

# Thermal and Dynamic Mechanical Properties of Organic–Inorganic Hybrid Composites of Itaconate-Containing Poly(butylene succinate) and Methacrylate-Substituted Polysilsesquioxane

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**ABSTRACT:** Itaconate-unit-containing poly(butylene succinate) (PBSI) was synthesized by the reaction of 1,4-butanediol, succinic acid, and itaconic acid in a molar ratio of 2.0 : 1.0 : 1.0, and the obtained PBSI was reacted with methacryl-group-substituted polysilsesquioxane (ME-PSQ) in the presence of benzoyl peroxide (BPO) at 130°C to produce PBSI/ME-PSQ hybrid composites. The thermal and dynamic mechanical properties of the PBSI/ME-PSQ hybrid composites were investigated in comparison with those of PBSI cured at 130°C in the presence of BPO. As a result, the hybrid composites showed a much higher thermal degradation temperature and storage modulus in the rubbery state than the cured PBSI (C-PBSI). The thermal degradation temperature and storage

modulus of the hybrid composites increased with increasing ME-PSQ content. The glass-transition temperature, measured by dynamic mechanical analysis of the hybrid composites, somewhat increased with increasing ME-PSQ content. However, the glass-transition temperatures of all the hybrid composites were lower than that of C-PBSI. Although the IR absorption peak related to C=C groups was not detected for C-PBSI, some olefinic absorption peaks remained for all the hybrid composites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2159–2164, 2008

**Key words:** biodegradable; crosslinking; nanocomposites; polyesters; thermal properties

## INTRODUCTION

Biodegradable polyesters such as polylactide (PLA),<sup>1</sup> poly(butylene succinate) (PBS),<sup>2</sup> poly(butylene adipate/terephthalate),<sup>3</sup> poly(ethylene terephthalate/succinate),<sup>4</sup> and poly( $\epsilon$ -caprolactone)<sup>5</sup> have been extensively investigated since the 1970s to reduce the environmental pollution caused by plastic waste. Recently, biobased polymers derived from renewable agricultural and biomass feedstock have been gathering much attention as sustainable and ecoefficient products that can replace products based exclusively on petroleum feedstock.<sup>6,7</sup> With respect to biodegradable polyesters, PLA is produced from starch via fermentation. In addition, PBS can be also prepared from renewable plant resources.<sup>8,9</sup> Thus, succinic acid (SA) can be prepared by the fermentation of starch, and SA can be converted to 1,4-butanediol (BD) by hydrogenation.<sup>10</sup> However, PBS has poorer mechanical and thermal properties than PLA and other conventional petrochemical polyest-

ers, although PBS is more flexible than PLA. Many efforts have been devoted to improving the mechanical and thermal properties of PBS. Among them, the reinforcement of biobased plastics with layered silicates or biofibers is expected to be a desirable method without the ecoefficiency being sacrificed. There have already been some reports on nanocomposites of PBS with organomodified montmorillonites.<sup>11–14</sup> However, it is very difficult to prepare completely exfoliated and homogeneously dispersed nanocomposites and to get superior interfacial adhesiveness.

Organic–inorganic hybrid composites through the reaction of polysilsesquioxanes  $[(RSiO_{3/2})_n]$  with organic functional groups with organic monomers, oligomers, and polymers possessing functional groups are expected to have increased performance capabilities with respect to the former nonhybrid nanocomposites.<sup>15–20</sup> We already reported the crosslinking reaction and biodegradability of itaconate-unit-incorporated poly(butylene succinate) (PBSI) prepared by the reaction of SA, BD, and itaconic acid (IA),<sup>21</sup> all of which are inexpensive and can be derived from biomass resources.<sup>22</sup> The itaconate C=C bond of PBSI can be reacted with acryl groups incorporated into polysilsesquioxanes. This study

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describes the synthesis and properties of new organic-inorganic hybrid composites of PBSI and methacryl-group-substituted polysilsesquioxanes (ME-PSQ) prepared from relatively inexpensive 3-(trimethoxysilyl)propyl methacrylate (TMSPM).

