Effect of Silicone Oil on the Morphology and Properties of Polycarbonate

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ABSTRACT: Two types of silicone oil, poly(dimethyldiphenyl siloxane) (PDMDPS) and poly(dimethyl siloxane) (PDMS), were added to polycarbonate (PC), and the morphological, mechanical, rheological, and thermal changes of the PC/silicone oil were investigated. A scanning electron microscope showed that the dispersed droplets of the silicone oils in the PC matrix and the size of the dispersed phases were enlarged with increasing amounts of silicone oil. A transition from brittle to ductile failure was observed with increasing PDMDPS. The impact strength of neat PC at $-30°C$ was 8 kg_f cm/cm, which increased to 52 kg_f cm/cm with the addition of PDMDPS. It appears that, at low temperature, the phenyl group in PDMDPS is more effective for toughening. A higher decomposition temperature and the bulkier molecular structure of PDMDPS, compared to PDMS, resulted in a smaller increase in the melt flow index of PC/PDMDPS than for PC/PDMS. The glass transition temperature, initiation temperature of thermal weight loss, and heat distortion temperature of PC/silicone oil systems were decreased with an increase in the silicone oil. The blending of PC with PDMDPS provided a practical way to develop a combination of high tensile strength and impact strength at a low temperature with applicable comprehensive properties. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3439–3446, 2008

Key words: impact strength; polycarbonate; silicone oil; low temperature property

INTRODUCTION

Polycarbonate (PC) is an engineering plastic widely used in the automotive industry, for data storage, in electronics and in construction. Most commercialized polycarbonates are bisphenol-A polycarbonate, which has the advantageous properties of superior heat resistance, transparency, dimensional stability and self-extinction. The Young's modulus and strength of PC is comparable to other engineering plastics, and its impact strength is very high. The impact strength of PC without a notch is one of the highest among engineering plastics at ambient temperature, whereas the impact strength at low temperatures lessens and sharply decreases as the radius of a notch decreases.[1–3] Generally, the application of PC, particularly in the automotive industry, is limited by the impact strength at low temperatures.

There have been many studies on the impact toughening of PC by blending it with other poly-mers. Many of these studies have focused on rubber blends.[3–7] It has been shown that the addition of a small amount of acrylonitrile-butadiene-styrene (ABS) and core-shell rubbers to PC can improve impact strength.

Silicone oils are with high thermal stability, excellent weather resistance, fine electrical insulation, and good stability at low temperatures.[8,9] Si—O is a main chain of silicone oil; the Si atom-attached chemical groups rotate around the Si—O chain and occupy more space. The additional space makes interaction forces between surrounding molecules, and the silicone oil decreases. The larger groups connected with the Si atom, the more the organic nature of molecules is displayed. The most common groups attached with the Si atom are methyl and phenyl.[10]
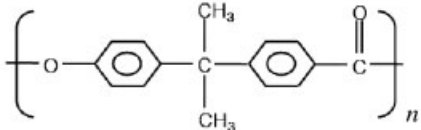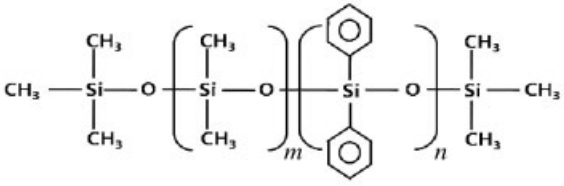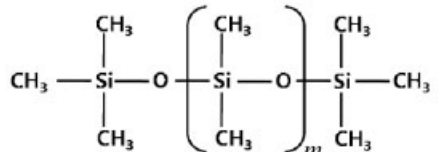
We used two silicone oils: polydimethyldiphenyl siloxane (PDMDPS) and polydimethyl siloxane (PDMS). PDMDPS has a higher decomposition temperature than PDMS.[11–14] The bulky rigid phenyl groups attached to the Si atom in PDMDPS are responsible for the differences in thermal properties.[15]

In this study, PDMS and PDMDPS were added to PC, and tensile strength and impact strength at low temperatures were investigated. Also, the effect of silicone oil on morphology, melt flow index, and thermal properties in PC/silicone oil were discussed.

TABLE I
Materials Properties[16,17]

Polymer	T_g (°C)	M_w (g/mol)	M_v (g/mol)	M_n (g/mol)	Refractive index
Polycarbonate	151	22,800	21,400	9,760	1.585

Silicone oil	T_g (°C)	Kinematic viscosity (cst)	Spe. gravity (g/cm²)	Color	Surface tension (dyne/cm)	Refractive index
Poly(dimethyl diphenyl siloxane)	−65	400	1.07	Transparent	22.7	1.505
Poly(dimethyl siloxane)	−123	1,000	0.975	Pale yellow	21.2	1.403

EXPERIMENTAL

Materials

The unmodified PC resin used in this study was Trirex 3022A (Samyang, Korea) with a glass transition temperature of 151°C. The silicone oils used were PDMDPS and PDMS (Shin-Etsu, Japan). The structures and properties of the PC and silicone oils are shown in Table I.

