

Rheological properties and thermal degradation behaviors of sonochemically treated polycarbonate/polysiloxanes blends

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Abstract

Two polysiloxanes having different chemical structures were blended with polycarbonate (PC) under ultrasonic irradiation in solution. The polysiloxanes used were poly(methylphenyl siloxane) and vinyl-terminated poly(dimethyl siloxane). It was of primary interest to investigate the effect of polysiloxane structure on the rheological properties of PC/polysiloxane blends. It was found that a small amount (1.5 phr) of polysiloxanes greatly altered the melt viscosities and elasticity of PC. In particular, incorporation of poly(methylphenylsiloxane) led to a notable increase in elasticity with greater shear sensitivity of PC. The observed rheological behaviors of PC/polysiloxane blends were partly explained in conjunction with the tendencies found in ultrasonic degradation of polysiloxanes. Thermal stability and morphology in sonicated blends of PC/polysiloxane blends were also discussed.

Keywords : polycarbonate, polysiloxane, ultrasound, degradation

1. Introduction

Polycarbonate (PC) is a tough, transparent, and widely used engineering thermoplastic resin. Despite of its excellence in mechanical performance, numerous attempts have been made to improve the low temperature impact resistance, notch sensitivity and thermal stability, which were mostly done by introducing polysiloxane units in PC chains (Pesetskii *et al.*, 2000; Grubbs and Kleppick, 1982; Ma *et al.*, 1997). In order to generate copolymers of PC and polysiloxane, either PC or polysiloxane was chemically modified for successful reactions between the two. For example, PC-poly(dimethylsiloxane) (PDMS) multi-block copolymers were made by reacting (nitrophenylcarbonate)-terminated PC and (bisphenol A)-terminated PDMS (van Aert *et al.*, 2001). Besides the improvement of mechanical properties, alteration of thermal degradation and flame retardance in PC was another important aspect of preparing block copolymers of PC-PDMS with a dimethylsiloxane block size of 15-350 units. These copolymers were prepared by using PC oligomer and reactive PDMS (Nodera and Kanai, 2006a; 2006b). For electric applications, where high flame retardancy and environmental compatibility are critical, the PC-PDMS block copolymer turned out to be a promising alternative to halogen containing or phosphorous based flame retardant PC. For exam-

ple, PC-PDMS block copolymers with DMS units of 40-130 had high limiting oxygen index values with 1.0 wt % PDMS. A major role of PDMS units was to form good thermal insulators through the reaction of PC and PDMS in combustions.

In this study, modification of PC was done by blending with polysiloxane under ultrasonic irradiation without any functionalization of either component. The motivation for this attempt was based on the previous studies where sonochemical treatment provided a useful mean to produce PC based copolymer and transform the molecular architecture of PC as well (Kim *et al.*, 2007; Choi *et al.*, 2007). In here, two polysiloxanes of different chemical structures were incorporated in chloroform as a solvent for the mixture. The purpose of imposing ultrasound to the solution was to generate the macroradicals of PC and polysiloxane respectively, and mutual coupling between those macroradicals was expected to form PC-polysiloxane copolymers.

Despite of the abovementioned benefits owing to the existence of siloxane in PC phase, relatively little attention was focused on the rheological behaviors of polysiloxane containing copolymers or blends of PC. No doubt, such information is valuable to process siloxane containing PC either in solution or melt state. It was, therefore, a major objective of this study to investigate rheological properties of the PC/polysiloxane blends prepared by sonochemical mixing. The thermal degradation of the blends was also examined to reveal the influence of ultrasonic irradiation

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Table 1. Materials used in this study

Name	Abbreviation	Structure	Viscosity (cSt)	Source
Divinyl terminated polydimethylsiloxane	VT-PDMS		400	Momentive
Poly(methylphenylsiloxane)	PMPS		500	Aldrich

on the thermal stability of the material. It is expected that the results found from this study will provide useful information for the development of advanced PC by the incorporation of siloxane based polymers.