## EXPERIMENTAL

### Materials

SA, BD, IA, titanium tetra-*n*-butoxide, and benzoyl peroxide (BPO) were purchased from Kanto Chemical (Tokyo, Japan). TMSPM and 10 wt % tetramethylammonium hydroxide (TMAOH) in water were purchased from Sigma-Aldrich Japan Co., Ltd. (Tokyo, Japan).

### Preparation of PBSI

The synthetic scheme of PBSI is shown in Figure 1. The BD/SA/IA feed molar ratio was 2.0 : 1.0 : 1.0. The synthetic procedure was as follows: To a mixture of BD (29.7 g, 0.330 mol), SA (19.5 g, 0.165 mol), and IA (21.5 g, 0.165 mol) was added titanium tetra-*n*-butoxide (35 mg, 0.10 mmol) as a catalyst, and condensation polymerization was carried out at 150°C under 150 Torr for 5 h and then at 160°C under 30 Torr for 6 h. After cooling to room temperature, the product was dissolved in chloroform (5 mL) and precipitated with methanol (1.0 L). The precipitate was washed with methanol and dried at room temperature *in vacuo* to give PBSI (22.4 g) as a yellow powder in a 39% yield.

### Preparation of ME-PSQ

Figure 2 shows the synthesis procedure for ME-PSQ, which is referred to the literature<sup>23</sup> of the synthesis of poly(amimopropyl/phenyl)silsesquioxanes by the reaction of  $\gamma$ -aminopropyltriethoxysilane and phenyltriethoxysilane in a mixture of ethanol and water with TMAOH. To a mixture of ion-exchanged water (25 mL), ethanol (75 mL), and a 10 wt % tetramethylammonium hydroxide aqueous solution (1.0 mL, 1.1 mmol) was added TMSPM (20 mL, 84 mmol). The mixture was stirred for 24 h at room temperature and allowed to stand for 1 day. The

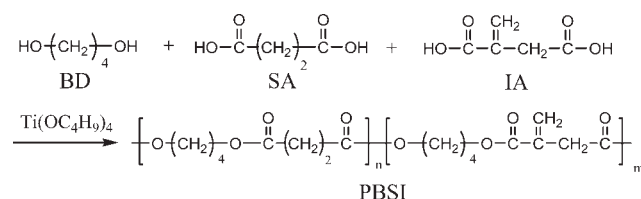


Figure 1 Synthetic scheme of PBSI.

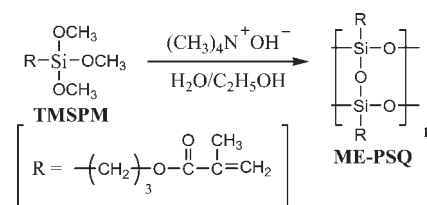


Figure 2 Synthetic scheme of ME-PSQ.

formed precipitate was collected by decantation, washed by vacuum filtration with ion-exchanged water/ethanol (one-third by volume), and then washed again with ethanol. The rinsed product was dried *in vacuo* for 24 h at room temperature to give ME-PSQ (8.4 g) as a colorless, viscous liquid in a 56% yield.

### Preparation of PBSI/ME-PSQ hybrid composites

To a solution of PBSI (1.00 g) and ME-PSQ (0.56 g) in tetrahydrofuran (THF; 25 mL) was added BPO (78 mg), and the mixture was stirred for 12 h at 40°C. The obtained solution was poured onto a Teflon plate, dried at room temperature for 1 day, and further dried *in vacuo* at room temperature. The mixture was put in an electric oven, heated at 80°C for 8 h, and then at 130°C for 2 h to give a PBSI/ME-PSQ hybrid composite (hybrid I). In a similar manner, except for the use of 1.12 or 2.24 g of ME-PSQ and 106 or 162 mg of BPO, PBSI/ME-PSQ hybrid composites (hybrid II and hybrid III) were prepared. For comparison, PBSI (1.00 g) was cured in the presence of BPO (50 mg) under the same conditions used for the preparation of the hybrid composites. The abbreviation for the cured PBSI is C-PBSI.