Sample preparation

To enhance the mixing of the PC and silicone oil, granule type PC was used. The PC and silicone oil were mixed using a Henzel mixer at 60 rpm for 6 min. PDMDPS and PDMS were added up to 10 wt %, and the mixture of PC/silicone oil was fed into an extruder.

A twin screw extruder (SM-Tech, Korea) with a diameter of 35 mm was used to mix the PC and silicone oil. The processing temperature was 265°C, and the rotational speed of the screw was maintained at 150 rpm. The mixed PC/silicone oil were subsequently quenched in water and palletized. Specimens for mechanical tests were injection molded after drying the pellets at 130°C for 4 h.

Physical measurements

A field emission scanning electron microscope (FE-SEM), Jeol JSM-6700F, was used to examine the extent of phase separation in the blends by examining the fracture surfaces of the blends. Fractured samples at room temperature and at −30°C by impact test were coated with platinum and used for morphology observation.

Mechanical properties were measured by a universal test machine (Zwick, England). Impact strength was measured at −30°C and at ambient temperature (25°C) based on ASTM D256 using an impact tester from the Tinius Olsen Company. The size of the impact test was 3.18 mm × 12.66 mm × 6.3 mm.

Melt flow index is defined by the weight of a polymer extruded through a standard cylindrical die at a standard temperature in a laboratory rheometer carrying a standard piston and load in 10 min. The melt-flow index was measured using an MP600 from the Tinius Olsen Company at 300°C at 1.2 kg of load.
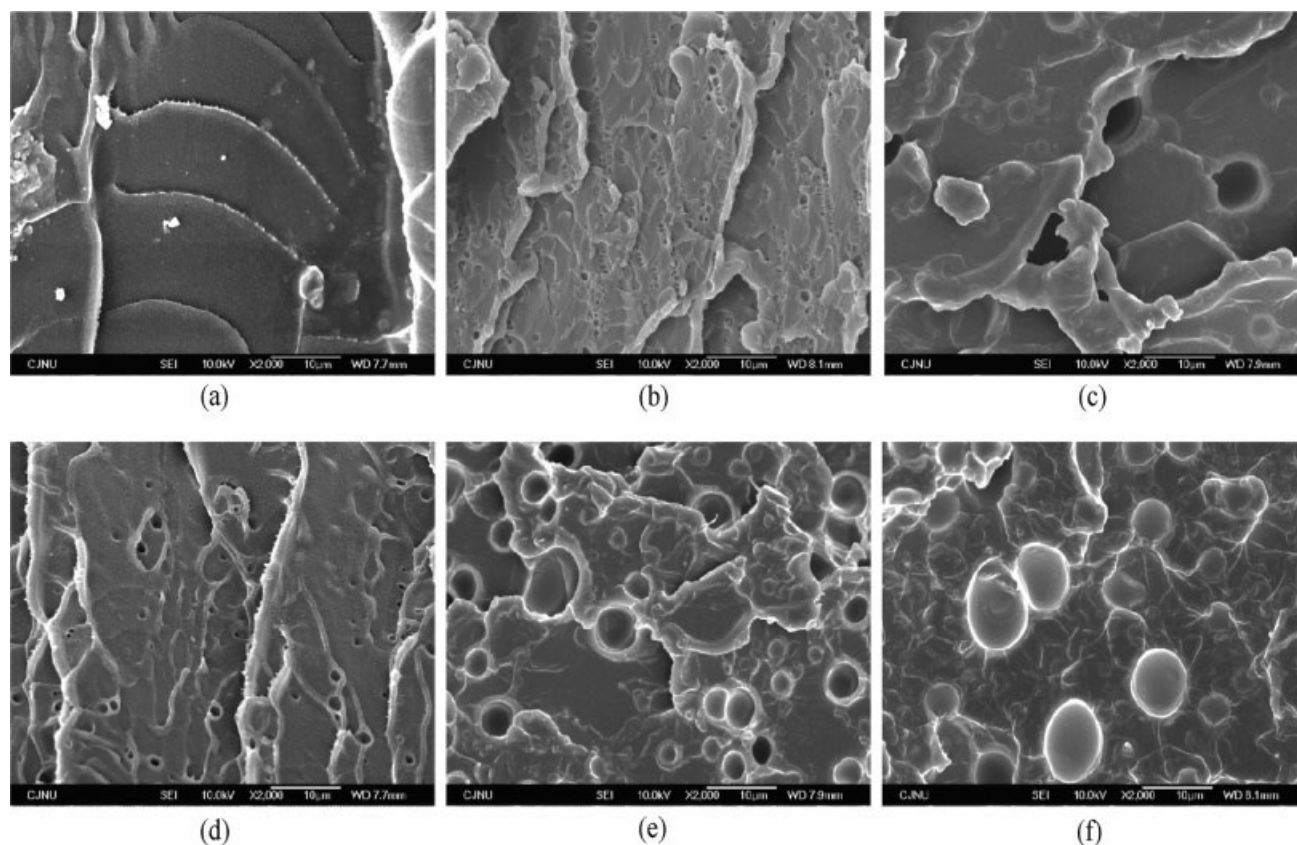
Figure 1 Fracture surfaces of PC/silicone oil at room temperature (×2000). (a) PC control, (b) PC/PDMDPS (1 wt %), (c) PC/PDMDPS (5 wt %), (d) PC/PDMS (0.3 wt %), (e) PC/PDMS (5 wt %), and (f) PC/PDMS (10 wt %).

