Crystallization Kinetics and Tensile Modulus of Blends of Metallocene Short-Chain Branched Polyethylene with Conventional Polyolefins

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ABSTRACT: In this study, blends of metallocene short-chain branched polyethylene (SCBPE) with low-density polyethylene (LDPE), high-density polyethylene (HDPE), polystyrene (PS), ethylene–propylene–diene monomer (EPDM), and isotactic polypropylene (iPP) were prepared in weight proportions of 80 and 20, respectively. The crystallization behaviors of these blends were studied with polarized light microscopy (PLM) and differential scanning calorimetry. PLM showed that SCBPE/LDPE, SCBPE/HDPE, and SCBPE/EPDM formed band spherulites whose band widths and sizes were both smaller than that of pure SCBPE. No spherulites were observed, but tiny crystallites were observed in the completely immiscible SCBPE/PS, and the crystallites in SCBPE/iPP became smaller; only irregular spherulites were seen. The crystallization kinetics and me- chanical properties of SCBPE were greatly affected by the second polyolefin but in different way, depending on the phase behavior and the moduli of the second components. SCBPE may be phase-miscible in the melt with LDPE, HDPE, and EPDM but phase-separated during crystalliza- tion. A big change in the crystal morphology and crystalli- zation kinetics existed in the SCBPE/iPP blend. The me- chanical properties of the blends were also researched with dynamic mechanical analysis (DMA). DMA results showed that the tensile modulus of the blends had nothing to do with the phase behavior but only depended on the modulus of the second component. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1816–1823, 2005

Key words: blends; crystallization; morphology

INTRODUCTION

Recently, the single-site feature of the metallocene catalyst led to a new type of short-chain branched polyethylene (SCBPE) that has a narrow molecular weight distribution and a uniform short-chain branch distribution. Because of its superior mechanical and thermal properties, SCBPE has received a lot of inter- est both industrially and academically.[1–5] At the same time, the narrow molecular weight distribution and uniform short-chain branch distribution of SCBPE re- sults in poor processability, which has made its appli- cation limited. However, this shortcoming could be overcome by blending SCBE with other polymers to achieve suitable combinations of physical properties and better processing characteristics. First, the misci- bility of blends must be considered because it affects not only the melt processing and melt rheology but also the properties of the products. Wignall and Almo[6] investigated the solid-state morphology of blends of linear and model SCBPE [high-density polyethylene (HDPE)/SCBPE] by differential scanning calorimetry (DSC), transmission electron microscopy (TEM), small-angle neutron scattering, and small-angle X-ray scattering. Their results indicated that the mixtures were homogeneous in the melt for all compositions when the ethyl branch content in the copolymer was low (i.e., lower than 4 branches/100 backbone carbon atoms for a weight-average molecular weight similar to 10^{-5}). However, because of the structural and melt- ing point differences between HDPE and SCBPE, the components may phase segregate in the solid state. Cho[7] reported the melt rheology and mechanical properties in SCBPE/low-density polyethylene (LDPE), SCBPE/HDPE, and HDPE/LDPE. Their re- sults showed that all three blends might have been miscible in the melt. However, the SCBPE/LDPE and HDPE/LDPE blends exhibited two crystallization temperatures (T_c's), indicating that those blends dis- played phase separation on cooling from the melt. Rana[8,9] also studied the phase behavior of HDPE/ SCBPE from its morphology and found that this blend could undergo cocrystallization or phase separation during the molten mixing, depending on the compo-

sitions and processing conditions. The morphology for polypropylene–polyethylene blend controlled by time–temperature–miscibility was investigated by Shanks et al.[10] The crystallization rate (half-time) for isotactic polypropylene (iPP) in iPP/HDPE, iPP/ LDPE, iPP/very low density polyethylene (VLDPE), and iPP/VLDPE was very similar to that of the pure polypropylene, suggesting that the two polymers in the blends were immiscible. The crystallization rate of iPP in iPP/SCBPE greatly decreased, broad diffuse spherulites formed, and iPP became a continuous phase. They proposed that iPP and SCBPE were miscible, and so iPP crystallizes as in dilute solution. Yang[11] studied morphology development when blending SCBPE and polystyrene (the minor phase) in a Haake internal mixer. The blends showed a bimodal particle size distribution of the minor phase during the initial stage of morphological development. These observations suggest that the main function of compatibilizer during blending was in reducing the interfacial tension between two immiscible polymer phases.

