

# Properties of Poly(butylene terephthalate) Chain-Extended by Epoxycyclohexyl Polyhedral Oligomeric Silsesquioxane

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**ABSTRACT:** Epoxycyclohexyl polyhedral oligomeric silsesquioxane (epoxy-POSS) was used to prepare a chain-extended poly(butylene terephthalate) (PBT) with a twin-screw extruder. The effect of epoxy-POSS on the melt flow index, mechanical properties, rheological behavior, and thermal properties of chain-extended PBT was investigated. PBT had an intrinsic viscosity of 1.1 dL/g and a carboxyl content of 21.6 equiv/10<sup>6</sup> g, but the PBT chain-extended with 2 wt % epoxy-POSS had an intrinsic viscosity of 1.7

dL/g and a carboxyl content lower than 7 equiv/10<sup>6</sup> g. After the addition of epoxy-POSS, the melt flow index of PBT dramatically decreased, the elongation at break increased greatly, the tensile strength increased slightly, and the thermal stability was also improved. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 825–830, 2008

**Key words:** polyesters; reactive extrusion; polyhedral oligomeric; silsesquioxane; chain extender

## INTRODUCTION

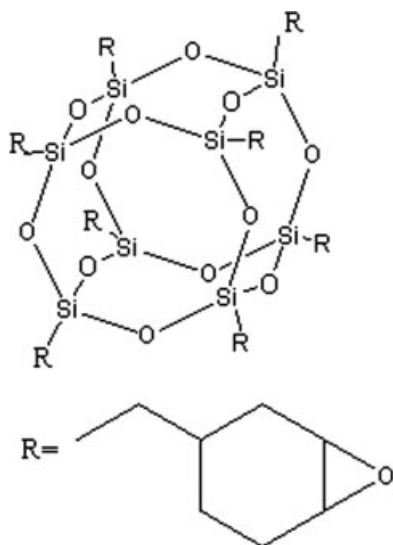
In recent years, the area of polymeric nanocomposites has provoked much interest. Polyhedral oligomeric silsesquioxane (POSS) based materials, both as organic–inorganic hybrids and as polymer nanocomposites, have been studied widely. The POSS molecule contains a basic polyhedral silicone–oxygen nanostructure skeleton or cage with a precisely defined Si–Si diameter of 0.53 nm. The cage may have 8 or 12 Si atoms (with a Si/O ratio of 2 : 3) located at the corner of the cage, which are surrounded by 8 or 12 organic groups, respectively (Fig. 1).<sup>1</sup> POSS molecules are physically large with respect to monomer dimensions and nearly equivalent in size to most polymer segments. POSS can be effectively incorporated into polymers by copolymerization, grafting, or even blending through traditional processing methods. POSS and its derivatives have been reported as candidates for modifying a wide range of thermoplastics, such as polyolefin,<sup>2–4</sup> polystyrene,<sup>5</sup> poly(methyl methacrylate),<sup>6</sup> polycarbonate,<sup>7</sup> poly(ethylene terephthalate),<sup>8–10</sup> and polyamide,<sup>11</sup> and a few thermoset systems.<sup>12–14</sup> The incorporation of POSS or its derivatives into poly-

mers can lead to some dramatically improved properties, such as increases in the use temperature, oxidation resistance, and surface hardening and improved mechanical properties, as well as reductions in flammability, heat evolution, and viscosity during processing.<sup>15</sup>

Poly(butylene terephthalate) (PBT) is well known as a commercial engineering plastic with widespread applications in fibers, automobile parts, and engineering components. It is produced by the transesterification and then polycondensation of a mixture of dimethyl terephthalate and 1,4-butanediol *in vacuo*. However, the general grades of PBT have relatively low molecular weights and cannot meet the requirements of some application fields. Therefore, great efforts have been made to increase its molecular weight. The use of a so-called chain extender<sup>16–24</sup> has been considered a rather attractive method. It is reported that the most effective ones are those that react with the carboxyl end groups and liberate byproducts (addition type) such as diepoxies. The diepoxies can react with both carboxyl and hydroxyl groups. From these reactions, new hydroxyl groups are formed that can lead to branching or even crosslinking. However, it has been reported that a limited degree of branching gives a poly(ethylene terephthalate) melt the ability to be molded in a very fine closed-cell foam.<sup>25</sup> Bikaris and Karayannidis<sup>21–23</sup> synthesized three types of diepoxies and used them as chain extenders for PBT and poly(ethylene terephthalate). Guo<sup>24</sup> described a high-reactivity diepoxy,

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**Figure 1** Schematic diagram of POSS. R is an epoxy-cyclohexyl group.

diglycidyl tetrahydrophthalate, as a chain extender that could react with the hydroxyl and carboxyl end groups of PBT at a very fast reaction rate and a relatively high temperature.

