

Synthesis and Characterizations of Branched Poly(butylene succinate) Copolymers with 1,2-Octanediol Segments

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Received 14 September 2009; accepted 22 January 2010

DOI 10.1002/app.32168

Published online 13 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Branched poly(butylene succinate) (PBS) copolymers were synthesized, from succinic acid (SA), 1,4-butanediol (1,4-BD), and 1,2-octanediol (1,2-OD) through a two-step process containing esterification and polycondensation, with different mole fractions of 1,2-OD segments. The branched PBS copolymers were characterized with $^1\text{H-NMR}$, differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), thermogravimetric analysis (TGA), dynamic rheological testing, and tensile properties analysis. The results of DSC and WAXD show that, with the increasing of the 1,2-OD segments content, the glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), and the degree of crystallinity (X_c) decrease. While the crystal structure of PBS does not change by intro-

ducing 1,2-OD segments. The results of TGA and dynamic rheological testing indicate that the thermal stability of neat PBS is improved with the addition of 1,2-OD segments. The incorporation of 1,2-OD segments has some effects on the rheological properties of PBS, such as complex viscosities ($|\eta^*|$), storage modulus (G'), and loss modulus (G''). Tensile testing demonstrates that the elongation at break is improved significantly with increasing 1,2-OD segments content, but without a notable decrease of tensile strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2538–2544, 2010

Key words: poly(butylene succinate); branched copolymer; crystallization behavior; rheological property; tensile property

INTRODUCTION

Recently, biodegradable polymers have attracted great attention because of their environmental compatibility, among which the aliphatic polyesters are the most studied materials and regarded as high performance, environment friendly, and low cost biodegradable plastics.^{1–4} Compared with other aliphatic polyesters, poly(butylene succinate) (PBS) exhibits not only relative higher melting point but also better thermomechanical, processing, and biodegradation properties. Consequently, PBS has been commercialized as a commodity polymer (e.g. BionolleTM) and is usually synthesized through the polycondensation reaction of succinic acid (SA) and 1,4-butanediol (1,4-BD).^{5,6} However, insufficient stiffness, low melt viscosity, and especially poor impact strength have limited its application range. Therefore, various approaches have been explored to overcome these disadvantages.^{7–11} For example, Zhao et al.¹² synthesized PBS through chain-extending

method, and showed that the intrinsic viscosities and molecular weights were enhanced compared with the neat PBS. However, transesterification reaction also occurred during the chain-extension process. Guo and coworkers^{13,14} had studied the composition and physical properties of PBS and its copolyesters poly(butylene succinate-co-propylene succinate), but the mechanical properties and rheological behaviors were not reported for the copolymers. Chae et al.¹⁵ investigated the mechanical properties of PBS copolymers, indicating that the addition of 2-methyl succinate segments could enhance the toughness of neat PBS, whereas the melt viscosity and melting temperature decreased considerably.

Apart from these researches, focusing on synthesizing PBS copolymers, introducing branched chains into the PBS is another route for improving the performance of PBS. Branched polymers possess higher melt strength and melt viscosity than those of linear polymer. In addition, branching can bring the tension stiffening effect, which can effectively help in the uniform stretching properties during film blowing processing. Particularly, branching can improve the tear strength of polyesters so as to resist propagation of cracks created by sharp objects. According to the size of chain branches, branched polymers can be divided into short-chain branches and long-chain branches. Short-chain branches reduce the degree of

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50673050.

crystallinity, while long-chain branches increase melt viscosities and endow elongational viscosities with tension stiffening behavior.^{16,17} Many researches have been devoted to trace the effect of branched chains on the structure and properties of aliphatic polyesters. Kim et al.¹⁸ prepared branched PBS copolymers by introducing trimethylol propane. The corresponding results showed that branching can change the rheological properties of PBS, whereas the mechanical properties were not reported. Jin et al.^{19,20} examined the effect of ethyl and *n*-octyl branches on the properties of PBS, indicating that the introduction of ethyl branches as well as *n*-octyl branches into PBS improved the biodegradation properties, the elongation at break, and tear strength without notable decrease of tensile strength and tensile modulus. However, branched PBS copolymers exhibited lower melt viscosity than that of linear PBS, which is unfavorable for the processing properties of PBS. In addition, Jin et al.²¹ also synthesized branched PBS copolymers with *N*-hexenyl side branches, and showed that the branching improved the biodegradability of PBS.