In this article, we report our recent efforts to improve the mechanical and processing properties of SCBPE by blending it with other polyolefins. We first prepared SCBPE/HDPE, SCBPE/LDPE, SCBPE/ethylene–propylene–diene monomer (EPDM), SCBPE/ polystyrene (PS), and SCBPE/iPP blends and then investigated the crystallization and mechanical properties of these blends by polarized light microscopy (PLM), DSC, and dynamic mechanical analysis (DMA). We tried to probe the phase behavior from the information given by DSC, PLM, and DMA and to better understand the crystallization behaviors, mechanical properties, and miscibility of these blends.

EXPERIMENTAL

Materials

Selected characteristics for the polymers used in this study are given in Table I. SCBPEs made with a metallocene single-site catalyst were available from the Research Institute of Petroleum Processing (Beijing, China). The molecular weight of SCBPE was 5.8×10^4, and the branch content was 25 branches/1000 backbone carbon atoms. The SCBPE was used without any fractionation, and its polydispersity was 3.0.

Blend preparation

SCBPE with HDPE, LDPE, EPDM, PS, or iPP was molt-blended in proportion to the weight ratio 80/20. All of the blends were mixed in a Haake Rheomix (Paramus, NJ) at 50 rpm. The mixing temperature was 190°C, and the mixing time was 10 min.

TABLE I
Characteristics of the Materials in this Study

Sample ID	Trademark	Melt index (g/10 min)	Manufacturer
m-SCBPE	LH-113	1.3	Research Institute of Petroleum Processing (Beijing, China)
LDPE	1F7B	7.0	Yan Shan Petroleum Chemical (Beijing, China)
HDPE	5000S	6.9	Qi Lu Petroleum Chemical (Zibo, China)
iPP	1300	1.0	Yan Shan Petroleum Chemical (Beijing, China)
PS	PG-33	12	
EPDM	3745	—	Japan Synthetic Rubber Co. Ltd. (Tokyo, Japan)

Instrument and measurements

DSC measurements were conducted on a PerkinElmer Pyris I (Norwalk, CT) differential scanning calorimeter. The specimens weighed in the range 3–5 mg. During the measurement, dried N_2 gas was purged at a constant flow rate. In the case of isothermal crystallization, the sample was kept at a temperature of 20°C above the melting point of the sample for 5 min to remove residual crystals, which could have been seeds for the crystallization. Then, they were cooled rapidly to the predetermined T_c at a rate of 100°C/min, and the temperature was held constant until the crystallization was completed. Thereafter, the specimens were heated again without prior cooling to obtain the DSC endotherms at a rate of 10°C/min. The temperature reading and calorific measurement were calibrated with a standard indium.

PLM, with a camera attached to the microscope, was used to observe the microscopic morphology. Thin films were prepared by the melt-pressing of a small amount of the sample between the cover glass and the glass slide at a temperature of 20°C above the melting point of the sample; then the sample was quenched to room temperature.

DMA was conducted with a Rheometrics RSAIII solids analyzer (New Castle, DE) in the range 10^{-1} to 10^{-2} s^{-1} at constant temperatures 50 and 100°C. All of the specimens were rectangular with a 7.9-mm width, 48-mm length, and 0.8-mm thickness.