Epoxy-functionalized POSS has been widely studied in epoxy resins as a nanofiller and cure accelerator.<sup>13,26</sup> To date, there have been few reports about epoxy-functionalized POSS chain-extended polyesters. Here, epoxy-cyclohexyl polyhedral oligomeric silsesquioxane (epoxy-POSS; a mixture of  $n = 8$ ,  $n = 10$ , and  $n = 12$ ; a schematic diagram of  $n = 8$  is shown in Fig. 1) was selected as an effective chain extender for PBT. The epoxy-POSS could easily react with the carboxyl group and hydroxyl group, leading to the chain extension of PBT. As expected, the mechanical and thermal properties of PBT were improved when epoxy-POSS was added.

## EXPERIMENTAL

PBT (grade 4500) was supplied by Jiangyin Yongtong Chemical Co. (Jiangsu Province, China). Epoxy-POSS (grade EP0408) was supplied by Hybrid Plastic (Michigan, USA). PBT pellets were dried at 120°C for 4 h in a vacuum oven before processing to remove water. A master batch of epoxy-POSS in PBT (2 wt %) was prepared by the mixing of PBT and a POSS/trichloromethane solution first and then drying at 80°C for 12 h in a vacuum oven.

The blends were extruded with a Berstoff twin-screw extruder (type ZE25, Berstoff Corp. Hanover, Germany, length/diameter ratio = 41, screw diameter = 25 mm) at a screw speed of 200 rpm and torques of 40–50%. The temperature profile of the barrel was 40–230–230–235–235–240–240–245–250°C

from the hopper to the die. The extrudates were cooled in a water bath, pelletized, and dried in an air oven at 80°C for 8 h. Injection molding was carried out in a plastic injection-molding machine (HTB110X/1, Ningbo Haitian Co., Jiangsu Province, China) to obtain specimens for tests of the tensile strength, elongation at break (ASTM D 638; thickness = 3.2 mm), flexural modulus and strength (ASTM D 790; thickness = 3.2 mm), and impact strength (ASTM D 256; thickness = 3.2 mm). The barrel temperature profile of the injection molding was 240–250–250–250–260°C, and the mold temperature was 60°C.

The carboxyl end group content in PBT was measured according to the Pohl method.<sup>27</sup> The solution viscosity was measured at  $25 \pm 0.1^\circ\text{C}$  with an Ubbelohde viscometer (Shanghai Medical Group, Shanghai, China) on a solution of 60 : 40 (w/w) phenol/tetrachloroethane at a polymer concentration of about 0.5 wt %. The insoluble part of the samples was removed by filtration and weighed. The intrinsic viscosity ( $[\eta]$ ) of each sample was calculated with a single-point measurement:

$$[\eta] = [2(\eta_{sp} - \ln \eta_{sp})]^{0.5}/c$$

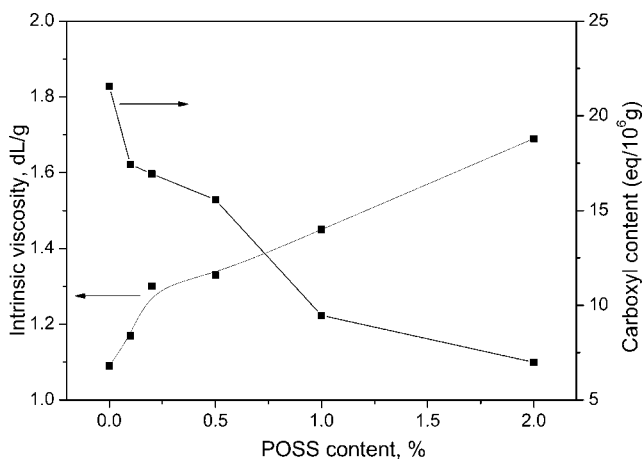
where  $\eta_{sp}$  is the specific viscosity and  $c$  is the concentration. The degree of crosslinking (DC),<sup>28</sup> defined as the percentage of the insoluble gel, was determined as follows: 250 mg of PBT was dissolved in 25 mL of 60 : 40 (w/w) phenol/tetrachloroethane at 120°C for 4 h. After the removal of the soluble portion by filtration, the insoluble gel was washed well with acetone, dried, and weighed.