This article will report our results on the synthesis and characterizations of a series of branched PBS copolymers, with 1,2-octanediol as a branching agent, by a two-step process consisting of esterification and polycondensation. The main objective is to study the effect of chain branches on the structure, thermal behaviors, rheological properties, and tensile properties of neat PBS and branched PBS copolymers. Moreover, it is also important to correlate chains branching structure to macroscopic properties of branched PBS copolymers.

EXPERIMENTAL

Materials

SA was provided by Hexing Chemical Corporation (China) and was used as received. 1,4-BD was supplied by Tianjin Chemical Corporation (China), 1,2-octanediol (1,2-OD) was provided by Realsun Chemical Industry Corporation (China). Tetra-*n*-butyl-titanate (Ti(OBu)₄) as a catalyst was obtained from Beijing Chemical Company (China). Other chemicals and solvents were used as received without further purification.

Synthesis of branched PBS copolymers

Neat PBS and branched PBS copolymers were synthesized using a two-step reaction of esterification and polycondensation in melting state. As an example, synthesis process of branched PBS copolymer containing 15 mol % of 1,2-OD segments is described as follows. In the process of esterification, the reactor

was a three-necked flask with a mechanical stirrer, nitrogen inlet, and a condenser in a temperature-controlled oil bath. The reaction mixture, SA (47.3 g, 0.40 mol), 1,4-BD (33.66 g, 0.374 mol), 1,2-OD (9.66 g, 0.066 mol), was added into the reactor. Under N₂ gas atmosphere, the temperature was increased slowly to 145°C until the acid component melted completely. Water resulted from the reaction was collected using a trap device. Esterification reaction was considered as completed when no more water was produced, The weight of H₂O collected was around 95% of its theoretical value. For the polycondensation process, the catalyst Ti(OBu)₄ was added first and the temperature was gradually raised to the final reaction temperature of 220°C at pressure below 0.5 mmHg and maintained at this condition for 4 h, after the polymerization, the highly viscous product was cooled in the flask under nitrogen atmosphere.

The synthesized copolymer was dissolved in chloroform and then precipitated into excess amount of ice-cold methanol. The precipitate was washed with methanol and dried in vacuum at room temperature for 24 h. All the other polyesters were synthesized following the same procedure. The synthesized branched PBS copolymers are denoted PBSOS-5, PBSOS-10, and PBSOS-15, respectively, where "OS" in the sample code represents the 1,2-OD segments and the numbers following "OS" represent the mole fractions of 1,2-OD segments.

Characterization and measurements

¹H-NMR spectra were taken with a Varian VXR-Unity (500 MHz) using CDCl₃ as the solvent and tetramethylsilane as the internal standard of chemical shift. DSC experiment was performed using a Shimadzu DSC-60 differential scanning calorimeter under a nitrogen atmosphere in the temperature range from 30 to 160°C. The branched PBS copolymers were scanned from 30 to 160°C (Run I), remaining at 160°C for 5 min to eliminate the thermal and mechanical history, and then cooled to 30°C at a rate of 10°C/min, after that the samples were reheated to 160°C at a rate of 10°C/min (Run II). Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60 thermogravimetric analyzer by heating the samples to 550°C at a rate of 20°C/min under nitrogen atmosphere. Wide angle X-ray diffraction (WAXD) analysis was performed at room temperature using an X-ray diffractometer (Rigaku, D/max-RB) with CuK α radiation at a scanning rate of 6°C/min. All rheological measurements were performed on a strain-controlled rheometer (Anton Paar, MCR301) using parallel plates (25 mm diameter) at 140°C. Testing sample disks with a thickness of 1.5 mm and a diameter of 25 mm were prepared