RESULTS AND DISCUSSION

Crystal morphology

To investigate the morphological changes of SCBPE after blending with other polyolefins, a PLM experi-
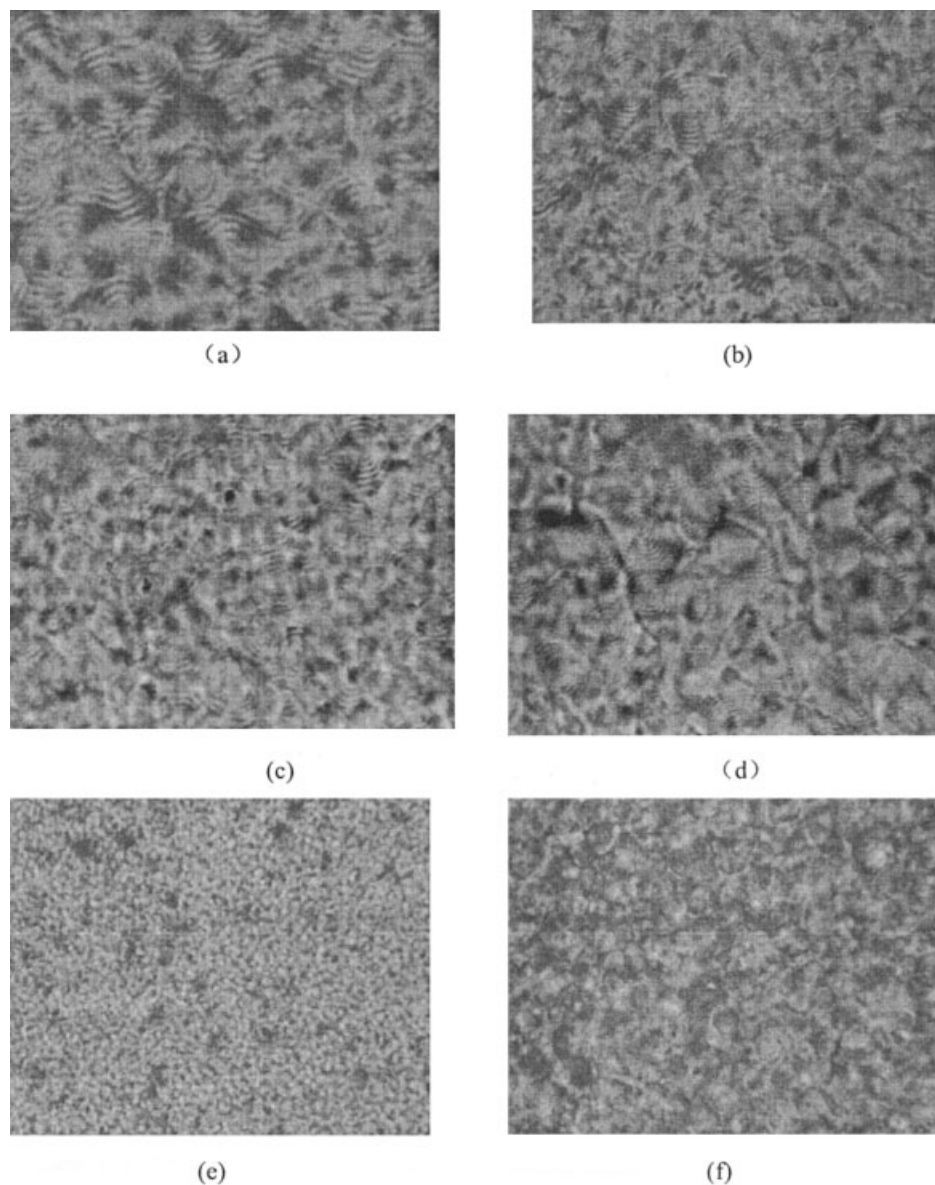
Figure 1 PLM micrographs of SCBPE and its blends with other polyolefins: (a) pure SCBPE, (b) SCBPE/HDPE, (c) SCBPE/LDPE, (d)SCBPE/EPDM, (e)SCBPE/iPP, and (f) SCBPE/PS.

ment was carried out for all of the blends and for pure SCBPE as well. The photographs are shown in Figure 1. As shown in Figure 1(a), in the PLM photograph of pure SCBPE appears well-defined spherulites with banded structure because of its low branch content. With the addition of 20% HDPE, LDPE, and EPDM to pure SCBPE, the morphology also had band spherulites, but both the sizes of the spherulites and the width of the banded structure decreased, as shown in Figure 1(b–d). No spherulites were observed, but tiny crystallites were observed in the SCBPE/PS blend, and also some transparent PS particles of various sizes were seen, which indicated a macroscopic phase separation between PS and SCBPE. The reason for the lack of spherulites and the presence of tiny crystallites