The tensile and flexural tests were carried out at room temperature with an Instron (Instron Corp., Tucson, AZ) 4465 tester at speeds of 50 and 2 mm/min, respectively. The Izod impact tests were carried out on Ray-Ran testing equipment (Ray-Ran Test Equipment, Ltd., Warwickshire, United Kingdom). A minimum of five specimens were tested for each reported value of the tensile, flexural, and impact strengths. The melt flow index (MFI; ASTM 1238) was measured with a 5MPCA MFI testing instrument (Ray-Ran Test Equipment Ltd., Warwickshire, United Kingdom) with a 2.16-kg load at 250°C.

The thermal properties of PBT at the processing temperature were tested in terms of the torque change in the mixing chamber of a Haake RC90 rheometer (Haake Co., Offenburg, Germany) at 250°C and 60 rpm.

The melt viscosity was measured with an Instron 4467 capillary rheometer (Instron Corp.) at 240°C. The capillary die had a length/diameter ratio of 40/1 and an entrance angle of 180°. The Rabinowitch and Bagley corrections were applied to all the experimental data.

The thermal properties were measured with a PerkinElmer (Waltham, MA) Pyris 1 differential scan-



**Figure 2** Variation of the intrinsic viscosity and carboxyl group content of PBT with the epoxy-POSS content.

ning calorimeter. The samples were first heated at a rate of 20°C/min from 25 to 250°C, maintained there for 2 min to remove the thermal history, and cooled at a rate of 10°C/min to 25°C. The cooled samples were then reheated at a rate of 10°C/min to 250°C to obtain the melting temperature and crystallization temperature.

## RESULTS AND DISCUSSION

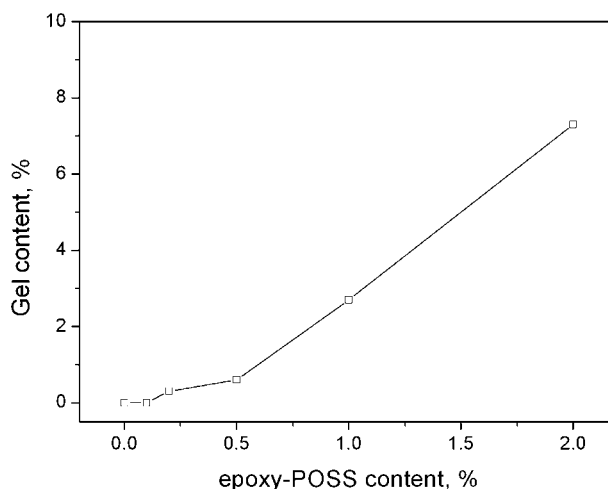
### Chain extension of PBT by epoxy-POSS

The theoretical amount of the chain extender ( $w_{\text{theo}}$ ) to be added to PBT was calculated as follows:<sup>16</sup>

$$w_{\text{theo}}(\%) = \frac{1}{8} G \times CC_0 \times 10^{-4}$$

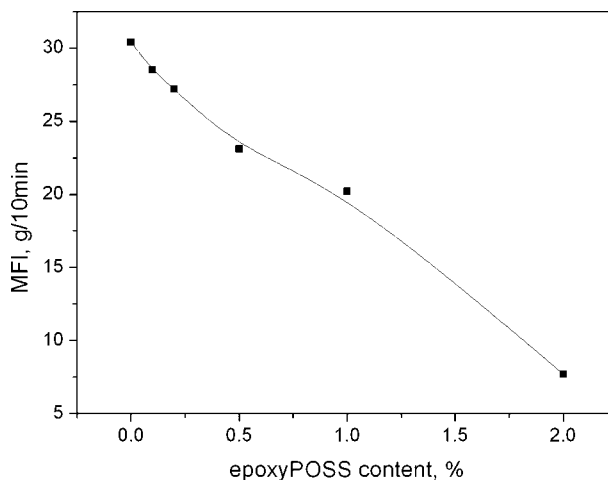
where  $G$  is the molecular weight of the chain extender ( $G = 1416$  for epoxy-POSS with eight Si atoms) and  $CC_0$  is the carboxyl content of the initial PBT, as stated in Figure 2. Thus,  $w_{\text{theo}}$  was 0.38% in this case.

