

CRYSTALLIZATION AND MECHANICAL PROPERTIES OF BLENDS OF METALLOCENE SHORT CHAIN BRANCHED POLYETHYLENE WITH CONVENTIONAL POLYOLEFINS*

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Abstract Metallocene-catalyzed short chain branched polyethylene (SCBPE) was blended with LDPE, HDPE, PS, EPDM and *i*PP in the weight proportions of 80 and 20. The crystallization and mechanical properties of these blends were studied by PLM, DSC and DMA. It has been observed in PLM that SCBPE/LDPE, SCBPE/HDPE and SCBPE/EPDM can form band spherulites whose band width and size are both smaller than that of the pure SCBPE. Tiny crystallites are observed in the completely immiscible SCBPE/PS blend. The crystallites in SCBPE/*i*PP are very small and only irregular spherulites are seen. The crystallization kinetics and mechanical properties of SCBPE are greatly affected by the second polyolefin, but in a different way, depending on the phase behavior and the modulus of the second components. SCBPE may be phase miscible in the melt with HDPE, LDPE and EPDM and co-crystallize together with HDPE or LDPE during cooling. A big change of crystal morphology and crystallization kinetics is seen in SCBPE/*i*PP blend compared with pure SCBPE and the lowest $\tan\delta$ is also seen for this system. DMA results show that the tensile modulus of the blends has nothing to do with phase behavior, but only depends on the modulus of the second component.

Keywords SCBPE, Crystallization, Morphology, Tensile modulus

INTRODUCTION

Recently, the single-site feature of metallocene catalyst has been found to lead to a new type of short-chain branched polyethylene (SCBPE), which has a narrow molecular weight distribution (MWD) and uniform short chain branch (SCB) distribution. Due to its superior mechanical and thermal properties, SCBPE has received a lot of interest, both industrially and academically^[1–5]. At the same time, the narrow molecular weight distribution and uniform short chain branch distribution of SCBPE result in a poor processibility, which made its application limited. However, this shortcoming could be overcome by blending it with other polymers in order to achieve suitable combinations of physical properties and better processing characteristics. First of all, the miscibility of blends must be considered because it affects not only the melt processing and melt rheology but also the properties of products. Concerning the blends between polyolefins, one must mention the co-crystallization phenomenon. It is a very interesting phenomenon and frequently investigated for blends of different types of polyethylene^[6–9]. It was concluded that composition distribution has a great influence on co-crystallization in LDPE/SCBPE blends^[10]. Wignall *et al.*^[11] have investigated the solid state morphology of blends of linear and model short-chain branched polyethylene (HDPE/SCBPE) by DSC, TEM, SANS and SAXS. And the results indicated that the mixtures are homogeneous in the melt for all compositions when the ethyl branch content in the copolymer is low (*i.e.* lower than 4 branches/100 backbone carbon atoms for a molecular weight of M_w similar to

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10^5). However, due to the structural and melting point differences between HDPE and SCBPE, the components may phase segregate in the solid state. Cho *et al.* investigated the melt rheology and mechanical properties of SCBPE/LDPE, SCBPE/HDPE, HDPE/LDPE^[12]. Their results showed that SCBPE/LDPE and HDPE/LDPE blends exhibited two crystallization temperatures, indicating that those blends displayed phase separation upon cooling from the melt. Rana^[13, 14] also studied the phase behavior of HDPE/SCBPE blends from their morphology and found that the blends could undergo co-crystallization or phase separation during the molten mixing, depending on the compositions and processing conditions. The morphology of *i*PP/PE blends controlled by time-temperature-miscibility was investigated by Shanks^[15]. The crystallization rates (half time) for *i*PP in *i*PP/HDPE, *i*PP/LDPE, *i*PP/VHDPE and *i*PP/VLDPE were very similar to that of the pure polypropylene, suggesting that the two polymers in the blends were immiscible. The crystallization rate of *i*PP in *i*PP/SCBPE was found to be greatly decreased, and broad diffuse spherulites formed and *i*PP became a continuous phase. They proposed that *i*PP and SCBPE were miscible in that *i*PP crystallizes as in dilute solution. Yang *et al.* have studied the morphological development during blending SCBPE with polystyrene (the minor phase) in a Haake internal mixer^[16]. 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 lies in reducing the interfacial tension between two immiscible polymer phases.