in the SCBPE/PS blends was not clear and is worth further investigation. Interestingly, no spherulites were seen in SCBPE/iPP either [Fig. 1(e)]. One could also see some black blocks of various sizes dispersed in the matrix covered with little bright dots. The little bright dots were due to the little crystalline grains for both SCBPE and iPP, whereas the black blocks were attributed to the amorphous phases, which were not crystallized under the experimental conditions. This may have also been caused by the phase miscibility in the melt state between SCBPE and iPP, as suggested by Shanks.[10] One only can obtain very limited information of crystal morphology and phase morphology via PLM; TEM or atomic force microscopy must be used for more detailed information.
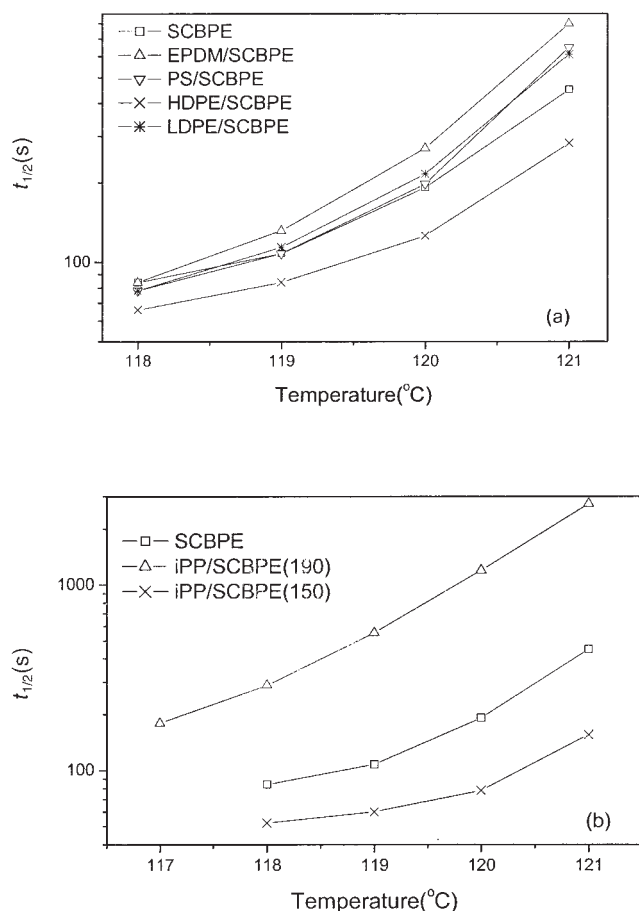
Figure 2 $t_{1/2}$ values as a function of T_c for (a) SCBPE and the blends except SCBPE/iPP and (b) SCBPE/iPP melted at two temperatures before crystallization.

Isothermal crystallization

Figure 2(a) shows a plot of the isothermal crystallization half-time ($t_{1/2}$) versus the isothermal temperature. The value of $t_{1/2}$ can be used to qualitatively analyze the crystallization rate. The lower the value of $t_{1/2}$ is, the faster the rate of crystallization will be. At the same T_c, the $t_{1/2}$'s of SCBPE/LDPE and SCBPE/PS blends did not change very much compared with pure SCBPE. The similar $t_{1/2}$ values of SCBPE/PS and pure SCBPE could be easily understood as a result of the phase separation between SCBPE and PS. However, LDPE could have been phase miscible with SCBPE in the melt state as suggested by the PLM results. The similar $t_{1/2}$ values of SCBPE/LDPE and pure SCBPE observed here might have been due to the cocrystallization of SCBPE and LDPE (see Fig. 3). There was also an enhanced crystallization rate in the SCBPE/HDPE blend and a decreased crystallization rate in the SCBPE/EPDM blends. Because of the linear structure of HDPE, its molecular motion was easier than that of pure SCBPE, and it crystallized first in the blends. The preformed crystallites served as nuclei for SCBPE,

which enhanced the crystallization rate and led to a decrease in $t_{1/2}$ of SCBPE/HDPE. Although EPDM copolymerized with ethylene, propylene, and 2-butylene has some polyethylene chain segments in the backbone, which can results in entanglement of chains of SCBPE and EPDM (phase miscible), when the blends were cooled down, SCBPE crystallized but EPDM was rejected out of the crystal. Hence, the $t_{1/2}$ of SCBPE/EPDM was larger than that of pure SCBPE at the same temperature. The crystallization of SCBPE/iPP showed a very interesting phenomenon; this is shown in Figure 2(b). There are two curves of SCBPE/iPP in Figure 2(b). One curve marked with SCBPE/iPP (150) means that the blend was melted at 150°C and cooled to the predetermined T_c's for crystallization. The other marked with SCBPE/iPP (190) indicates that the blend was melted at 190°C before crystallization. Compared with pure SCBPE, the $t_{1/2}$ of SCBPE/iPP (150) decreased, whereas that of iPP/SCBPE (190) increased greatly. For example, at 118°C, $t_{1/2}$ of SCBPE/iPP (150) was 53 s, whereas the $t_{1/2}$ of SCBPE/iPP (190) was 288 s, compared with 84 s of pure SCBPE. Because the melting point of pure iPP was about 160°C, at 150°C PP was not entirely melted and still had crystal grains as nucleating agents that made the rate of crystallization rate of SCBPE accelerate and shortened the $t_{1/2}$. However, iPP and SCBPE were both molten at 190°C, and the increase of $t_{1/2}$ of SCBPE/iPP (190) once again suggested that iPP became miscible with SCBPE when it was melted but could not become miscible at 150°C where it was not melted.