2. Experimental

PC used in this study was a low viscosity grade (Panlite L-1225Y, Mn=9,200) made by Teijin (Japan). For polysiloxanes, divinyl-terminated poly(dimethyl siloxane) (VT-PDMS) was supplied from Momentive and poly(methylphenyl siloxane) (PMPS) were purchased from Aldrich. The details of chemical structure and viscosity information were summarized in Table 1. The concentration of polysiloxanes was 1.5 and 3 phr, respectively. In order to assess the rate of ultrasonic degradation, 2.5×10^{-4} M of 1,1-diphenyl-2-picrylhydrazyl (DPPH) was added during sonication of polysiloxanes solutions, as practiced by Bawn and Mellish (1951). Since DPPH acts as a radical scavenger during sonication, radical formation kinetics can be obtained by monitoring the concentration profile of the active radical scavenger DPPH by ultraviolet-visible spectrometry. DPPH was obtained from Aldrich and was used as received. All other chemicals were obtained commercially and used without further purification.

The reactions were carried out in a probe batch reactor (Suslick), where a horn type ultrasonic homogenizer (Sonics & Materials, Inc., VCX 750) was used. The reactor was surrounded by a thermostatted water bath to maintain the temperature of 5°C throughout reaction. The equipment is capable of automatic tuning and the horn consists of a titanium tip with 1/2" in diameter. The frequency of ultrasound was 20 kHz and the amplitude was varied to control the intensity of ultrasound. The sonication intensity at 50% of the maximum amplitude was found to be around 27 W/cm², which was determined by calorimetric method. Sonication

time was set to 3 min and 5 min, respectively. The on/off ratio of ultrasound irradiation was fixed as 7:3. Before sonication, the reactor was deoxygenated by bubbling with nitrogen gas for 3 min. During the reaction, argon was bubbled continuously through the solution at a flow rate of 45 ml/min to attain a condition of stable cavitation. Before subsequent experiments, all the samples were dried in a vacuum oven at 80°C overnight.

The samples obtained from the ultrasonic treatment were compression-molded at 260°C for 5 min. Disk-shaped specimens with a thickness of 2 mm and a diameter of 25 mm were prepared. An ARES rotational rheometer (Rheometric Scientific) was used to measure the complex viscosity and complex modulus. The measurements of the dynamic viscosities were performed in a parallel-plate fixture (diameter=25 mm) with a gap distance of 1.2 mm. The strain was kept at 10% to ensure linear viscoelasticity. The frequency range was 0.1-100 rad/s, and the temperature was 260°C. The work was conducted under a nitrogen atmosphere to prevent degradation.

A TA 2950 thermal analyzer was used to investigate the thermal stability of the modified PC. Experiments were carried out on about 2 mg samples under nitrogen at a heating rate of 10°C/min up to 800°C. Glass transitions were measured by differential scanning calorimetry using a TA 2910 at a heating rate of 10°C/min.

The phase morphology of the blends was examined by using a scanning electron microscopy (SEM, JEOL JSM-5800) after coating the fracture surface of the sample with gold.

3. Results and discussion

Fig. 1 shows the effect of sonication time on the complex viscosities of PC/polysiloxane blends prepared from sonicated mixing process. After 3 min of sonication, it was