To study the thermal stability of the blends, a thermogravimetric analyzer (Scinco, Korea) was used. A 10–15 mg sample was used under nitrogen atmosphere at a heating rate of 10°C/min from room temperature to 700°C. Differential scanning calorimetry (using Model: DSC 2010, TA, USA) thermograms over a temperature range of −150 to 250°C were used to measure the glass transition temperature. The nitrogen gas was circulated at a flow rate of 60 mL/min, and the heating rate was 10°C/min.

A three-point loading fixture was used for heat deflection temperature measurements on injection-molded bars. The heat deflection temperature was measured at a load of 18.6 kg_f/cm^2 and heating rate of 2°C/min (Model: 3M-2, Toyoseiki, Japan).

RESULTS AND DISCUSSION

The fractured surface of the impact-tested specimen was observed using FE-SEM. Figure 1 shows the fracture surfaces of neat PC and PC/silicone oil systems, which were tested at room temperature. Neat PC showed a smooth and characteristic wavelike ductile fracture, whereas PC/PDMDPS showed a microheterogeneous phase separation. The silicone oil droplets were dispersed in the continuous phase of PC. The degree of phase separation and the number and size of droplets increased as the silicone oil content was increased. The uniform fracture surface was observed at 1 wt % of PDMDPS, whereas the distinctive droplets of 5 μm diameter were observed at 5 wt % of PDMDPS. The number of droplets induced from the silicone oil increased, and the droplets were enlarged, which was not observed in the neat PC. Increasing the fraction of the dispersed phase resulted in an increase in the size of the coalescing particles.[18] The phase separation of the PC/silicone oil was more distinctive in PDMS than in PDMDPS. A clear phase separation was observed, even at 1 wt % of PDMS. A similar separated domain was observed in the PC/liquid crystal polymer; the uniformly dispersed phase indicated good dispersion.[19] The T_gs from the differential scanning calorimetry (DSC) and the sharp decrease of impact strength are related to the phase separation of the silicone oil. The chain mobility of silicone oil at low temperatures and the rough fracture surfaces are the main reasons for the increase in impact strength and tensile strength.