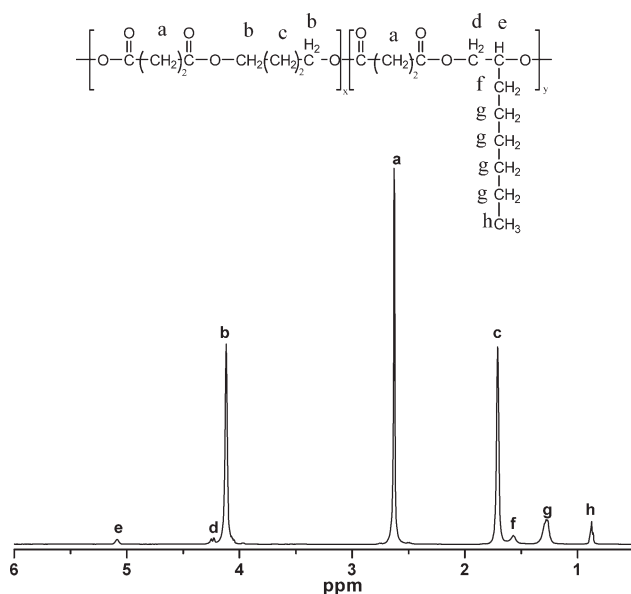


Figure 1 The $^1\text{H-NMR}$ spectrum of PBSOS-15.

by compression molding of the samples at 150°C for 8 min. Small-amplitude oscillatory shear ($\gamma = 0.5\%$) measurements were conducted within a frequency range from 0.1 rad/s to 100 rad/s. The tensile properties of neat PBS and branched PBS copolymers were obtained with a Gotech tester at room temperature and at a crosshead speed of 10 mm/min according to ASTM D638.

RESULTS AND DISCUSSION

Chain structure of branched PBS copolymers

Neat PBS and branched PBS copolymers were synthesized via bulk polymerization using SA, 1,4-BD, and in the cases of copolymers, 1,2-OD. The $^1\text{H-NMR}$ was used to study the chemical structure and composition of branched PBS copolymers. The $^1\text{H-NMR}$ spectrum of PBSOS-15 is shown in Figure 1. As can be seen, the peak appearing at 2.63 ppm (Proton *a*) corresponds to the methylene protons in SA units. The peaks at 1.71 ppm (Proton *c*) and 4.12 ppm (Proton *b*) originate from the central and terminal protons of 1,4-BD segments. The peaks at 4.25 ppm (Proton *d*) and 5.09 ppm (Proton *e*) originate

TABLE I
Composition and Zero Shear Viscosities (η_0) of Neat PBS and Branched PBS Copolymers

Samples	Composition of reaction mixture (mol %)	Composition of copolyester (mol %) ^a	Zero shear viscosity η_0 (Pa s) ^b
PBS	100/0	100/0	1063
PBSOS-5	95/5	95/5	1340
PBSOS-10	90/10	91/9	444
PBSOS-15	85/15	86/14	776

^a determined by $^1\text{H-NMR}$.

^b determined by rheological testing within a shear rate range of 10–0.01 1/s (testing temperature at 140°C).

from $-\text{CH}_2-$ and $-\text{CH}-$ in the 1,2-OD units, respectively, according to the integrated intensity of *e* peak ($-\text{CH}-$ in the 1,2-OD units) relative to that of *a* peak (methylene peak in the SA units), the 1,2-OD segments content in the copolymers can be determined. The feeding ratio and the copolymers composition are shown in Table I. Based on the above results, the structure and composition of branched PBS copolymers were confirmed.

Table I also shows the change in zero shear viscosities (η_0) of neat PBS and branched PBS copolymers. It is known that the value of η_0 indirectly reflects the change of molecular weight of polymer.^{22,23} From Table I, it can be seen that the values of η_0 of copolymers varied between 444 and 1340 Pa s, first being increased and then decreased with the increasing of 1,2-OD segments content. When the content of 1,2-OD segments is 5 mol %, the value of η_0 was higher than that of others, while the PBSOS-10 has the lowest among the three copolymers studied.