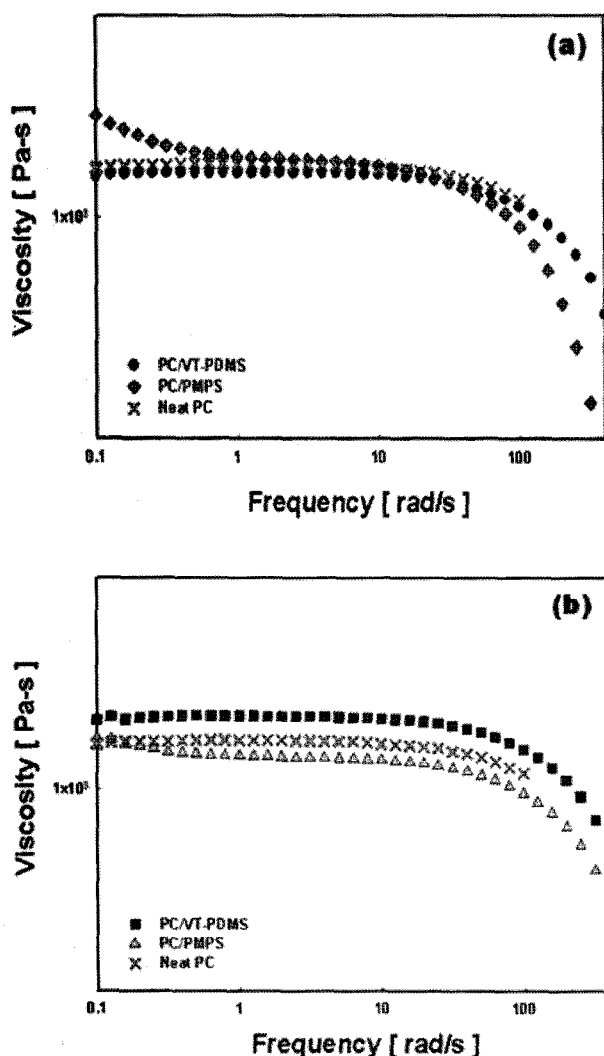


Fig. 1. Effect of polysiloxanes and sonication time on the complex viscosities of PC/polysiloxane (1.5 phr) blends. (a) sonication time=3 min, (b) sonication time=5 min.

found that the shear sensitivity of PC was apparently altered, when 1.5 phr of PMPS was added. The melt viscosities of PC/VT-PDMS blend were slightly higher than those of neat PC, but the shear dependency remained similar. As the sonication time increased from 3 min to 5 min, somewhat different trends were found. The melt viscosities of PC/VT-PDMS blend increased further, whereas those of PC/PMPS blend and its shear dependency were reduced. When PC or polysiloxanes molecules are under the influence of sonication, the molecules are expected to undergo chain scissions, which leads to reduction in the viscosity (Kim *et al.*, 2007; Price *et al.*, 1996). From the FTIR analysis for the simply mixed and sonicated blends (Choi, 2009), it was found that the main site of chain scission is C-O bond of carbonate linkage in PC, while Si-O-Si linkage is broken in polysiloxane, as revealed by reduction in peak intensity around 1780 cm^{-1} and 1080 cm^{-1} , respec-