The number and size of droplets increased as the PDMS increased, and ~ 10 μm of domains were
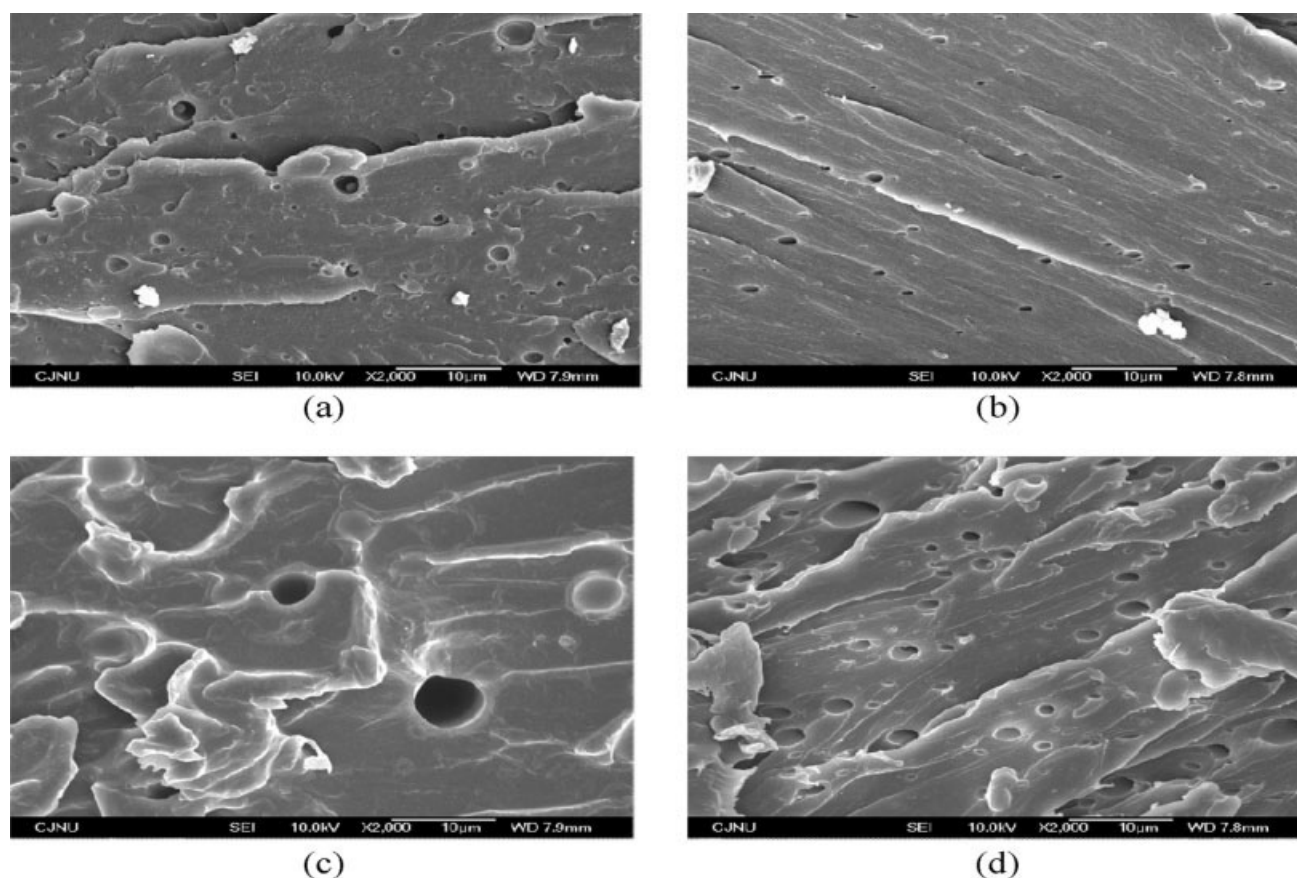
Figure 2 Morphology of fractured surface at −30°C (×2000). (a) PC/PDMDPS (1 wt %), (b) PC/PDMS (1 wt %), (c) PC/ PDMDPS (5 wt %), and (d) PC/PDMS (5 wt %).

observed. Figure 2 shows the fractured images of PC/PDMDPS and PC/PDMS at −30°C. Rough surfaces at room temperature changed to smooth surfaces by brittle-type failure at −30°C. The main mechanism of toughening in PC is matrix shear yielding, and it is related to the rough surfaces.[20] The PC/ PDMDPS showed rougher surfaces, and the PC/ PDMS showed brittle failure and a smooth surface.

PC/PDMS systems in Figure 2(b,d) showed many droplets, and they had lower impact strength, whereas the PC/PDMDPS in Figure 2(a,c) had a higher impact strength. The higher chemical affinity of phenyl groups between PC and PDMDPS, and the smaller number of droplets in the PC/PDMDPS than in the PC/PDMS, with the same amount of silicone oil, suggests a higher impact energy.

Tensile strengths of PC/silicone oil systems obtained by increasing the fraction of PDMDPS and PDMS are shown in Figure 3. At varied temperatures, the tensile strengths were different, which corresponded to different material characteristics. At room temperature, the tensile strength of neat PC was 680 kg$_f$/cm^2, and it decreased gradually with an increase in the amount of silicone oil. The tensile

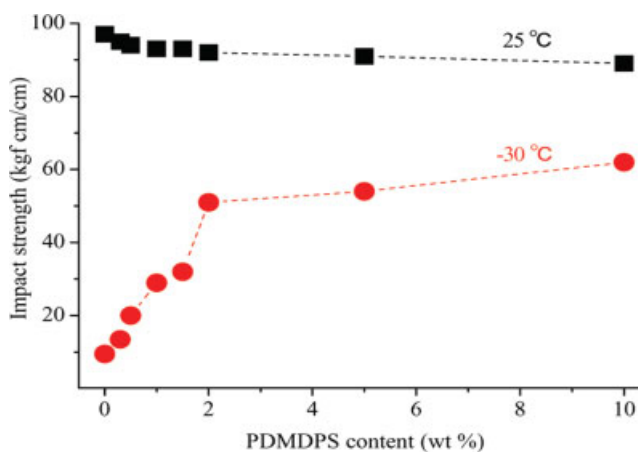strength of PC/PDMDPS was 600 kg$_f$/cm^2 at 10 wt % of PDMDPS. At −30°C, neat PC had a tensile strength of 550 kg$_f$/cm^2, and the maximum tensile strength of PC/PDMDPS was 620 kg$_f$/cm^2 at 5 wt % of PDMDPS. This decreased to 500 kg$_f$/cm^2 at 10 wt %. With a large amount of PDMDPS loading, injection-molded samples delaminated at the surfaces, and these samples had lower tensile strength. The phase separation may be related to the lower tensile strength.