Crystallization behaviors of neat PBS and branched PBS copolymers

The melting and crystallization behaviors of neat PBS and branched PBS copolymers were investigated via DSC analysis. The related thermal parameters are summarized in Table II. From Figure 2(a) and Table II, it is shown that there is a significant shift of the melting point to lower temperatures with increasing 1,2-OD segments content. Taking the PBSOS-15 as an example, the melting temperature of

TABLE II
Thermal Parameters of Neat PBS and Branched PBS Copolymers

Samples	$T_m(^{\circ}\text{C})$ run I/run II	$\Delta H_m(\text{J/g})$ run I/run II	$T_c(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})^a$	$\Delta T(^{\circ}\text{C})$	$X_c(\%)$	$T_{5\%}(^{\circ}\text{C})$	$T_{50\%}(^{\circ}\text{C})$	$T_{90\%}(^{\circ}\text{C})$
PBS	115.2/114.1	96.8/76.9	73.5	-31.8	40.6	69.9	332	401	426
PBSOS-5	109.9/109.4	83.4/73.2	66.4	-33.6	43.0	66.5	362	408	432
PBSOS-10	104.4/104.1	74.3/59.6	59.9	-34.4	44.2	54.2	357	404	429
PBSOS-15	100.1/100.0	57.2/45.4	56.4	-33.4	43.6	41.3	355	403	428

^a determined by dynamic mechanical thermal analyzer (Anton Paar, MCR301) with a strain of 0.1%, the temperature range is between -80 and 60°C with a heating rate of $2^\circ\text{C}/\text{min}$.