In this paper, 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/EPDM, SCBPE/PS and SCBPE/*i*PP blends, then investigated the crystallization and mechanical properties of these blends by PLM, DSC and DMA. We are trying to probe the phase behavior from the information given by DSC, PLM and DMA, for a better understanding of the crystallization behavior, mechanical properties and miscibility of these blends.

EXPERIMENTS

Materials

Some selected characteristics of the polymers used in this study are given in Table 1. Metallocene SCBPE with 1-hexene as comonomer was obtained from the Research Institute of Petroleum Processing, China. The molecular weight of SCBPE is 5.8×10^4 and the average branch content is 25 branches/1000 backbone carbon atoms. SCBPE was used without any fractionation, and its polydispersity is 3.0.

Table 1. Characteristics of materials used in the experiments

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

Blend Preparation

SCBPE was melt-blended with HDPE, LDPE, EPDM, PS and *i*PP in the weight ratio of 80/20, respectively. All blends were mixed in a Haake Rheomix at 50 r/min for 10 min at a temperature of 190°C.

Instruments and Measurements

DSC measurements were conducted on a Perkin-Elmer Model Pyris I differential scanning calorimeter. The specimens were weighed in the range of 3–5 mg. During the measurement, dried N₂ 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 a sample for 5 min to remove residual crystals, which may become the seeds for crystallization. Then the sample was cooled rapidly to the predetermined crystallization temperature T_c at a rate of 100 K/min and the temperature held constant until crystallization was complete. Thereafter the specimens were heated again

without prior cooling to obtain the DSC endotherms at a rate of 10 K/min. The temperature reading and calorific measurement were calibrated by using standard indium.

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

The dynamic mechanical analysis (DMA) was conducted by using a Rheometrics Solids Analyzer RSAIII in the frequency range of 10^{-1} to 10^2 s $^{-1}$ at constant temperatures of 50°C and 100°C. All the specimens were rectangular-shaped with 7.9 mm width, 48 mm length and 0.8 mm thickness.

RESULTS AND DISCUSSION

Crystal Morphology

For a polymer blend containing a crystalline component, one must know at what temperature the component will crystallize during cooling. If two components can crystallize, one should know whether they crystallize at the same temperature or co-crystallize together. The crystal morphology will be different in these two cases. To investigate the morphological change of SCBPE after blending with other polyolefins, a PLM experiment was carried out for all the blends and pure SCBPE as well. The photographs are shown in Fig. 1. As can be seen in Fig. 1(a), the PLM photograph of pure SCBPE exhibits well-defined spherulites with banded structure due to its low branch content. On addition of 20% HDPE, LDPE and EPDM to pure SCBPE, the morphology also shows band spherulites, but both the size of spherulites and width of banded structures decrease, as shown in Figs. 1(b), (c) and (d). Tiny crystallites are observed in the SCBPE/PS blend together with transparent PS particles of various sizes, which indicates that a macroscopic phase separation occurs between PS and SCBPE as expected. The reason why there are no spherulites but tiny crystallites in SCBPE/PS blends is not clear and needs further investigation. It is interesting that no well defined spherulites can be seen in SCBPE/*i*PP blends (Fig. 1e). One can also see some black blocks of various sizes dispersed in the matrix covered with little bright dots. The little bright dots are due to little crystalline grains of SCBPE or *i*PP, whereas the black blocks are attributed to the amorphous phases, which are not crystallized under the experimental conditions. This may be caused by the phase miscibility in the melt state between SCBPE and *i*PP, as suggested by Shanks^[10]. It should be mentioned that one can only obtain very limited information about crystal morphology and phase morphology (in macroscopic)