Tensile strength with various amounts of PDMS is shown in Figure 3(b). By increasing the PDMS content, the tensile strength of PC/PDMS at room temperature was similar to that of the PC/PDMDPS; however, the tensile strength of the PC/PDMS was higher up to 5 wt % of PDMS at −30°C. The addition of silicone oil with the lower glass transition temperature induced toughening during tensile loading at a low temperature, and tensile strength increased. The lower T_g of PDMS, compared to that of PDMDPS, led to the higher tensile strength of PC/PDMS at low temperatures. The tensile strength of the PC/PDMS at 10 wt % of PDMS at −30°C was not measurable due to the severe delamination of the injection-molded sample.
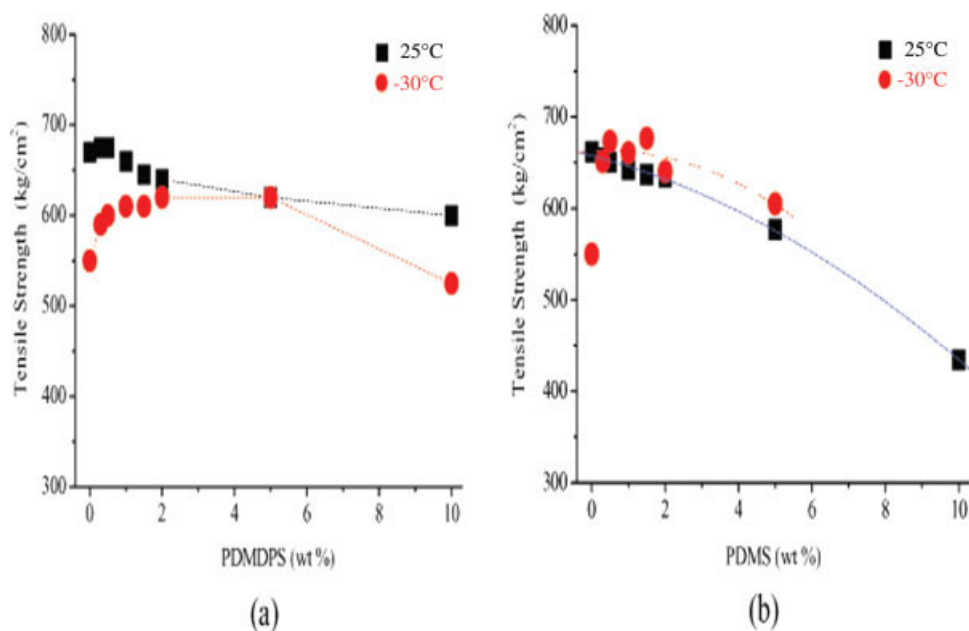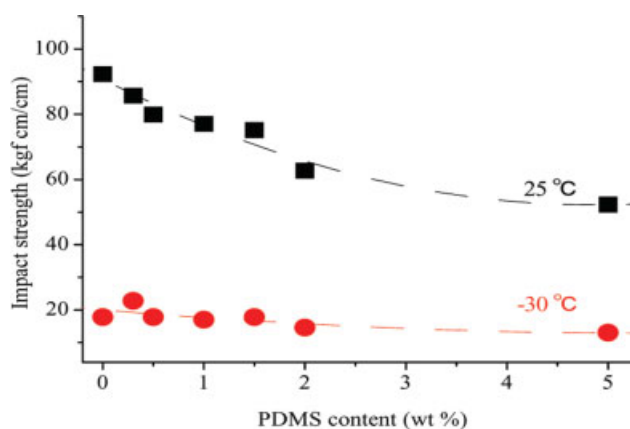
Figure 3 (a) Tensile strength as a function of PDMDPS, and (b) tensile strength as a function of PDMS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Notched Izod impact strengths of the PC/PDMDPS at room temperature and at $-30°C$ are shown in Figure 4. The impact property of PC showed a significant drop by decreasing the test temperature. The impact strength of neat PC was 97 kg_f cm/cm and 8 kg_f cm/cm at room temperature and at $-30°C$, respectively. As the PDMDPS increased, there was a slight decrease in the impact strength at room temperature, but there was a sharp increase in impact strength to 60 kg_f cm/cm at $-30°C$. In particular, at $-30°C$, adding less than 2 wt % made the PC/PDMDPS blends ductile without any significant sacrifice in other properties.

