worthy of some further discussion. A large number of studies have been conducted in the

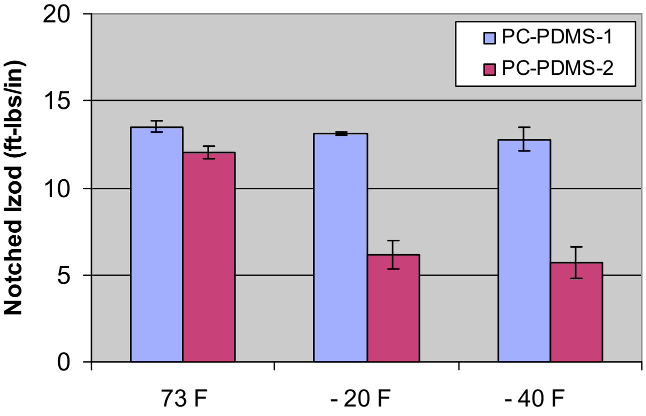

Fig. 10. Notched Izod impact toughness of two PC—PDMS blends at three different temperatures, 73 °F, −20 °F and −40 °F. PC—PDMS-1 is a blend of PC with a reactive siloxane SGM-36 and PC—PDMS-2 is a physical blend of PC with a non-reactive siloxane 4-7034 INT. Error bars represent one sigma standard deviation of five independent measurements.

past to address the rubber particle size dependence on impact toughening of glassy polymers [42]. When rubber particles are too small (e.g., <0.1 μm), they are either unable or ineffective to cavitate because the critical stress to induce cavitation may lie above the shear yield stress of the matrix polymer or the cavitation rate is too slow to extend throughout the entire gage length. In another extreme, when the particle size is too large (e.g., >1 μm), rubber particles cavitate and initiate crazes which then turn into propagating mciro-cracks and ultimately failures. Thus, the optimum size of rubber particles for impact toughening is believed to be in the range of 0.2–0.4 μm [42]. Looking at the particle size of PDMS in the reactive blend PC–PDMS-1 and non-reactive blend PC–PDMS-2 in Fig. 6a and b, respectively, it is clear that the reactive blending provides a near optimum dispersion of PDMS for good impact toughening, whereas the non-reactive blend contains large PDMS particles with a majority of them having a particle size at least 2∼3 μm in diameter. It is thus not surprising to see the inferior impact property of non-reactive PC–PDMS blend as shown in Fig. 10.

The effectiveness of using a reactive PDMS to improve the low temperature toughness of a polycarbonate as a function of PC molecular weight has also been examined. Fig. 11 shows the notched Izod impact toughness of blends prepared by extrusion compounding 5 wt% of SGM-36 into four different polycarbonate homopolymers. The molecular weight of polycarbonates after reactive blending ranged from about 14,500 to 30,000 g/mol. The notched Izod toughness of blends showed a strong dependence on the molecular weight of the polycarbonate matrix polymer. As the molecular weight of polycarbonate exceeds 20,000 g/mol, PC–PDMS blends are ductile at least down to −40 °F, suggesting that the critical polycarbonate molecular weight for the blend to be ductile is considerably lower than that for standard polycarbonates. However, for the blend with the lowest polycarbonate molecular weight (14,500 g/mol), its notched Izod toughness is only 2 ft-lbs/in at room temperature. This blend was found to be brittle throughout the entire temperature range. Thus, the base property of polycarbonate must be taken into account when designing a new PC–PDMS blend.

The mechanism for the enhanced ductility in the reactive blend of PC–PDMS is likely similar in nature to PC-*co*-PDMS copolymers made by interfacial copolymerization. In the case of a blend, the extremely low glass transition temperature of PDMS plus a well dispersed morphology provides an effective impact modification of the base polycarbonate, which lowers the ductile-to-brittle transition temperature (DBTT). In the case of a copolymer, the incorporation of siloxane into the polycarbonate backbone has been reported to decrease the DBTT of the polycarbonate [43,44]. At an extreme case, 25 wt% of siloxane incorporation can effectively decrease the DBTT to −110 °C [44]. Such remarkably low temperature ductility contrasts impressively with typical polycarbonate homopolymers with the lowest DBTT at around −20 °C.

3.4. *Rheological properties of PC–PDMS blends*

The use of silicone or silicone copolymers as processing aids for thermoplastic extrusion has been studied for various polymer systems [45,46]. According to Yilgor and coworkers, these additives have an effect on reducing the adhesion between the polymer and the barrel walls which improves flow of the molten polymer in the extruder barrel [45]. In this study, we found the incorporation of PDMS into polycarbonate also had a profound effect on the rheological properties of polycarbonate. The rheological behavior of PC–PDMS blends is not only different from polycarbonate homopolymer, but is also markedly different from PC-*co*-PDMS copolymers made by interfacial copolymerization.