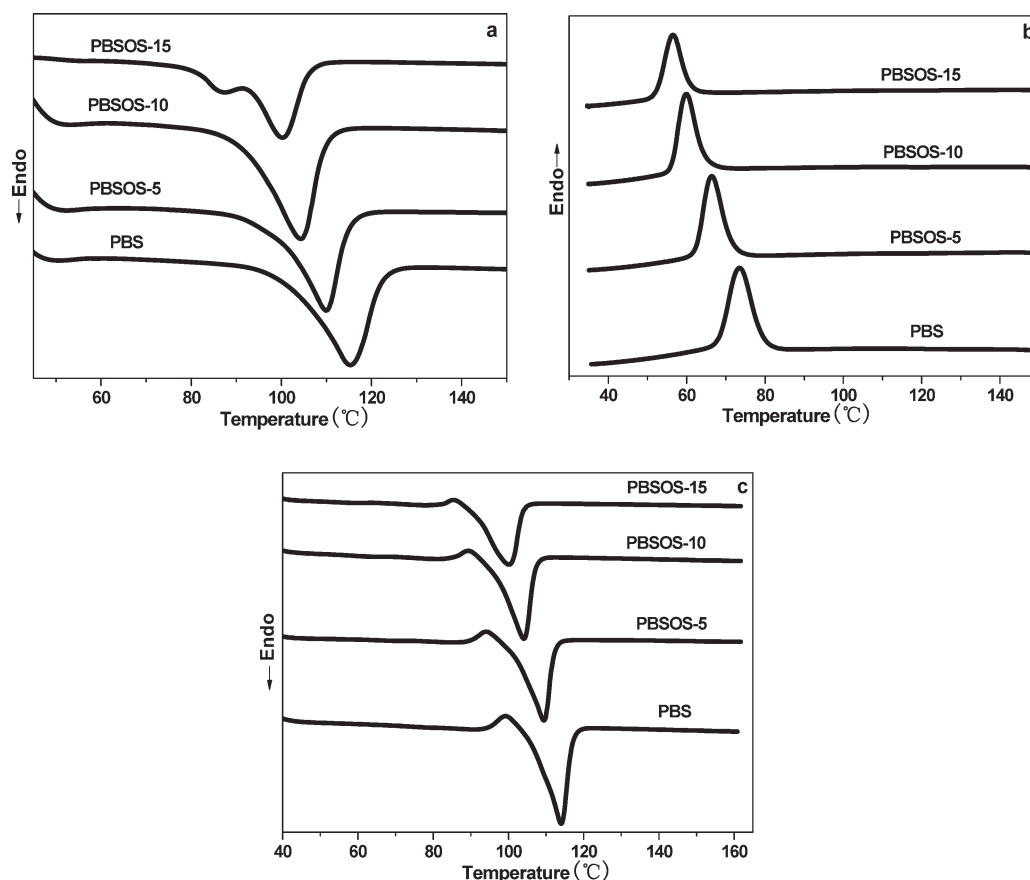


Figure 2 DSC thermograms of neat PBS and branched PBS copolymers with different 1,2-OD segments content: (a) the first heating curves, (b) cooling curves, and (c) the second heating curves.

the branched PBS copolymers decreased to 100°C, about 15°C lower than that of neat PBS. Also it can be seen that two endothermic peaks appear as the 1,2-OD segments content reaches up to 15 mol %, and these two melting peaks were attributed to the melting-recrystallization-remelting process of the lamellar crystals with different metastability, which has been reported for PBS and its copolymers.^{24–26}

From Figure 2(b), it can be seen that the crystallization temperatures of branched PBS copolymers are all lower than that of neat PBS, and decrease gradually with the increasing of 1,2-OD segments content, indicating that the introduction of 1,2-OD segments hindered the crystallizability of PBS. The supercooling degree ($\Delta T = T_m - T_c$) is an important parameter for determining the crystallizability of polymers.²⁷ Generally speaking, the larger ΔT value, the lower the crystallizability. As shown in Table II, ΔT value of PBS increases with increasing the 1,2-OD segments content. These results indicate that the crystallizability of branched PBS copolymers is much lower than that of neat PBS and the effect would become more and more significant with increasing 1,2-OD segments content. Also, the glass transition temperature (T_g) of branched PBS copolymers decrease slightly with the increasing of the 1,2-

OD segments content, indicating an increase of the chain segments mobility of PBS due to the addition of alky branching chains. From the DSC thermograms of different samples during the second heating process, the melting temperature (T_m) and the crystallinity degree (X_c) of branched PBS copolymers are lower than those of neat PBS, and decrease with increasing 1,2-OD segments content, due to the hindrance in crystal growth caused by the presence of foreign segments and branched chains that produced from 1,2-OD segments in the branched PBS copolymers.

X-ray diffraction analysis of neat PBS and branched PBS copolymers

The crystal structure is an important factor affecting the mechanical properties and biodegradability of the polymer. The diffraction diagrams of neat PBS and branched PBS copolymers with various 1,2-OD segments content are shown in Figure 3. The diffraction peaks for neat PBS appear at $2\theta = 19.61^\circ$, 22.18° , 22.67° , 26.08° , and 29.15° , which can be identified to a monoclinic crystal lattice with $a = 5.23 \text{ \AA}$, $b = 9.08 \text{ \AA}$, $c = 10.79 \text{ \AA}$, and $\beta = 123.87^\circ$.²⁸ With increasing 1,2-OD segments content, the peak at $2\theta = 22.18^\circ$

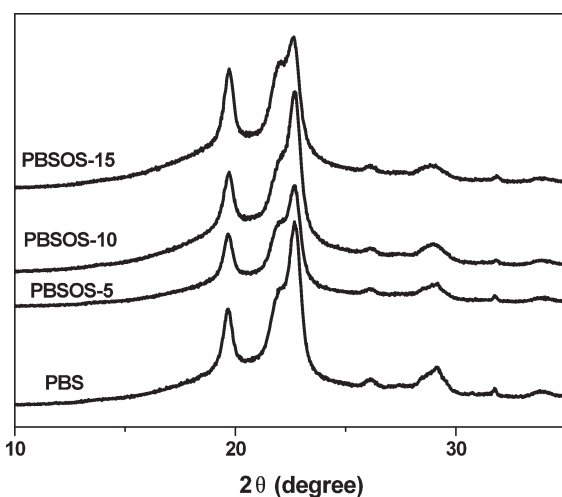


Figure 3 Wide angle X-ray diffractograms of neat PBS and branched PBS copolymers with different 1,2-OD segments content.

becomes more pronounced. The positions of the peaks on the diffractograms of branched PBS copolymers show that branched PBS copolymers have a monoclinic crystal lattice similar to neat PBS, which indicates that the 1,2-OD segments are excluded from the crystalline region of the lamellae in the crystallized copolymers.