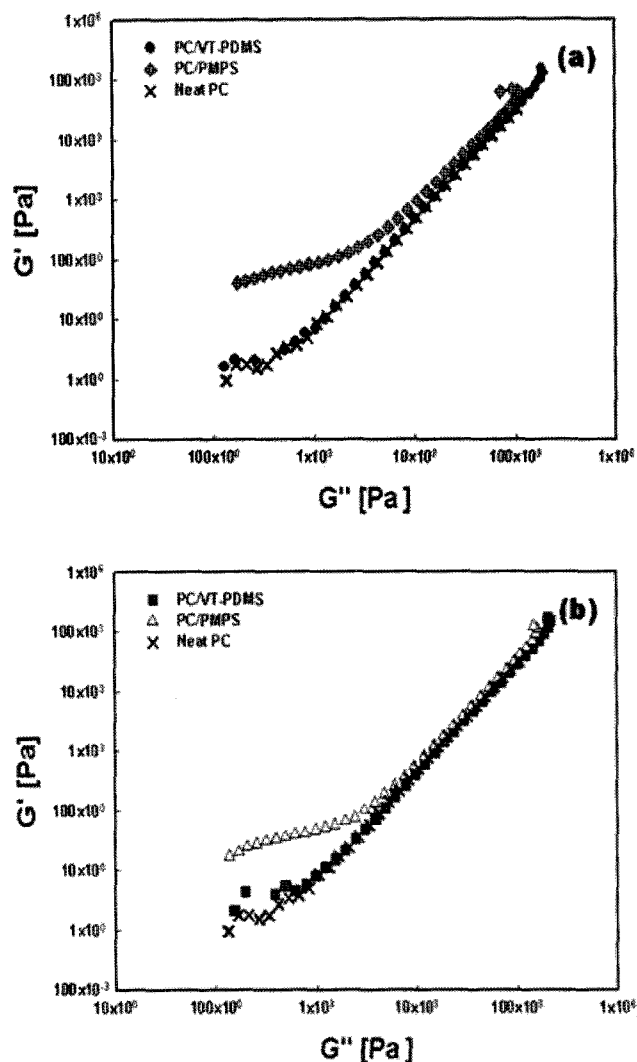


Fig. 2. Cole-Cole plots for PC/polysiloxane (1.5 phr). (a) sonication time=3 min, (b) sonication time=5 min.

tively. It is evident from Fig. 1 that systematic changes within the samples were indeed occurring during ultrasound assisted mixing process depending upon the kind of polysiloxanes. The viscosity variation shown in Fig. 1 supports a possibility that the mutual combination of macroradicals of PC and polysiloxane proceeded during sonicated mixing. In fact, from the Soxhlet extraction using toluene, the amount of free polysiloxane which is unbound to PC was measured, where little change in sample weight was occurred after extraction. It is, however, noted that the coupling of different kind of macroradicals does not necessarily follow the linear fashion, as will be further discussed later. Fig. 2 shows the modified Cole-Cole plots for the modified PC and neat PC. At a given G'' , G' 's of the PC modified by PMPS for 3 and 5 min of sonication are higher than those of neat PC and PC/VT-PDMS blends. Although the viscosities of PC/VT-PDMS were higher than those of

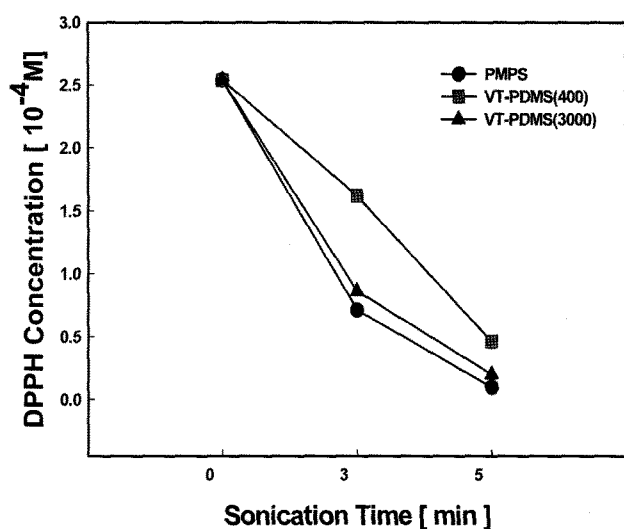


Fig. 3. Concentration of the radical scavenger 1,1-diphenyl-2-picrylhydrazyl (DPPH) in sonication time.

PC/PMPS blends prepared from the same duration of sonication, the elasticity of PC/VT-PDMS blend was lower than that of PC/PMPS blend. By examining the trends found in Figs. 1 and 2, it is surmised that branched structure was generated during sonication of PC/PMPS blends, whereas a linear type chain extension prevailed in PC/VT-PDMS blends. Obviously, it is a difficult task to exactly picture the transformation of chain structure within the limited data. Nevertheless, a plausible explanation for this notion follows in terms of characteristic features in ultrasonic degradation of polysiloxanes used in this study.