Nonisothermal crystallization

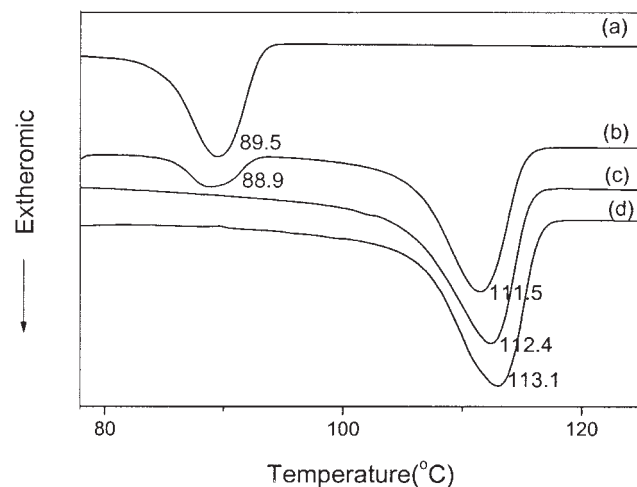Because the components of the SCBPE/LDPE, SCBPE/HDPE, and SCBPE/iPP blends could both

Figure 3 DSC cooling curves of (a) LDPE, (b) unmixed SCBPE/LDPE, (c) mixed SCBPE/LDPE, and (d) SCBPE.
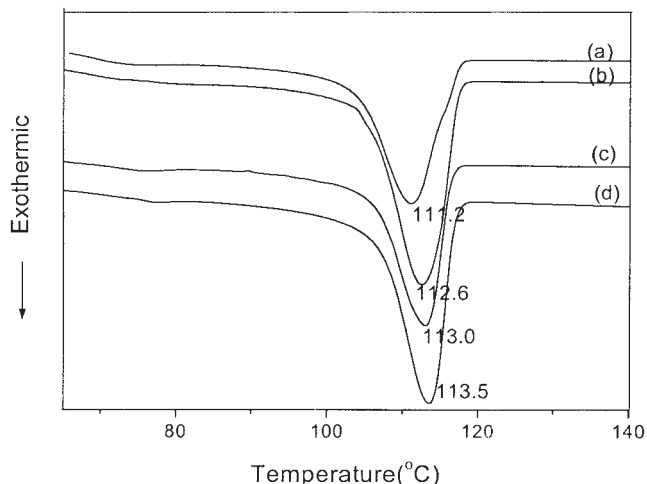
Figure 4 DSC cooling curves of (a) HDPE, (b) unmixed SCBPE/HDPE, (c) mixed SCBPE/HDPE, and (d) SCBPE.

crystallize during cooling, the crystallization behavior in these blends was quite complicated. To further elucidate the effect on the crystallization behavior of SCBPE by LDPE, HDPE, and iPP, we prepared two kinds of samples. One was called the unmixed sample, which was made by just putting SCBPE and the second component together in the same weight proportion (SCBPE/iPP = 80:20) without melt-blending. The others were called the mixed samples, which were made by melt-blending SCBPE with the second component together in the same weight proportion. Again the DSC measurement was carried out in the manner of nonisothermal crystallization. the unmixed, mixed, and pure samples were kept at 190°C for 5 min and were then cooled at a rate of 20°C/min. Figure 3 illustrates the DSC cooling curves of LDPE, SCBPE/ LDPE (unmixed), SCBPE/LPE (mixed), and SCBPE. It was evident that the curve of unmixed SCBPE/LDPE had two crystallization peaks. One was 88.9°C, and the other was 111.5°C. Compared with the peak temperature of pure LDPE (89.5°C) and that of pure SCBPE (113.1), it was clear that in the curve of unmixed SCBPE/LDPE, the higher temperature was the T_c of SCBPE and the lower one was that of LDPE. Because the macroscopic phase separation existed between SCBPE and LDPE in SCBPE/LDPE (unmixed), SCBPE and LDPE could crystallize during crystallization, and the two crystallization peaks in the DSC curve were seen. However, there was only one crystallization peak in the DSC curve of SCBPE/LDPE (mixed), whose temperature was 112.4°C, that is, near to the peak temperature of pure SCBPE. The phenomenon indicated again that SCBPE was miscible with LDPE to some degree in the melt in the mixed sample, which was in agreement with the PLM pictures. This result was also in good agreement with Xu et al.'s[12] finding that the most linear part of LDPE was incor-

porated into the lamellae of ethylene–butene copolymers, thus forming a cocrystallization that depended on the molecular structure of polymers, such as branch content, molecular shape, and molecular weight. The hypothesis of LDPE incorporated into the SCBPE lamellae could be also possibly proved by a comparison of the values of blend crystallization enthalpy with that of the SCBPE. To do this, a systematic study is needed on the change of enthalpy as function of blend composition for the blends. This work is being undertaken by our group.