There was a transition from brittle to ductile failure as the silicone oil was increased. Figure 5 shows the notched impact strength as a function of PDMS. The impact strength decreased to 50 kg_f cm/cm when the amount of PDMS was increased to 5 wt % at room temperature. The impact strength of PC/PDMS was less than 20 kg_f cm/cm, even at a higher loading of PDMS at $-30°C$, and it was lower than the impact strength of PC/PDMDPS. The large difference in impact strength between PC/PDMS and PC/PDMDPS, especially at $-30°C$, may be due to the structure of silicone oil. The rigidity and a chemical affinity between PC and PDMDPS due to the phenyl group made the PC/PDMDPS much tougher
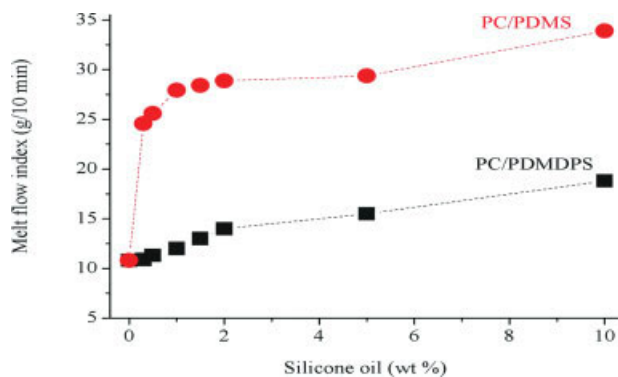

Figure 4 Notched Izod impact strength of PC/PDMDPS blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 Notched Izod impact of PC/PDMS blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
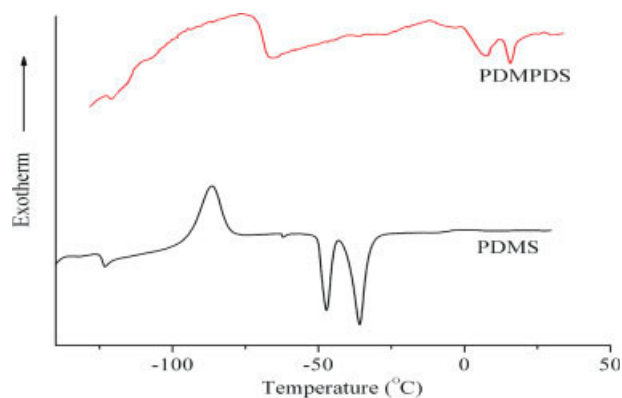
Figure 6 Comparison of melt flow index. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 DSC traces of PDMDPS and PDMS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

than the PC/PDMS at low temperatures. It is hypothesized that the phenyl group in the PDMDPS produced the higher impact strength in the PC/PDMDPS than in the PC/PDMS at low temperature and induced a small decrease in impact strength at room temperature.

As the amount of PDMDPS and PDMS to PC was increased, the melt-flow index also increased, as shown in Figure 6. The melt-flow index of neat polycarbonate was 10.8 g/10 min. It increased to 18.8 g/10 min and 33.5 g/10 min at 10 wt % of PDMDPS and PDMS, respectively.

The smaller side groups of PDMS compared to the bulky phenyl groups in PDMDPS may be a reason

for the higher melt flow index. The lower decomposition temperature, lower T_g, and the side groups of PDMS that were smaller than those of PDMDPS caused the higher melt flow index of PC/PDMS with a small addition of PDMS.