In view of chemical structure in PMPS, formation of macroradicals may be more favorable due to the existence of phenyl group attached to Si, simply because the radicals are stabilized by delocalization owing to the electron richness of phenyl group compared to methyl group. In an attempt to clarify this issue, radical formation of polysiloxanes used in this study has been assessed by measuring intensities of DPPH at 520 nm in ultraviolet-visible spectroscopy analysis. In order to delineate the effect of molecular weight, a high viscosity grade of VT-PDMS (3000 cSt) was also tested here. Concentration variation of active DPPH in sonication time was displayed in Fig. 3. For the given sonication time of 5 min, concentration of macroradicals was higher (lower concentration of active DPPH) for PMPS, compared to VT-PDMS. It is well known that the initial degradation rate is higher for the sample with higher molecular weight (Mason and Lorimer, 2002). A consistent trend was also confirmed here in examining the degradation rate of VT-PDMS, as was previously observed from a study on the ultrasonic degradation of a series of homologous PDMS by Price *et al.* (1996). However, it is pointed out from Fig. 3 that ultrasonic degradation of polysiloxanes considered here seems

to be more strongly controlled by the chemical structure of substituents attached to Si. In other words, stable nature of macroradicals leads to higher degradation rate in PMPS over the high viscosity grade VT-PDMS, at least during the early stage of degradation process. Furthermore, steric hindrance due to the phenyl ring near the end of a macroradical may also play a role in the evolution of chain structure. Such structural feature would prefer a route involving hydrogen abstraction from methyl groups of PC or PMPS rather than direct coupling between the macroradicals, which then offers active sites for chain branching and is responsible for the observed rheological behaviors of PC/PMPS blends. An analogous argument can be found from a study on the development of branched PC (Kim *et al.*, 2007).

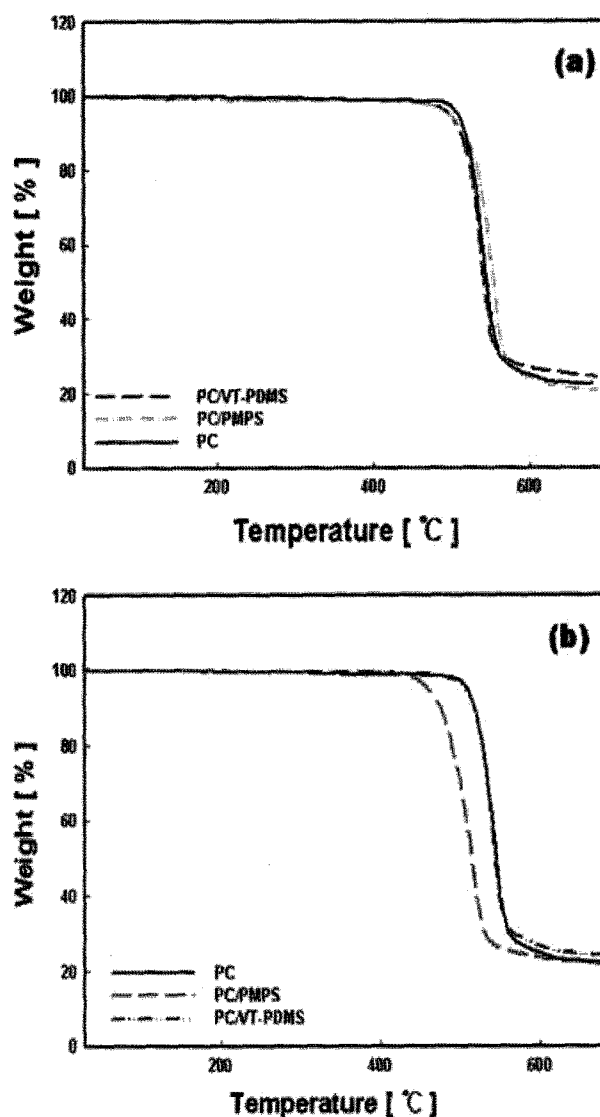


Fig. 4. TGA data for neat PC and PC/polysiloxane blends (sonication time=5 min) for polysiloxane concentration of (a) 1.5 phr and (b) 3 phr.