The same experiment has been done on SCBPE/ HDPE, as shown in Figure 4. Because the peak temperature of pure HDPE (112.6°C) was similar to that of pure SCBPE (113.0), the DSC curve of HDPE/SCBPE did not show apparent two peaks but rather a wide peak with a little shoulder peak for both the mixed and unmixed samples. The curve of mixed sample was narrower than that of the unmixed blend, which indicated that the size of crystal was uniform in the mixed sample. In the course of crystallization, HDPE molecules first crystallized because of its linear structure. However, the peak temperature of SCBPE was close to that of HDPE, and the weight proportion of SCBPE was more than that of HDPE, which caused the merging of two crystallization peaks. This may have also simply been due to the cocrystallization, as suggested from the PLM results. Kwag et al.[15] reported that the phase morphology of blend of metallocene SCBPE and HDPE appeared as a homogeneous single phase, which showed that HDPE/SCBPE was miscible. Choi[13] observed that when the branch content of SCBPE was about 40 branched/1000 backbone carbon atoms, the blend of SCBPE and HDPE was phase-separated in the melt. The results of Rana and Lee[14] showed that HDPE/SCBPE was thermodynamically immiscible when the branch content of SCBPE was above 40 branched/1000 backbone carbon atoms but
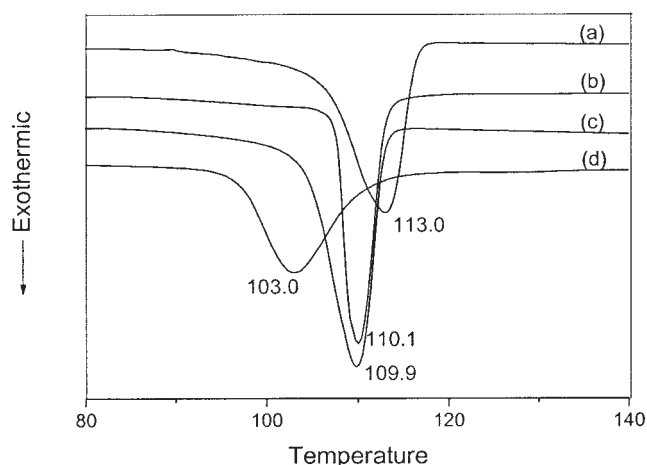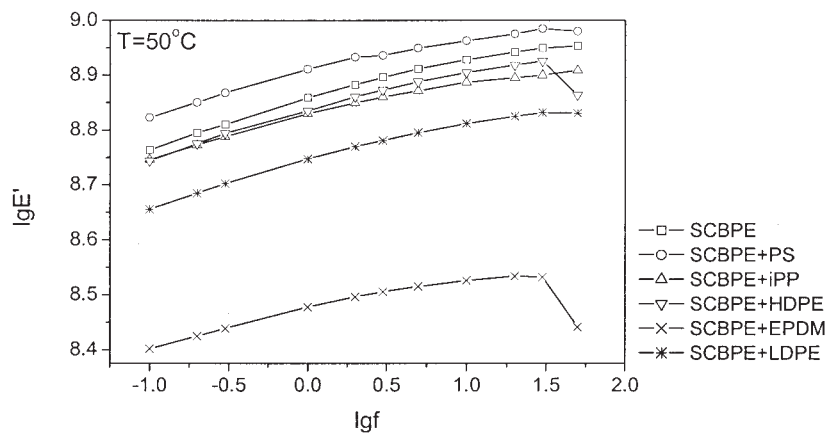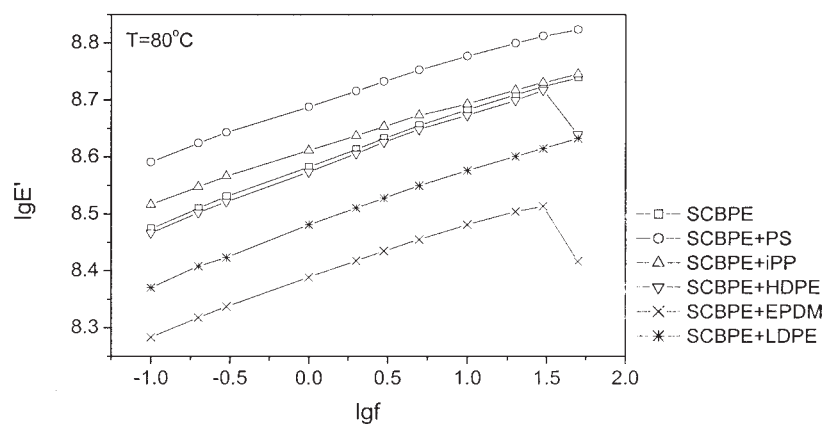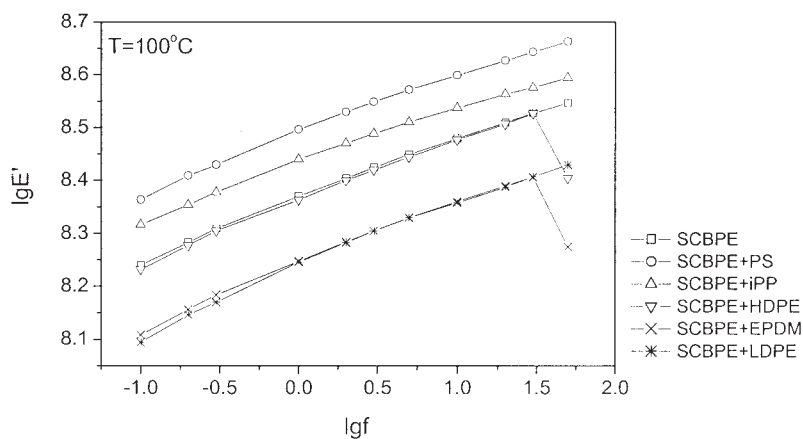