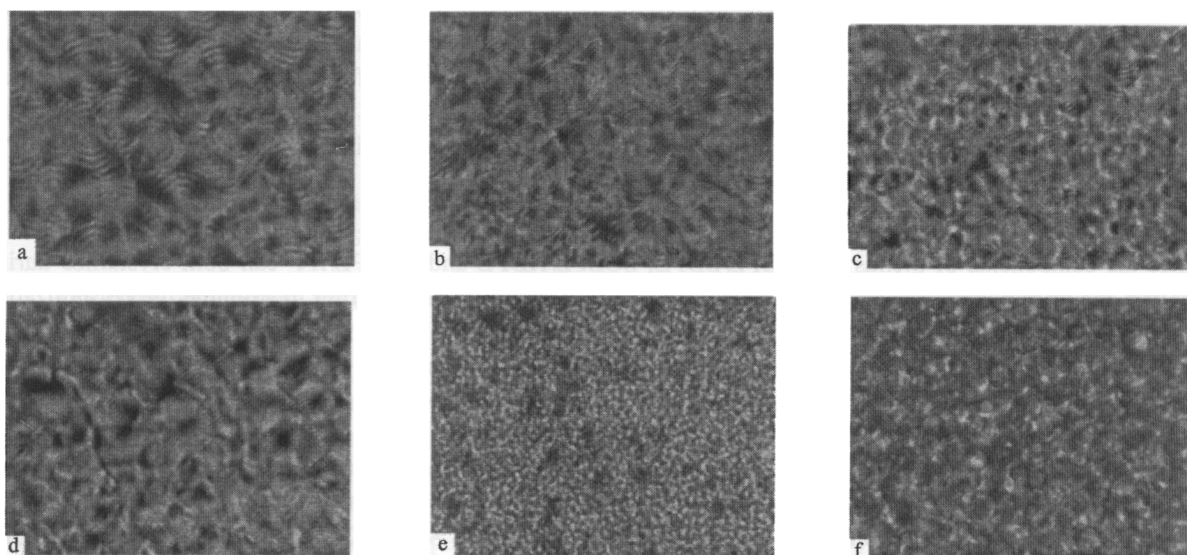


Fig. 1 PLM micrographs of SCBPE, and its blends with other polyolefins

a) Pure SCBPE; b) SCBPE/HDPE; c) SCBPE/LDPE; d) SCBPE/EPDM; e) SCBPE/*i*PP; f) SCBPE/PS

by PLM observation, and transmission electron microscopy (TEM) or atomic force microscope (AFM) must be used for observing more detailed microscopic structure (microscopically). Obviously, it is not possible to co-crystallize SCBPE together with *i*PP. But co-crystallization between SCBPE and HDPE or LDPE is possible and was further studied by DSC (see below).