As far as the viscosity data for 5 min sonication are concerned, it is not clear why both shear dependency and viscosity values were decreased in PC/PMPS blend, while viscosities of PC/VT-PDMS were continuously increased for the same processing condition. It is also noted from Fig. 2(b) that the elasticity of PC/PMPS blend somewhat decreased whereas that of PC/VT-PDMS was slightly increased. Although the detailed mechanism remains a topic of debate, it is considered that substantial chain scission in larger molecules grown earlier underwent upon further exposure to high-intensity ultrasound in PC/PMPS system. In contrast, vinyl groups located at the ends of VT-PDMS may promote chain extension with either macro-radicals of itself or PC. Due to the lack of rigorous analysis on the molecular structure of the sonicated blends, further studies are underway.

Thermal degradation behavior of PC/polysiloxane blends were presented in Fig. 4. Since, in principle, radical species are generated to achieve transformation of molecular structure, one may suspect that such radicals may affect somewhat adverse effects in the thermal stability of the modified PC. It was found from Fig. 4(a) that the sonochemical modification of PC with polysiloxanes resulted in slight decrease of initial degradation temperature when 1.5 phr of polysiloxane was added. As the concentration of polysiloxane was increased up to 3 phr, the initial degradation temperature was reduced from 522°C to 494°C in PC/PMPS blend, while the thermal stability of PC/VT-PDMS and neat PC was quite similar, as shown in Fig. 4(b). From a study on the effect of phenyl group on the thermal stability of polysiloxane (Zhou *et al.*, 2006), it was reported that the onset of degradation under nitrogen atmosphere took place at lower temperatures when phenyl content was

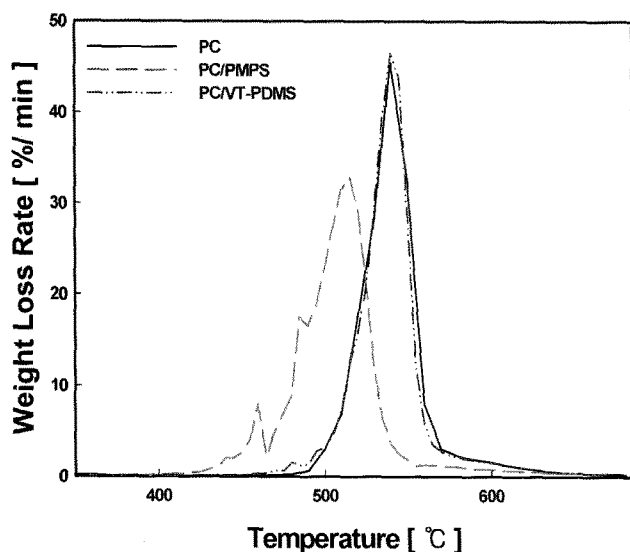


Fig. 5. Weight loss rate for PC and PC/polysiloxane blends (polysiloxane concentration = 3 phr) versus temperature by TGA.

increased. Thus, it is considered that the sonication imposed during mixing was not a major cause to deteriorate the thermal stability of the PC/polysiloxane blends. Moreover, the analysis on the rate of weight loss indicated that the degradation rate is retarded as the temperature increases (Fig. 5). This is a quite important consideration on the flame retardance of polymeric materials. Although the amount of char formation is an important concern as well, the rate of weight loss of PC-PDMS block copolymers was reasonably well correlated with limiting oxygen