The variation of the intrinsic viscosity and carboxyl end group content of PBT is shown in Figure 2. The intrinsic viscosity increased gradually from 1.1 to 1.7 dL/g and the carboxyl end group content decreased from 21.6 to 7.0 equiv/10<sup>6</sup> g when the epoxy-POSS content increased from 0 to 2%. The epoxy group can react with both the carboxyl group and hydroxyl group of PBT at high temperatures but reacts more preferentially with the carboxyl group than the hydroxyl group. Therefore, the chain-extended PBT has a relatively low carboxyl group concentration. According to Figure 2, the probed high viscosity and low carboxyl content mean that epoxy-POSS successfully reacted with the carboxyl end group and extended the PBT chain.



**Figure 3** Effect of the epoxy-POSS content on DC.

However, because of more than two epoxy groups existing in the epoxy-POSS and the reactions between the epoxy group and the carboxyl or hydroxyl end group of PBT, the epoxy group of epoxy-POSS can further react with PBT to form a branched chain or crosslink. This reaction can cause some problems during the processing of PBT. The effect of the epoxy-POSS content on DC is displayed in Figure 3. DC was negligible when the epoxy-POSS content was less than 1% (2.6 times  $w_{\text{theo}}$ ); DC became 7.3% when the epoxy-POSS content was 2% (5.2 times  $w_{\text{theo}}$ ). Many researchers have reported that epoxy-functional POSS can react completely with the amide group in an epoxy resin.<sup>29,30</sup> Bikiaris and Karayannidis<sup>22</sup> reported that in the case of diepoxide chain-extended PBT, crosslinking appeared after 30 min or even a longer time of reaction when the diepoxide content was 2 times  $w_{\text{theo}}$ . In this study, DC was quite low even at a high POSS content (2.6 times  $w_{\text{theo}}$ ), and this



**Figure 4** Variation of MFI of PBT with the epoxy-POSS content.

**TABLE I**  
Effects of the Epoxy–POSS Content on the Mechanical Properties

Epoxy–POSS content (%)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Izod impact strength (J/m)
0	50.8	25.5	72.4	2112	51.0
0.1	51.9	47.6	76.5	2259	50.1
0.2	52.7	83.4	78.3	2252	52.4
0.5	53.3	76.3	77.2	2242	49.0
1	53.5	108.0	77.6	2253	51.7
2	53.3	90.8	77.2	2269	51.0

means that the branching reaction and the crosslinking reaction should be much slower than the linear chain-extension reaction because of steric hindrance and a short reaction time. This is favorable for the processing.

The variation of MFI of PBT with the epoxy–POSS content is shown in Figure 4. MFI linearly decreased with increasing epoxy–POSS content, and this was mainly attributed to the increase in the molecular weight of PBT.

### Mechanical properties of PBT

Table I shows the results for the tensile and flexural strength and notched Izod impact of the epoxy–POSS chain-extended PBT. An increase in the epoxy–POSS content resulted in a dramatic increase in the elongation at break, a slight increase in the tensile strength, flexural strength, and flexural modulus, and little change in the notched Izod impact strength.

Figure 5 shows the stress–strain curves of the epoxy–POSS chain-extended PBT. The stress–strain curves change with an increase in the epoxy–POSS content. The unmodified PBT was a quasibrittle polymer, and the elongation at break was about 25%. The elongation at break reached 130% when 1% epoxy–POSS was added, but the elongation at break