Fig. 12 compares the flow curves of the reactive PC–PDMS blend PC–PDMS-1 to several polycarbonate homopolymers at 300 °C. The shear viscosity of the PC–PDMS-1 blend (containing 5 wt% SGM-36) showed a strong shear thinning behavior across the entire shear rate range studied. In comparison to the base polycarbonate resin (i.e., PC-1), the entire flow curve of PC–PDMS-1 is down shifted by more than half an order of magnitude (Fig. 12). This reduction in viscosity is partially due to the degraded molecular weight of polycarbonate base polymer. Another interesting comparison can be made between PC–PDMS-1 and PC-2. They have about same melt flow rate (Table 1), yet PC–PDMS-1 showed a substantially stronger degree of shear thinning than PC-2. In fact, the viscosity of PC–PDMS-1 at high shear rates (> ca. 5000 1/s) was found to be even lower than that of PC-3, a commercial polycarbonate with the highest melt flow rate currently available in the market place. These results indicate superior flow characteristics can be achieved by reactively modifying polycarbonate with PDMS.

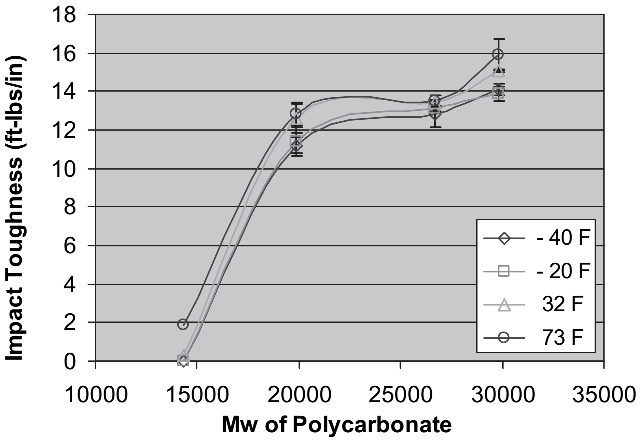

Fig. 11. Effect of polycarbonate molecular weight (M_w) on the impact toughness of PC–PDMS reactive blends at four different temperatures: −40 °F, −20 °F, 32 °F and 73 °F. All blends were reactive compounded with 5 wt% of SGM-36. The molecular weight of polycarbonate was characterized on the final injection molded specimens using GPC equipped with a UV detector. Error bars represent one sigma standard deviation of five independent measurements.

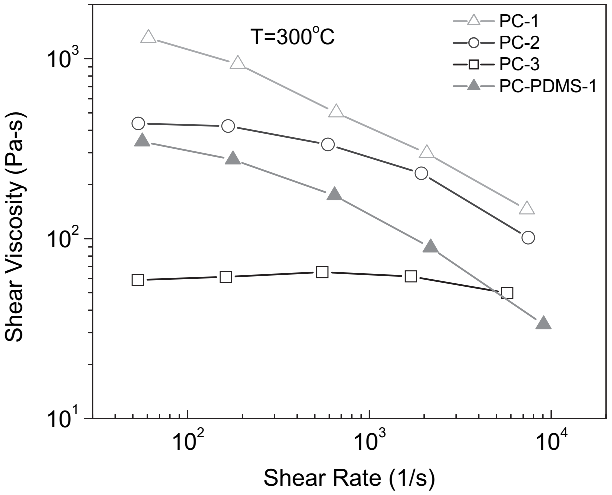

Fig. 12. Capillary shear viscosities of PC–PDMS-1 blend versus three different polycarbonate homopolymers, PC-1, PC-2 and PC-3. PC–PDMS-1 and PC-2 have about the same melt flow rate at 300 °C. All the viscosity measurements were carried out at 300 °C.

The relative degree of shear thinning exhibited by PC and PC–PDMS-1 blend is more evident from a flow curve when the shear viscosity is normalized to its zero shear viscosity. Fig. 13 shows the viscosity ratio at various shear rates with respect to the viscosity at the lowest shear rate accessible by the capillary rheometer for three polycarbonate homopolymers and PC–PDMS-1 blend. At the lowest molecular weight (PC-3), a nearly Newtonian behavior was observed. An increase of the molecular weight in polycarbonate leads to a systematic increase of shear thinning (PC-2 and PC-1), as expected. PC–PDMS-1 blend showed a strong degree of shear thinning that is approaching to the highest molecular weight polycarbonate (PC-1) despite of its relatively modest molecular weight (Table 1).