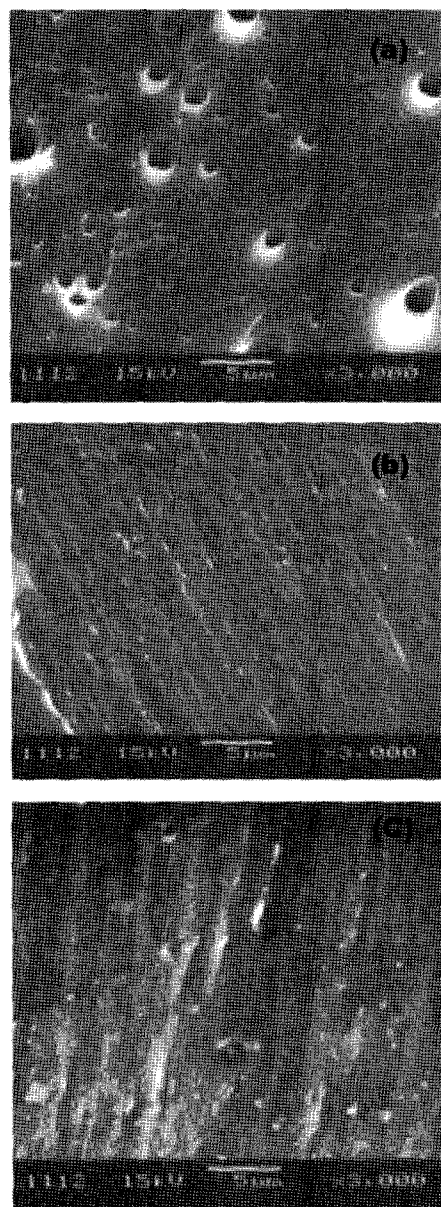


Fig. 6. SEM images for PC/polysiloxane (3 phr) blends prepared by (a) simple mixing of PC/PMPS (mixing time = 30 min), (b) sonicated mixing of PC/PMPS (sonication time = 5 min), (c) sonicated mixing of PC/VT-PDMS (sonication time = 5 min).

index (LOI) (Nodera and Kanai, 2006a). In their study, one important consideration was to focus on the role of bubbles generated during combustion. The bubbles served as thermal insulators to achieve the desirable level of flame retardance and sufficient melt tension was required to preserve the bubbles within the melt. In present study, the increased elasticity of PC/PMPS blend may be relevant to the deceleration of weight loss during thermal degradation. More detailed study on the degradation behavior and flame retardance of PC/polysiloxane blends are under consideration.

Morphology of the sonicated PC/PMPS and PC/VT-PDMS blends were investigated by SEM and their micrographs are displayed in Fig. 6. In a blend of PC/PMPS prepared from 30 min of stirring without sonication, numerous holes of 2.2 μm in average size are shown, which is a typical morphology revealed in an incompatible blend, indicating insufficient adhesion between PMPS domains and PC matrix. Such morphology was totally changed upon sonochemical treatment of the blends; most of the holes were disappeared and the appearance of surface became more homogeneous, compared to the simple blend. The data of glass transition shown in Table 2 also support the improvement of compatibility in PC/polysiloxane (1.5 phr) blends; as the sonication proceeds the glass transition temperature of PC (144°C) was decreased to 134 and 135°C in PMPS and VT-PDMS blend, respectively. Other examples of enhanced compatibility by sonochemical effect are found elsewhere (Kim *et al.*, 2002).

4. Conclusions

In summary, rheological behaviors of PC were remarkably changed by adding a small amount of polysiloxanes under sonication, depending upon the chemical structure of polysiloxanes and sonication time. The shear sensitivity and elasticity were increased in PC/PMPS blends, whereas the increase of melt viscosity was dominant in the blends

Table 2. Glass transition temperatures (T_g) of PC and its blends with polysiloxanes (1.5 phr)

Polymer	Sonication Time (min)	T_g (°C)
PC	-	144
	Simple Mixing	142
PC/PMPS	3	139
	5	134
	Simple Mixing	147
PC/VT-PDMS	3	144
	5	135

of PC/VT-PDMS in which the shear dependency remained similar to that of PC. The ultrasonic degradation of polysiloxane was dependent both on the molecular weight and backbone structure of polysiloxanes. Among the polysiloxanes used in this study, the rate of radical generation was highest for PMPS reflecting the stability of macro-radicals. Based on the rheological behaviors of the blends and characteristic feature of ultrasonic degradation of polysiloxanes, it was considered that the formation of branched structure is a feasible route in PC/PMPS blend. At a loading of 1.5 phr of polysiloxanes, thermal stability of sonicated blends was comparable to neat PC, although the initial degradation temperature was reduced for the blend containing 3 phr of PMPS. From the investigation of morphology and changes in the glass transition temperature, it was confirmed that ultrasonic irradiation during mixing process is a useful mean to increase the compatibility of PC/polysiloxane blends.

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