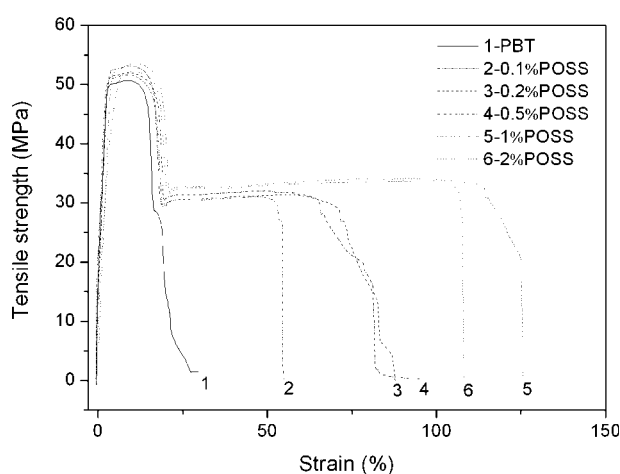
decreased slightly when 2% epoxy–POSS was added, probably because of the excessive crosslinking of PBT.

### Differential scanning calorimetry analysis

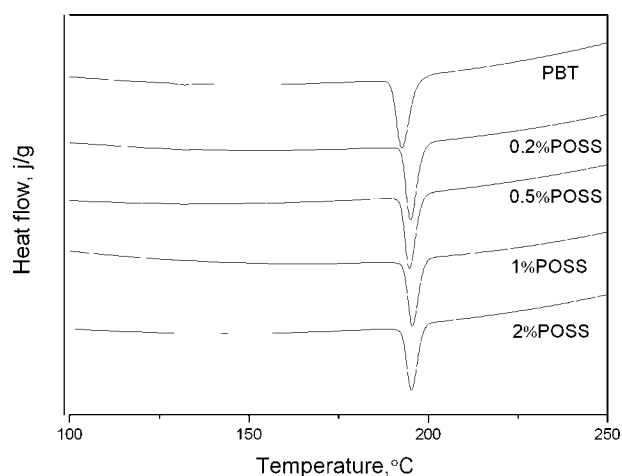
Figures 6 and 7 show the crystalline and melt curves of epoxy–POSS modified PBT, respectively. The melting temperature decreased as the epoxy–POSS concentration increased. This can be explained by the fact that, in addition to the extension of PBT chains, branches and crosslinks that attach to the polymer chains can be formed during the chain-extension reaction. The side branches are defects in the crystal lamellae; hence, the heavily chain-extended PBT has a lower melting point. That is also consistent with the fact that the chain-extended PBT has higher values of the crystallization temperature, as shown in Figure 6. The crystallization temperature increased with increasing POSS concentration, indicating that epoxy–POSS can act as an effective nucleating agent, accelerating the crystallization rate of PBT.

### Capillary rheological behavior

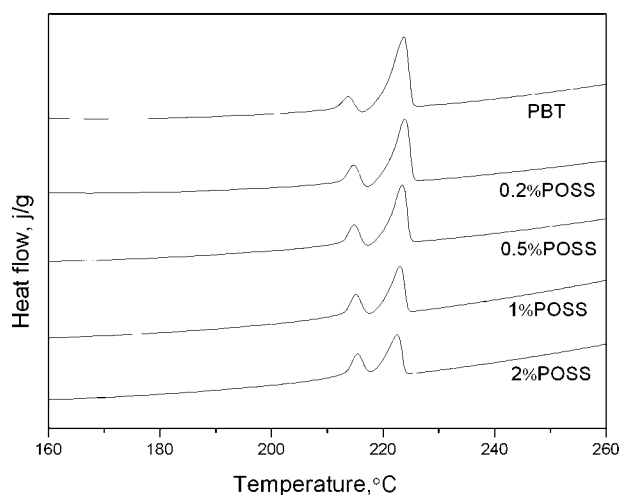
The apparent shear viscosity ( $\eta_a$ ) versus the shear rate ( $\dot{\gamma}$ ) of epoxy–POSS chain-extended PBT is shown in Figure 8. All the materials showed a shear-thin-



**Figure 5** Stress–strain curves of epoxy–POSS chain-extended PBT.



**Figure 6** Nonisothermal crystallization curves of epoxy–POSS chain-extended PBT.



**Figure 7** Reheating melting curves of epoxy-POSS chain-extended PBT.

ning behavior, and the viscosity decreased with an increasing shear rate. The bilogarithmic plots are based on a power-law model:

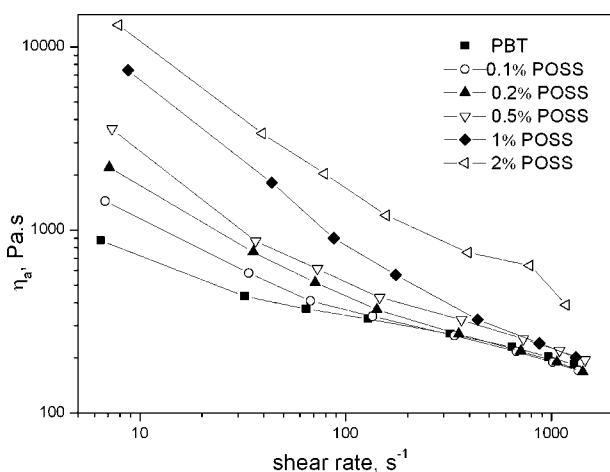
$$\eta_a = k\gamma^{n-1}$$

so

$$\log \eta_a = \log k + (n - 1) \log \gamma$$

where  $k$  is the consistency index and  $n$  is the power-law index.

Figure 8 shows that all the materials follow a power-law relationship at a low apparent shear rate. The value of the apparent shear viscosity at the same shear rate increased with increasing epoxy-POSS content because of the increase in the molecular weight of PBT. Table II lists the power-law indices of PBT. The power-law index gradually decreased with increasing epoxy-POSS content.



**Figure 8** Capillary rheological curves for epoxy-POSS chain-extended PBT.

**TABLE II**  
Power-Law Index of Epoxy-POSS Chain-Extended PBT

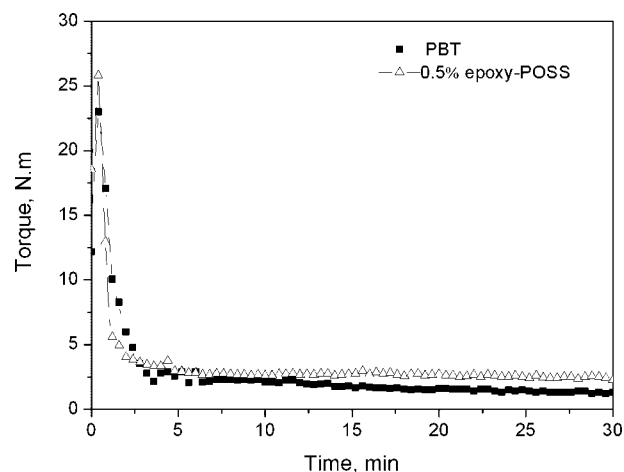
Epoxy-POSS content (%)	0	0.1	0.2	0.5	1	2
Power-law index	0.73	0.63	0.55	0.51	0.33	0.36

### Thermal properties

To test the thermal stability of the chain-extended PBT at the processing temperature, PBT pellets were mixed in a Haake mixer at 250°C. The torque curves are shown in Figure 9. The torque value of the chain-extended PBT was higher than that of the original PBT after they were completely melted. The torque values of PBT changed from 2.4 to 1.3 N m when the mixing time changed from 5 to 30 min, whereas that of chain-extended PBT changed only from 2.9 to 2.3 N m. These results indicate that the epoxy-POSS chain-extended PBT has better thermal stability than PBT, possibly because of the presence of a small amount of residual epoxy in the chain-extended PBT acting as a stabilizer and a lower concentration of carboxyl end groups on the PBT chains.<sup>24</sup>

### CONCLUSIONS

Epoxy-POSS chain-extended PBT was prepared in a twin-screw extruder. Epoxy-POSS is an effective chain extender for PBT. PBT had an intrinsic viscosity of 1.1 dL/g and a carboxyl content of 21.6 equiv/10<sup>6</sup> g, but the PBT chain-extended with 2 wt % epoxy-POSS had an intrinsic viscosity of 1.7 dL/g and a carboxyl content lower than 7 equiv/10<sup>6</sup> g. MFI of PBT dramatically decreased with increasing epoxy-POSS content. In addition, an increase in the epoxy-POSS content resulted in a dramatic increase in the elongation at break and a slight increase in the ten-



**Figure 9** Torque curves for PBT and 0.5% epoxy-POSS chain-extended PBT.

sile strength, flexural strength, and flexural modulus. The thermal stability was also improved.

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