DSC results of two silicone oils are shown in Figure 7. The glass transition temperature of PDMS was $-123°C$, and melting peaks were observed at $-47°C$ and $-36°C$. The PDMDPS showed T_g at $-65°C$, and it showed melting peaks at $9.2°C$ and $18.6°C$. The higher thermal properties of the PDMDPS imply that PC/PDMDPS has higher heat resistance properties than PC/PDMS.
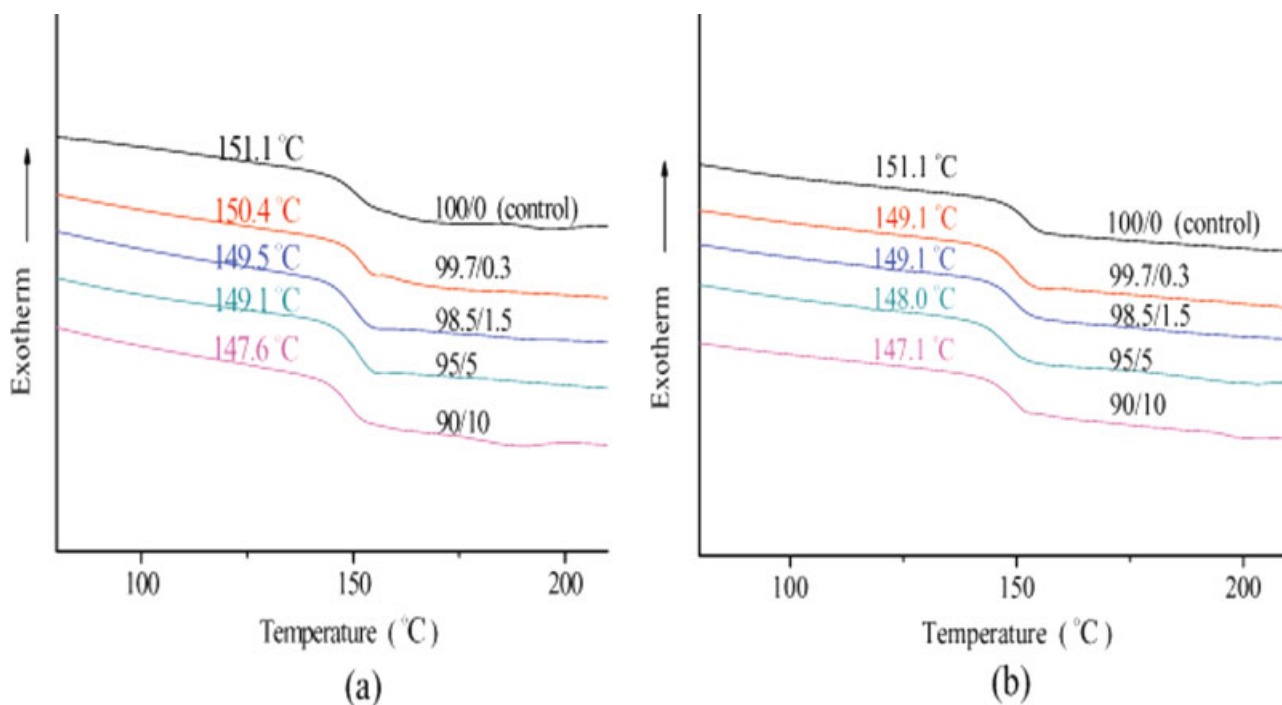
Figure 8 DSC traces of PC phase with silicone oil content in (a) PC/PDMDPS and (b) PC/PDMS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
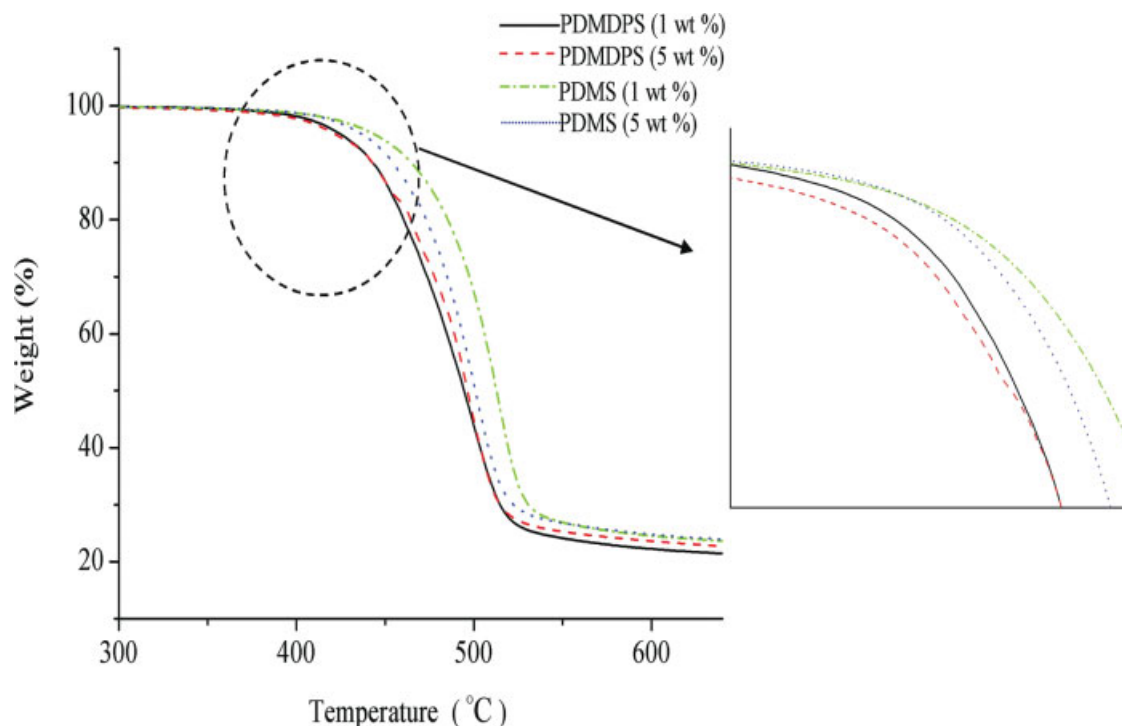
Figure 9 TGA graphs of PC/silicone oil. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