Figure 5 DSC cooling curves of (a) SCBPE, (b) mixed SCBPE/iPP, (c) unmixed SCBPE/iPP, and (d) iPP.

Figure 6 Plot of *E'* of SCBPE and the blends versus frequency at indicated temperatures (*T*'s) of (a) 50, (b) 80, and (c) 100°C.

was mechanically compatible, which was understood by their thermal and mechanical behaviors.

Figure 5 shows the results for the SCBPE/iPP blends. The crystallization peak of SCBPE was 10°C higher than that of iPP. Not only the crystallization of iPP/SCBPE (unmixed) but also that of iPP/SCBPE (mixed) showed one crystallization peak and almost the same crystallization peak temperature. We know that it should have been phase-separated in the un-mixed blend, but still only one peak was observed. So one must be very careful when dealing with the DSC crystallization cures, and one peak does not necessar-
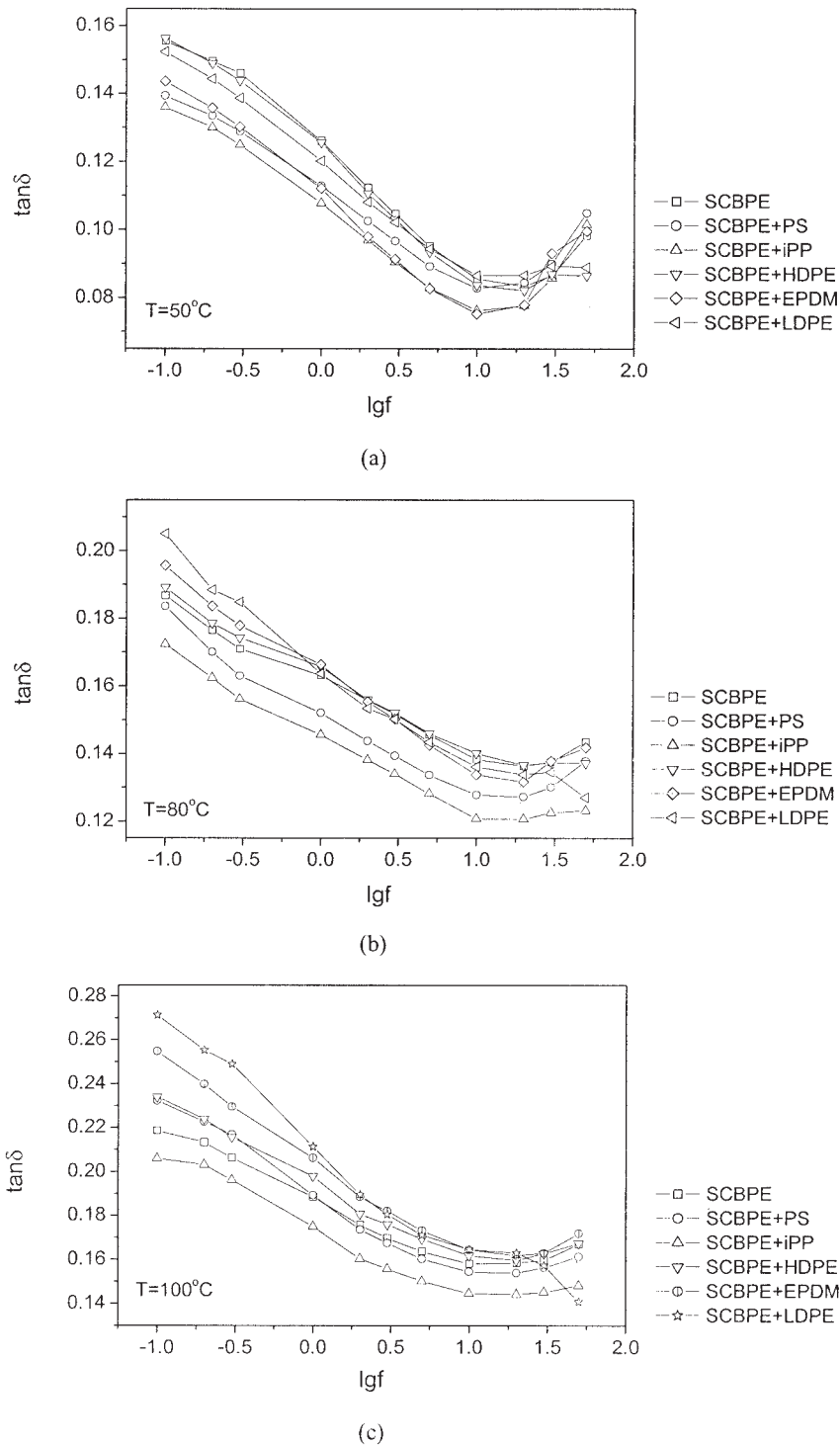
Figure 7 Plot of tan δ of SCBPE and the blends versus denary logarithm of frequency at indicated temperature (*T*'s) of (a) 50, (b) 80, and (c) 100°C.