Thermal stability of neat PBS and branched PBS copolymers

The thermal stability of branched PBS copolymers is an important parameter for their processing and applications. Figure 4 shows the TGA curves of neat PBS and branched PBS copolymers with different 1,2-OD segments content. It is shown that the thermal degradation curves of neat PBS and branched PBS copolymers are very similar to each other, all showing classic one-step degradation curves. Table II summarizes the thermal parameters, such as the temperature corresponding to the weight losses of 5, 50, and 90%, represent as $T_{5\%}$, $T_{50\%}$, $T_{90\%}$ under the nitrogen atmosphere, respectively. The initial thermal degradation can be represented by the value of $T_{5\%}$, which increases first and then decreases with the increasing of 1,2-OD segments content. For example, when the 1,2-OD segments content is 5 mol %, the temperature at initial thermal degradation ($T_{5\%}$) is improved from 332°C for neat PBS to about 360°C for the branched PBS copolymers, indicating again a higher thermal stabilities in the presence of 1,2-OD segments. The values of $T_{50\%}$ and $T_{90\%}$ of branched PBS copolymers show the similar tendency as $T_{5\%}$. The improvement in the thermal stabilities of branched PBS copolymers might be attributed to the existence of chains branches structure, which may retard the thermal degradation of

PBS chains,^{29,30} leading to the enhancement of thermal stabilities of branched PBS copolymers.

The rheological properties of neat PBS and branched PBS copolymers

The complex viscosities of neat PBS and branched PBS copolymers as a function of frequency are shown in Figure 5(a). The complex viscosities ($|\eta^*|$) of neat PBS and branched PBS copolymers decrease with the increasing of frequency, indicating a non-Newtonian behavior over the entire measured frequency range. The branched PBS copolymers exhibit higher value of $|\eta^*|$ than that of neat PBS over the entire frequency range. With increasing 1,2-OD segments content, the values of $|\eta^*|$ of branched PBS copolymers increase first and then decrease. Indicating that the entanglement effects between branching chains and the PBS matrix molecules. In addition, the zero shear viscosity (η_0) is also important. From Table I, the PBSOS-5 has the highest zero shear viscosity (η_0), which exhibits higher value of $|\eta^*|$ than that of neat PBS and other copolymers. In addition, the value of $|\eta^*|$ of PBSOS-10 is higher than that of PBSOS-15, although the former has lower zero shear viscosity (η_0) than the latter. This can be ascribed to the fact that the former has larger hydrodynamic volume than the latter, resulting in a higher degree of chain entanglement.³¹

The storage modulus (G') and loss modulus (G'') of neat PBS and branched PBS copolymers as a function of frequency are displayed in Figure 5(b, c). The values of G' and G'' of branched PBS copolymers significantly increase with the increasing of frequency, and this enhancing effect is more pronounced at low frequency. When the 1,2-OD segments content is 15 mol %, the behavior of increased in G' and G'' at low frequency became obvious, suggesting the increase in the interactions between 1,2-OD segments and the

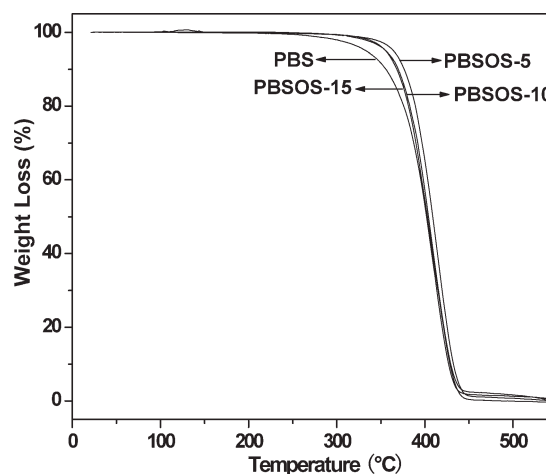


Figure 4 TGA curves for neat PBS and branched PBS copolymers.