### Measurements

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on a Bruker AV-400 (400 MHz) (Madison, WI) with CDCl<sub>3</sub> as a solvent. Gel permeation chromatography (GPC) of PBSI and ME-PSQ was carried out at 40°C on a Shimadzu LC-10A series apparatus (Kyoto, Japan) equipped with two PLgel 5- $\mu$ m mixed-D GPC columns (Polymer Laboratories, Ltd. (Amherst, MA); linear range of molecular weight = 200–400,000) and a refractive-index detector. Dimethylformamide (DMF) was used as an eluent at a flow rate of 0.5 mL/min. Polystyrene standards with a narrow molecular weight distribution [weight-average molecular weight ( $M_w$ ) = 580–377,400] were used for molecular weight calibration. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu FT-IR 8100 by the KBr pellet or attenuated total reflectance method. The differ-

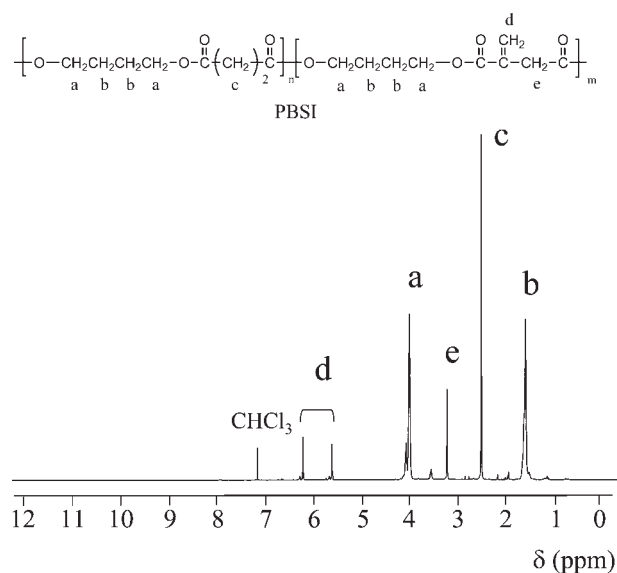


Figure 3  $^1\text{H}$ -NMR spectrum of PBSI in  $\text{CDCl}_3$ .

ential scanning calorimetry (DSC) measurements were performed on a PerkinElmer Pyris 1 differential scanning calorimeter (Yokohama, Japan) at a heating rate of  $20^\circ\text{C}/\text{min}$  in a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was performed on a Rheograph Solid (Toyo Seiki Co., Ltd., Tokyo, Japan) with a chuck distance of 20 mm, a frequency of 10 Hz, and a heating rate of  $2^\circ\text{C}/\text{min}$ . The 5% weight loss temperature was measured on a PerkinElmer TGA 7 thermogravimetric analyzer in a nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$ . Solubility was tested after a mixture of a sample (10 mg) and solvent (0.5 mL) was sonicated for 5 min and then allowed to stand for 24 h at room temperature.

## RESULTS AND DISCUSSION

### Characterization of PBSI

The number-average molecular weight ( $M_n$ ) and  $M_w$  values measured by GPC for PBSI prepared at the BD/SA/IA feed molar ratio of 2.0 : 1.0 : 1.0 were 4200 and 8300, respectively. Because the molecular weight and yield of PBSI were not so high, it was supposed that the unit ratio of the introduced BD, SA, and IA for PBSI was different from the feed molar ratio. Figure 3 shows the  $^1\text{H}$ -NMR spectrum of PBSI in  $\text{CDCl}_3$ . The  $^1\text{H}$  signals of butyleneoxy units can be observed at 4.0 (H-a) and 1.7 ppm (H-b). The signals of the butyleneoxy of butylene succinate unit cannot be distinguished from those of the butylene itaconate unit. A weak  $^1\text{H}$ -signal peak at 4.1 ppm is probably due to the H-a protons of the terminal hydroxylbutyl group. The ethylene protons of the succinate unit can be observed at 2.5 ppm (H-