ily mean the blend is miscible. Other instruments, including crystallization enthalpy, X-ray analyses, and TEM (or atomic force microscopy), are needed to determine the phase behavior.

Mechanical properties

Figure 6 shows the frequency dependence of the tensile storage modulus (E') of the blends at three fixed temperatures (50, 80, and 100°C). As seen in this figure, E' of all the samples increased with increasing frequency for all three temperatures, as we know increasing frequency is equal to a decrease in temperature. SCBPE/PS had the highest modulus, whereas SCBPE/EPDM had the lowest modulus, and others were in-between. We know that PS had the highest modulus and EPDM had the lowest modulus among

the materials used. This result indicated that tensile modulus of the blends had nothing to do with phase behavior (miscible or immiscible) or crystal morphology but only depended on the modulus of the second component. As the temperature increased, the modulus difference between SCBPE and the blends decreased because of the melting of SCBPE. The only exception was for SCBPE/PS, which showed more rigidity than the pure SCBPE with increasing temperature. This was probably because of the fact that the glass-transition temperature of polystyrene is about 100°C, and PS retains rigidity below the glass-transition temperature. Figure 7 shows the tan δ of the blends changes with increasing frequency, again at three fixed temperatures. There was a decrease in tan δ as frequency increased for all of the materials. A minimum was observed around 10 Hz. The curves overlapped at lower temperature s(50 and 80°C), and the difference between the tan δ became more obvious at the higher temperature (100°C). The value of tan δ for SCBPE/iPP was always the lowest among the samples at the three temperatures. Compared with E', the change in tan δ of SCBPE as when the second component was added was much more complicated and worth further investigation. It must be related to both the phase morphology and crystal morphology. Also, no transition peak was seen for any of the samples, so apparent molecular relaxation did not occur during the experiment. One may expect to collect more information on the phase behavior from tan δ because it is related to damping properties and is sensitive to phase morphology.

CONCLUSIONS

In summary, the crystallization and mechanical properties of SCBPE were greatly affected by a second polyolefin but in different way, depending on the phase behavior and the modulus of the second component. SCBPE was phase-miscible in melts with HDPE, LDPE, HDPE, and EPDM but was phase-separated during crystallization. There was a big change in the crystal morphology and crystallization kinetics of SCBPE/iPP blends. This needs to be studied further because the unmixed samples showed similar crystallization behavior as the mixed samples. The DMA results showed that the values of E' of all the blends decreased with increasing temperature at the fixed frequency, and the tensile modulus of the blends did not decrease with phase behavior but only depended on the modulus of the second component. Compared with E', the change in tan δ was much more complicated, and the lowest tan δ was seen for the SCBPE/iPP system.

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