DSC graphs of PC with silicone oil are shown in Figure 8. PC shows T_g at 151.1°C. A slightly lower T_g was shown as the PDMDPS was increased. The glass transition temperatures of the PC phase in PC/PDMDPS and PC/PDMS at a silicone oil content of 10 wt % were 147.6°C and 147.1°C, respectively. This indicates the solubilizing effects of low molecular silicone oils in a PC matrix. The small change of T_g supports the observation that PC and silicone oil are not miscible with each other. The reason for the larger peak shift of T_gs to a low temperature in the PC/PDMS is due to the T_gs of PDMS that are lower than those of PDMDPS.

Figure 9 shows the weight loss of PC/silicone oil systems at 1 and 5 wt % of silicone oil, measured up to 700°C at a heating rate of 10°C/min. It is known that PC starts to degrade at 430°C.[1] PC/silicone oil showed weight loss from about 400°C. The initial temperatures of weight loss were 350, 380, 400, and 410°C for PC/PDMPS (5 wt %), PC/PDMPS (1 wt %), PC/PDMS (5 wt %), and PC/PDMS (1 wt %), respectively. The weight losses at 450°C were 7, 9, 12, and 13% for PDMDPS (1 wt %), PDMDPS (5 wt %), PDMS (1 wt %), and PDMS (5 wt %), respectively.

In the same amount of silicone oil, the thermal degradation temperature and the amount of weight loss increased as the silicone oil increased. The lower viscosity of PDMDPS, 400 cst, was more compatible to that of PC/PDMDPS, as opposed to that of PMDS with a higher viscosity at 1000 cst. The PDMS showed more weight loss than PDMDPS at 450°C. This is due to the lower thermal stability of PDMS.[13]

Figure 10 shows the decrease in the heat deflection temperature of PC/silicone oil as a function of silicone oil. The heat deflection temperature of neat PC was 137°C, and it was lowered to 128°C and 120°C at 10 wt % of the PDMDPS and the PDMS, respectively. The bulky phenyl groups and higher T_gs led to the higher heat deflection temperatures of PC/PDMDPS than PC/PDMS.
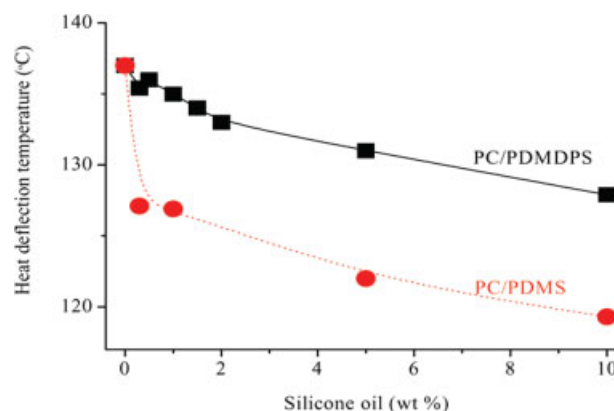
Figure 10 HDT as a function of silicone oil at 18.6 kg$_f$/cm^2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

Silicone oils were added to PC, and their effects on the morphology, mechanical, rheological, and thermal properties were investigated. FE-SEM analysis showed a phase separation of silicone oil in a PC matrix, and it was also confirmed by thermal characterization. Fracture surfaces of PC/PDMDPS and PC/PDMS showed a rough surface at room temperature and a relatively smooth surface at $-30°C$. The impact strength of PC at low temperatures was increased from 8 to 60 kg$_f$cm/cm by adding 10 wt % of PDMDPS. However, in PC/PDMS, the impact strength was not increased at low temperatures. The stability of the PDMDPS at low temperatures and its higher chemical affinity with PC, due to its phenyl groups, may be the reasons for the higher impact strength of PC/PDMDPS compared to PC/PDMS. The melt flow index increased with an increase in the silicone oil content. The PC/PDMDPS showed a little increase in the melt flow index due to the bulky structure and heat stability of PDMDPS, compared to PC/PDMS, which had small methyl groups attached on the Si-atom in PDMS.

By adding silicone oil to PC, the glass transition temperature, starting temperature of thermal weight loss and the heat deflection temperature of the PC/silicone oil systems were shifted to lower temperatures. The PC/PDMDPS showed higher heat resistance than the PC/PDMS. The higher chemical affinity and rigidity of the phenyl group in the PDMDPS led to the high impact strength of the PC/silicone oil systems at low temperatures with no significant decrease in other polycarbonate properties.

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