c), and aliphatic and olefinic protons of the itaconate unit can be observed at 3.2 (H-e) and 5.7 and 6.2 ppm (H-d). From the integral ratio of their  $^1\text{H}$  signals, the introduced unit ratio was calculated to be 2.9 : 1.7 : 1.0 BA/SA/IA. Although the SA/IA feed molar ratio was 1.0, the amount of actually introduced itaconate unit was lower than that of succinate unit. Also, the fact that BA/(SA + IA) was 2.9 : 2.7 indicated that the terminal group of PBSI was mainly a hydroxylbutyl group of the BA unit. However, we could not detect the  $^1\text{H}$  signals of the terminal hydroxyl or carboxylic acid groups, probably because of broadening, although the hydroxyl proton of BD and carboxylic proton of SA can be observed at 4.5 and 11.8 ppm, respectively. Assuming that both terminal groups of PBSI were hydroxylbutyl groups, the average unit numbers per molecule were calculated to be 14.5 for BD, 8.5 for SA, and 5.0 for IA from the introduced unit ratio of 2.9 : 1.7 : 1.0. From these values,  $M_n$  by the NMR method for PBSI was estimated to be 2500, which was somewhat lower than the  $M_n$  value (4200) by the GPC method using polystyrene standards.

### Characterization of ME-PSQ

Figure 4 shows the  $^1\text{H}$ -NMR spectrum of ME-PSQ prepared by the reaction of TMSPM and TMAOH in water/ethanol. The  $^1\text{H}$  signals observed at 3.6 ppm for methoxy protons of TMSPM almost disappeared for ME-PSQ, and all the protons of the methacryloxypropyl group can be observed, indicating the formation of silsesquioxanes. The  $M_n$  and  $M_w$  values measured by GPC with polystyrene standards for ME-PSQ were 5900 and 15,000, respectively. The GPC chart is shown in Figure 5. The shoulder peak indicated by mark a can be observed in a lower molecular weight region. The  $M_n$  and  $M_w$  values for part a are 1600 and 1800, respectively. The  $M_n$  value

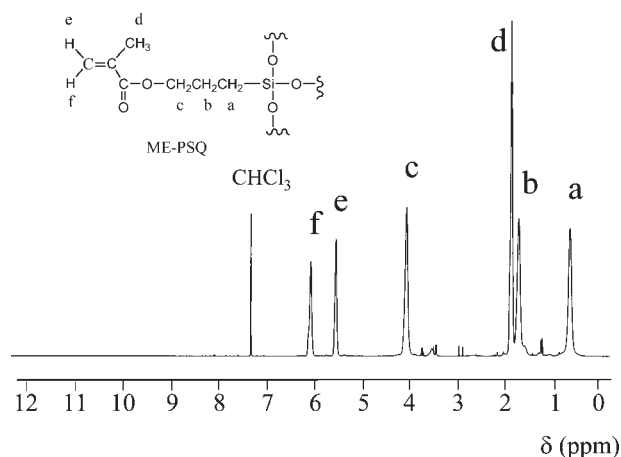
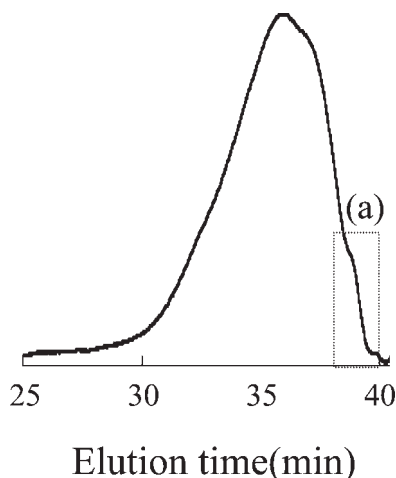


Figure 4  $^1\text{H}$ -NMR spectrum of ME-PSQ in  $\text{CDCl}_3$ .