The viscosity curve of PC–PDMS-1 was also compared to that of PC-*co*-PDMS copolymer and the PC–PDMS-2 blend as measured at $T = 300$ °C (Fig. 14). The rheology of two PC–PDMS blends are nearly identical to each other, but differ considerably from that of PC-*co*-PDMS copolymer, despite the fact that they all have about the same melt flow rate and approximately the same amount of PDMS in their composition. Less pronounced shear thinning was observed in the PC-*co*-PDMS copolymer. Further study has shown that the flow curve of the PC-*co*-PDMS copolymer is very similar to a polycarbonate homopolymer of the same melt flow rate (e.g., PC-2), except that PC-*co*-PDMS copolymer displays about 10–15% reduction in viscosity. The similarity in the flow curves between PC-*co*-PDMS copolymer and polycarbonate homopolymer suggests that the minor improvement of flow for the PC-*co*-PDMS copolymer is likely due to its lower glass transition temperature. Since the monomeric friction coefficient is likely lower for polydimethylsiloxane than bisphenol A PC, an incorporation of siloxane in the backbone of PC-*co*-PDMS chain would presumably result in an improved flow as well.

The strong shear thinning exhibited by both PC–PDMS blends in Figs. 13 and 14 is intriguing at first. Various possibilities could account for the shear thinning of a polymer system. From molecular structural standpoint of view, molecular weight change, grafting or block copolymer formation, branching, etc., can all lead to a change in rheological characteristics. However, none of those are believed to be the cause for superior flow characteristics of PC–PDMS blends we observed here. First, in the case of PC–PDMS reactive blend, the reduction in molecular weight of polycarbonate is expected to result in less shear thinning. This is contrary to our observation. Secondly, the chain scission of PC seems to be a dominate mechanism during the reactive blending of PC and PDMS. There is no apparent mechanism for branching or grafting which is a common cause for shear thinning. Thirdly, the flow curves are nearly identical for the reactive PC–PDMS blend and the non-reactive PC–PDMS blend that have a matching molecular weight in the polycarbonate major phase (Fig. 14). This indirectly suggests the molecular structure change in the reactive PC–PDMS blend (e.g., block copolymer formation) is not a major cause for high degree of shear thinning. Instead, the presence of un-grafted or free PDMS phase is likely the main contributing factor for high flow rheology of these blends.

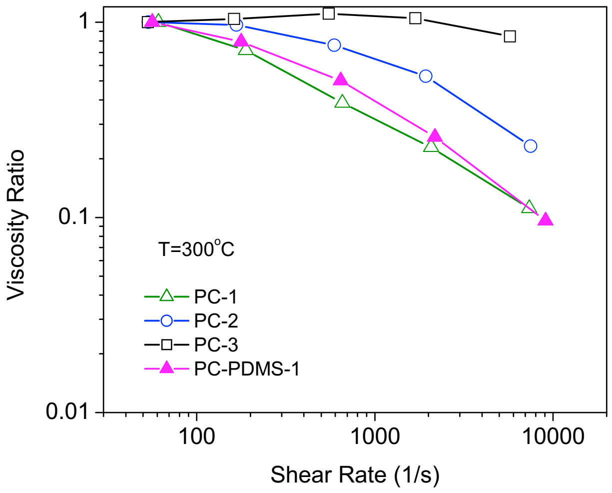

Fig. 13. Capillary shear viscosity normalized by the shear viscosity at the lowest shear rate accessible by the capillary rheometer which is at approximately 55 s^{-1}.

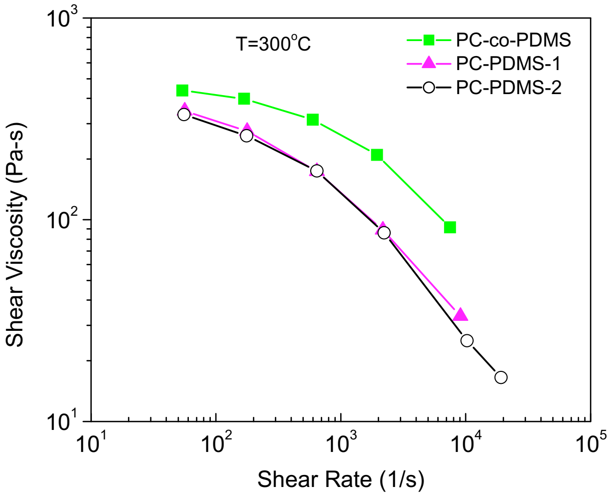

Fig. 14. Capillary shear viscosities of PC–PDMS-1 blend versus those of PC-*co*-PDMS copolymer and PC–PDMS-2 blend at 300 °C.