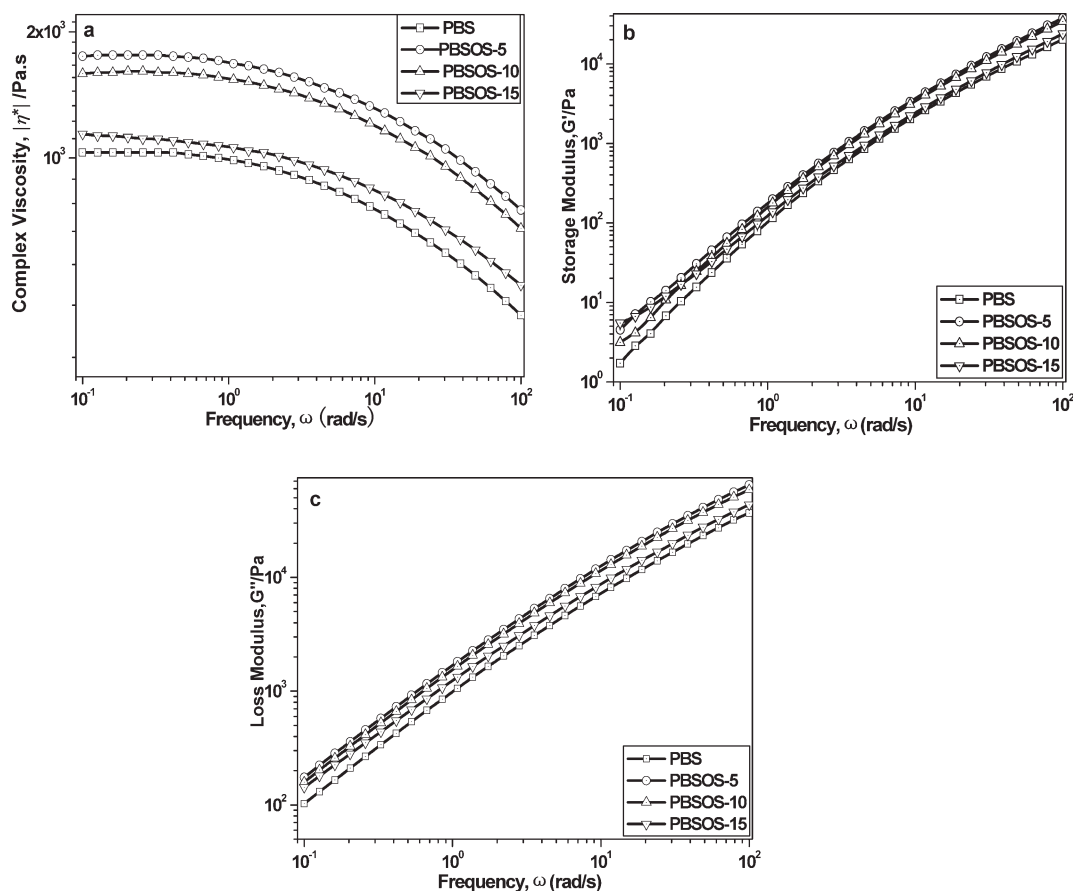


Figure 5 (a) Dynamic complex viscosities ($|\eta^*|$), (b) storage modulus (G'), and (c) loss modulus (G'') of neat PBS and branched PBS copolymers as a function of frequency.

PBS matrix. Also, the values of G' and G'' of branched PBS copolymers are higher than those of neat PBS over the entire frequency range. This indicates that the addition of 1,2-OD segments leads to more entanglement, which substantially enhances the interactions. With increasing the shear force, branched PBS copolymers showed almost similar or slightly higher G' and G'' values than those of neat PBS at high frequency, reflecting the disentangle-

ment of chain branches under the effect of the dominant shear force.