**Figure 5** GPC chart of ME-PSQ (refractive-index detector).

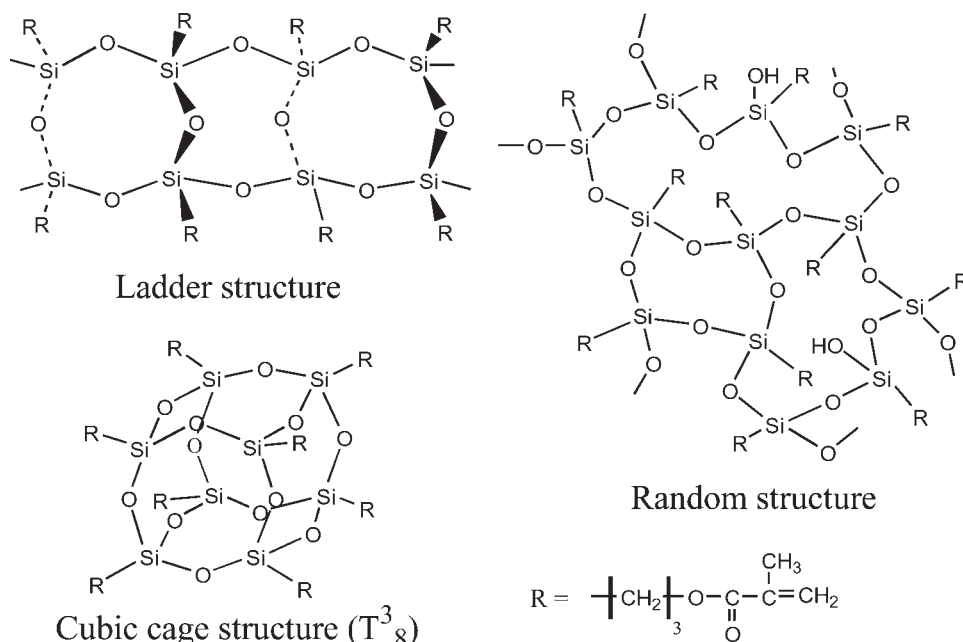
is close to the theoretical molecular weight (1432) of the corresponding fully condensed  $T_8^3$  cubic polyhedral oligomeric silsesquioxane (POSS) derivatives. However, the main GPC peak has a much higher molecular weight than the cubic POSS, and this indicates that the content of ladder and random polysilsesquioxanes shown in Figure 6 and/or POSSs ( $T_{10}^3$ ,  $T_{12}^3$ ,  $T_{14}^3$ , etc.) bigger than cubic  $T_8^3$  POSS is relatively large.

#### Synthesis and thermal properties of PBSI/ME-PSQ hybrid composites

The PBSI/ME-PSQ [1.00/0.56, 1.00/1.12, and 1.00/2.24 w/w (g/g)] hybrid composites (hybrids I, II, and III) were prepared by the reaction of PBSI and

ME-PSQ in the presence of BPO finally at 130°C. The feed molar ratios of itaconate/methacrylate were calculated to be 2.02/3.12, 2.02/6.24, and 2.02/12.48 for hybrids I, II, and III on the basis of the composition of PBSI estimated by  $^1\text{H-NMR}$ . The thermal properties of PBSI/ME-PSQ were investigated with respect to the cured PBSI without ME-PSQ (C-PBSI). All the hybrid composites and C-PBSI were insoluble in organic solvents such as acetone, DMF, chloroform, and THF, in which both PBSI and ME-PSQ dissolved; this suggested the formation of a crosslinked structure. Figure 7 shows FTIR spectra of the hybrid composites and C-PBSI. The absorption peak at  $1610\text{ cm}^{-1}$ , related to the itaconate and methacrylate  $\text{C}=\text{C}$  of PBSI and ME-PSQ, did not completely disappear for all the hybrid composites, and this indicated that some unsaturated  $\text{C}=\text{C}$  groups remained. Because the feed molar ratio of methacrylate to itaconate for the hybrid composites was much larger than 1, it is thought that some of the methacryl groups connected to a rigid polysilsesquioxane framework remained because of the steric hindrance. On the other hand, no  $\text{C}=\text{C}$  absorption peak was observed for C-PBSI, and this indicated that the itaconate  $\text{C}=\text{C}$  groups incorporated into the flexible PBS segment completely crosslinked.