Additional studies suggested that the shear thinning of PC–PDMS blends may be partially due to a wall slippage effect as a result of the migration of un-grafted PDMS in both blends to the capillary die wall. Evidence of PDMS migration to the surface was confirmed from an XPS study. The Si/C ratio was measured to be at 0.14 for an injection molded specimen. This is more than two orders of magnitude higher than the Si/C ratio calculated for the bulk phase, which is only at 0.011. Migrated PDMS is suspected to form sheet- or fibril-like domains near the capillary walls in response to high shear at the wall. The formation of a sheet-like morphology was inferred from the pearlescent appearance of injection molded parts made from PC–PDMS blends. A pearlescent appearance is typically indicative of the distinct light scattering of sheet- or fibril-like domains near the surface.

Furthermore, PDMS materials have very low viscosities at the polycarbonate processing temperatures (e.g., 300 °C), so they can act as a lubricant to allow the polycarbonate chains to slide past each other easily. Thus, the polymer melts in the capillary rheometer should experience a lower shear stress either due to wall slippage or lubricating effect, leading to a much stronger degree of shear thinning than a regular polycarbonate homopolymer.

The findings from this study are generally consistent with other literature data in terms of better processing or easy flow due to siloxane modification [32,33]. A recent study by Pesetskii showed polycarbonate blends comprising a small amount of an interfacial copolymerized PC–PDMS block copolymer were much more sensitive to shear stress than the polycarbonate homopolymer itself [33]. At low shear stress, the blend has a higher viscosity than the polycarbonate homopolymer, however, at high shear stress, the blend was found to have a substantially lower viscosity than the polycarbonate homopolymer. The on stream cross-sections of the blend extrudate showed fibril structures at a high shear rate ($>1500\ \mathrm{s}^{-1}$). Pesetskii and coworkers suggested that the fibrillation in the flow of PC–PDMS/PC blends was responsible for the reduced viscosity at high shear rate. This mechanism would also explain the strong shear thinning exhibited by PC–PDMS blends of the present study.

4. Conclusion

PC–PDMS blends prepared by reactive blending of polycarbonate and hydroxyl terminated polydimethylsiloxane of ultra-high molecular weight show promise to be an interesting class of new materials with both high flow and low temperature impact toughness. The transesterification between PC and PDMS results in an in situ compatibilized blend that is otherwise immiscible. By properly tuning the molecular weight of polycarbonate base polymer, a remarkable improvement in low temperature impact toughness was found with just about 5 wt% of PDMS incorporation. The blend is able to maintain its superior impact toughness from room temperature down to as low as −40 °C with essentially no reduction in noticed Izod toughness at low temperature. The extremely low glass transition temperature of PDMS plus a well dispersed morphology in the matrix polycarbonate is suspected to have a very effective impact modification to the base polycarbonate material, which lowers the ductile-to-brittle transition temperature.

The reactive PC–PDMS blends also show high flow characteristics relative to both polycarbonate homopolymer and PC-*co*-PDMS copolymer made by interfacial copolymerization. A strong degree of shear thinning was observed in PC–PDMS blends. This is quite different from both regular polycarbonate and PC-*co*-PDMS materials. The presence of free siloxane and the formation of PC–PDMS copolymer from the transesterification process have contributed to the easy flow property of such blends. In particular, the lubricating effect and the possible formation of sheet- or fibril-like domains due to the co-existence of PDMS and PC–PDMS copolymer could substantially reduce the shear stress of polymer melt experienced at high shear rates, resulting in the unusual shear thinning observed in this study.

This study demonstrated an economical route of modifying polycarbonate with an improved processing-property balance over conventional polycarbonates, copolymers and blends. One should be able to extend the reactive blending approach discussed in this paper to other siloxane systems. As long as the siloxane has a reactive group that can transesterify with polycarbonate in the melt state but not significantly degrade the molecular weight of polycarbonate, similar results in impact toughness and flow characteristics may be expected. Nevertheless, a careful balance would have to be exercised between siloxane molecular weight, functional groups, loading amount, and catalyst type and amount, etc. Depending on the specific type of chemistry between PC and PDMS, there is a possibility for the presence of un-grafted siloxane in the final blends as shown in this study. No attempt was made to quantify the amount of free siloxane in the current system, but their effect on fabrication and long term physical properties will be worthy of further investigation.

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