The tensile properties of neat PBS and branched PBS copolymers

The effects of 1,2-OD segments content on the tensile properties of branched PBS copolymers are shown in Figure 6. From Figure 6(a), it can be seen that the

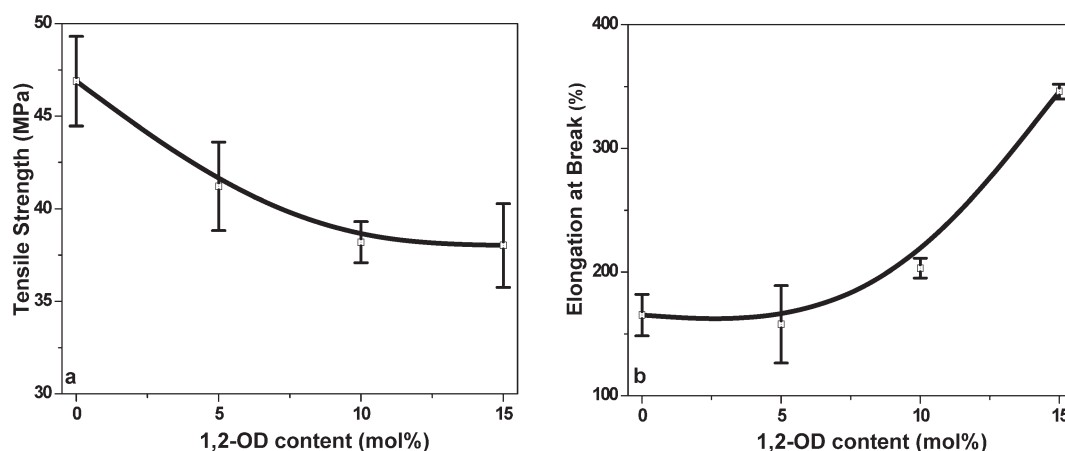


Figure 6 The tensile properties of neat PBS and branched PBS copolymers with different 1,2-OD segments content.

incorporation of 1,2-OD segments leads to decrease in the tensile strength of the material. As the 1,2-OD segments content is above 10 mol %, the decrease in tensile strength is not obvious with the increasing of the 1,2-OD segments content. The elongation at break of the samples is also obtained from the tensile measurements, as shown in Figure 6(b). It is shown that the addition of 1,2-OD segments will generally increase the elongation at break, and the elongation at break of PBS increases with increasing the 1,2-OD segments content. Upon addition of 15 mol % 1,2-OD segments, the value of the elongation at break of branched PBS copolymers can attain 345%, about 110% higher than that of neat PBS. The improvement in elongation at break of branched PBS copolymers can be understood as follows: on one hand, the addition of 1,2-OD segments increases the flexibility of polymer chains, the toughness is enhanced; on the other hand, the incorporation of 1,2-OD segments can decrease the degree of crystallinity, which leads to the improvement of toughness to a certain extent. The results of tensile testing show that the mechanical properties are closely dependent on the chemical structure and degree of crystallinity of polymers.

CONCLUSIONS

Branched PBS copolymers were synthesized via a two-step process of esterification and polycondensation using SA, 1,4-BD, and 1,2-OD. The chain structure, crystallization behaviors, thermal stabilities, rheological properties, and tensile properties of branched PBS copolymers were investigated in detail. The corresponding results show that the introduction of 1,2-OD segments decreases the glass transition temperature, melting temperature, crystallization temperature, and the degree of crystallinity of PBS. However, it also enhances the thermal stabilities of PBS. More importantly, the addition of 1,2-OD segments changes the rheological properties of PBS, such as complex viscosities ($|\eta^*|$), storage modulus (G'), and loss modulus (G''). Also, the elongation at break increases considerably with increasing the 1,2-OD segments content without notable decrease of the tensile strength.

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