Table I summarizes the glass-transition temperature ( $T_g$ ) measured by DSC for PBSI, C-PBSI, and PBSI/ME-PSQ hybrid composites. The cured C-PBSI showed much higher  $T_g$  values than PBSI because of the crosslinking reaction of the itaconate group. Hybrid I and hybrid II showed  $T_g$  values higher than that of PBSI but rather lower than that of C-PBSI. This result is in agreement with the results



**Figure 6** Probable structure of ME-PSQ.

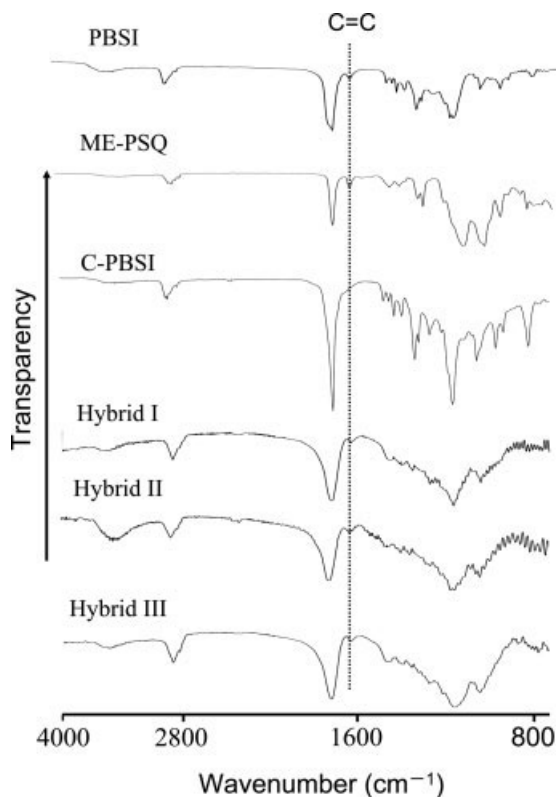


Figure 7 FTIR spectra of PBSI, ME-PSQ, C-PBSI, and PBSI/ME-PSQ hybrid composites.

of FTIR; that is, some unsaturated C=C groups remained for the hybrids. Also, it has been reported that the incorporation of POSS units into a epoxy-amine curing system often results in the lowering of  $T_g$ . The low  $T_g$ 's were attributed to the soft linkage between the epoxy groups and POSS and the low conversions of the epoxy curing reaction arising from steric hindrance.<sup>24-27</sup> The  $T_g$  value of hybrid II was a little higher than that of hybrid I, and this was reasonable because the ME-PSQ content of hybrid II was higher than that of hybrid I. However,  $T_g$  was not detected by the DSC method for hybrid III, which had the highest ME-PSQ content.

TABLE I  
 $T_g$  Values Measured by DSC and DMA and  $T_d$  Values Measured by TGA for PBSI, C-PBSI, and PBSI/ME-PSQ Hybrid Composites

Sample	$T_g$ (°C)		$T_d$ (°C)
	DSC	DMA	
PBSI	-43	—	304.2
C-PBSI	-15	10	333.6
Hybrid I	-25	-10	346.4
Hybrid II	-22	-1	378.2
Hybrid III	—	7	405.5

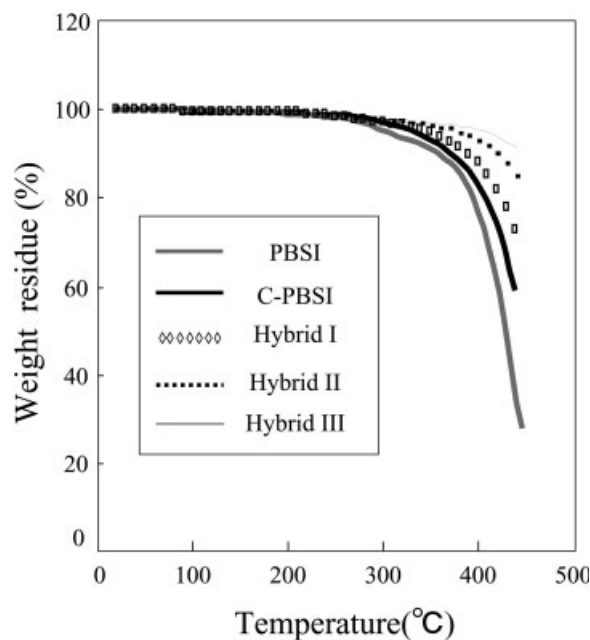
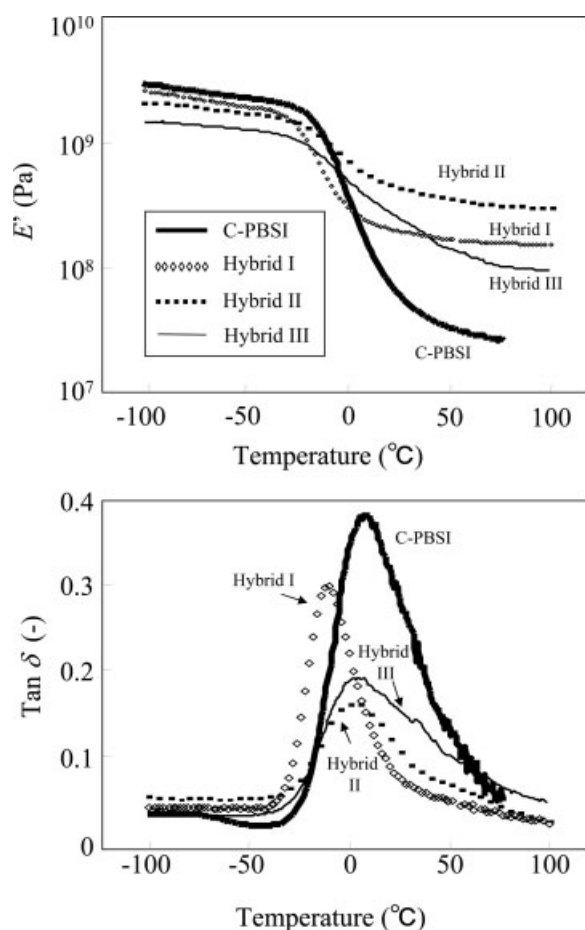


Figure 8 TGA curves of PBSI, C-PBSI, and PBSI/ME-PSQ hybrid composites.

Figure 8 shows thermogravimetric analysis (TGA) curves of PBSI, C-PBSI, and PBSI/ME-PSQ hybrid composites. The 5 wt % weight loss temperature ( $T_d$ ) of the hybrids increased with increasing ME-PSQ content, as shown in Table I. In particular,  $T_d$  of hybrid III was over 400°C. In contrast to the results of DSC, all the hybrid composites showed higher  $T_d$  values than C-PBSI. To improve  $T_d$ , the formation of a hybrid with ME-PSQ was very effective.

### Dynamic mechanical properties of PBSI/ME-PSQ hybrid composites

Figure 9 shows viscoelastic curves of C-PBSI and PBSI/ME-PSQ hybrid composites.  $T_g$ , which was not detected by DSC for hybrid III, was observed by DMA. The  $T_g$  measured by DMA of the PBSI/ME-PSQ hybrid composites increased with increasing ME-PSQ content (Table I). However, in agreement with the results of DSC, the  $T_g$  measured by DMA for all the hybrid composites was lower than that of C-PBSI. The storage modulus ( $E'$ ) of C-PBSI dropped around -10 to 10°C. The decrease of  $E'$  with rising temperature for all the hybrid composites was much less than that of C-PBSI. Among the hybrids, hybrid II showed the highest  $E'$  value in the rubbery state. The reason that hybrid III showed a lower  $E'$  value in the rubbery state may be attributed to the fact that excess ME-PSQ could not react with PBSI, and the unreacted ME-PSQ was phase-separated. Actually, hybrid I and II films were transparent, but a hybrid III film was translucent.



**Figure 9** Dynamic viscoelastic curves of C-PBSI and PBSI/ME-PSQ hybrid composites.

### CONCLUSIONS

Hybrid composites of PBSI with a BD/SA/IA unit ratio of 2.9 : 1.7 : 1.0 and ME-PSQ were prepared, and their properties were investigated in comparison with those of PBSI cured at 130°C in the presence of BPO. The hybrid composites (hybrids I, II, and III) showed much higher  $T_d$  and  $E'$  values in the rubbery state than the crosslinked PBSI, and their values increased with increasing ME-PSQ content. Although  $T_g$  measured by DMA for the hybrid composites somewhat increased with increasing ME-PSQ content,  $T_g$  was a little lower than that of the crosslinked PBSI. Consequently, the formation of hybrid composites of a biobased polyester and a polysilsesquiox-

ane is a very effective method for improving  $E'$  at an elevated temperature and  $T_d$ .

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