Isothermal Crystallization

Figure 2(a) shows a plot of isothermal crystallization half time ($t_{1/2}$) versus temperature. The value of half time can be used to qualitatively analyze the crystallization rate. The lower the value of $t_{1/2}$, the faster the rate of crystallization will be. At the same crystallization temperature, the $t_{1/2}$ of SCBPE/LDPE and SCBPE/PS blends does not change very much compared with pure SCBPE. The similar $t_{1/2}$ of SCBPE/PS and pure SCBPE can be easily understood as resulting from the phase separation between SCBPE and PS. However, LDPE could be phase miscible with SCBPE in the melt state as suggested from PLM results. The similar $t_{1/2}$ of SCBPE/LDPE and pure SCBPE observed here might be due to co-crystallization of SCBPE and LDPE (see Fig. 3–5). We also see an enhanced crystallization rate in SCBPE/HDPE blends and a decreased crystallization rate in SCBPE/EPDM blends. Due to the linear structure of HDPE, its molecular motion is easier than that of pure SCBPE and it crystallizes first in the blends. The pre-formed crystallites can serve as nuclei for SCBPE, which enhance the crystallization rate and lead to decreasing $t_{1/2}$ of SCBPE/HDPE, while EPDM, co-polymerized with ethylene, propylene and 2-butylene, has some polyethylene chain segments in the backbone, which can result in entanglement between chains of SCBPE and EPDM (phase miscible). When the blends are cooled down, SCBPE crystallizes but EPDM is expelled out of the crystal. Hence, the $t_{1/2}$ of SCBPE/EPDM is larger than that of pure SCBPE at the same temperature. The crystallization of SCBPE/*i*PP shows a very interesting phenomenon. This is shown in Fig. 2(b). There are two curves for SCBPE/*i*PP in Fig. 2(b). The curve marked with SCBPE/*i*PP (150) denotes that the blend was melted at 150°C and cooled to the predetermined crystallization temperatures for crystallization. The other marked with SCBPE/*i*PP (190) denotes that the blend was melted at 190°C before crystallization. Compared with pure SCBPE, the $t_{1/2}$ of crystallization of SCBPE/*i*PP (150) decreases while that of *i*PP/SCBPE (190) increases greatly. For example, at 118°C, $t_{1/2}$ of SCBPE/*i*PP (150) is 53 s whereas the $t_{1/2}$ of SCBPE/*i*PP (190) is 288 s compared with 84 s of pure SCBPE. Because the melting point of pure *i*PP is about 160°C, therefore, PP at 150°C is not entirely melted and still has crystal grains as nucleating agents that can accelerate the rate of crystallization of SCBPE and thus shorten the $t_{1/2}$. But when the blend is kept at 190°C, both *i*PP and SCBPE are in the molten state. The increase of $t_{1/2}$ of SCBPE/*i*PP (190) may be caused by the interaction (phase miscible) between SCBPE and *i*PP when both are melted. To verify that SCBPE co-crystallizes together with HDPE, LDPE or *i*PP, a subsequent heating experiment was carried out for the above crystallized samples. As shown in Fig. 3, the presence of only one melting peak for SCBPE/HDPE and SCBPE/LDPE blend but two melting peaks for SCBPE/*i*PP, indicates the possibility that SCBPE co-crystallizes together with HDPE or LDPE, but a separated crystal lamella is formed in the SCBPE/*i*PP blend.

Non-Isothermal Crystallization

Since the components of blends of SCBPE/LDPE, SCBPE/HDPE and SCBPE/*i*PP can both crystallize during cooling, the crystallization behavior in these blends is quite complicated. In order to examine the crystallization behavior of SCBPE after the addition of LDPE, HDPE and *i*PP, two kinds of samples were prepared. One is called the “unmixed sample”, which was made by just putting SCBPE and the second component together in the weight proportion of SCBPE/*i*PP = 80/20 without melt-blending. The other is called the “mixed sample”, which was made by melt-blending of SCBPE with the second component together in the same weight proportion as above. Again, DSC measurement was carried out in the manner of non-isothermal crystallization. The unmixed sample, the mixed sample and pure samples were kept at 190°C for 5 min, and then were cooled at a rate of 20 K/min. Figure 4 illustrates the DSC cooling curves of LDPE, SCBPE/LDPE (unmixed), SCBPE/LDPE (mixed) and SCBPE. It is evident that the curve of unmixed SCBPE/LDPE has two crystallization peaks, one at 88.9°C and the other at 111.5°C. Compared with the peak temperature of pure LDPE (89.5°C) and that of pure SCBPE (113.1), it is clear that in the curve of unmixed SCBPE/LDPE, the higher temperature is the

crystallization temperature of SCBPE and the lower one is that of LDPE. Since the macroscopic phase separation exists between SCBPE and LDPE in the SCBPE/LDPE (unmixed), SCBPE and LDPE can crystallize at two different temperatures during crystallization and two crystallization peaks are observable in the DSC curve. However, there is only one crystallization peak in the DSC curve for SCBPE/LDPE (mixed), whose temperature is 112.4°C, which is near the peak temperature of pure SCBPE. This phenomenon indicates again that SCBPE is miscible with LDPE to some degree in the melt in the mixed sample, and is in agreement with PLM pictures. This result is also in good agreement with Xu's finding that the most linear part of LDPE is incorporated into the lamellae of ethylene-butene copolymers thus undergoing co-crystallization that depends on the molecular structure of polymers such as branch content, molecular shape and molecular weight^[10]. The presumption of LDPE incorporated into the SCBPE lamellae could be also possibly proved by comparing the values of blend crystallization enthalpy with that of the SCBPE. A systematic study on the change of enthalpy as function of blend composition for the blends is being undertaken in our group.

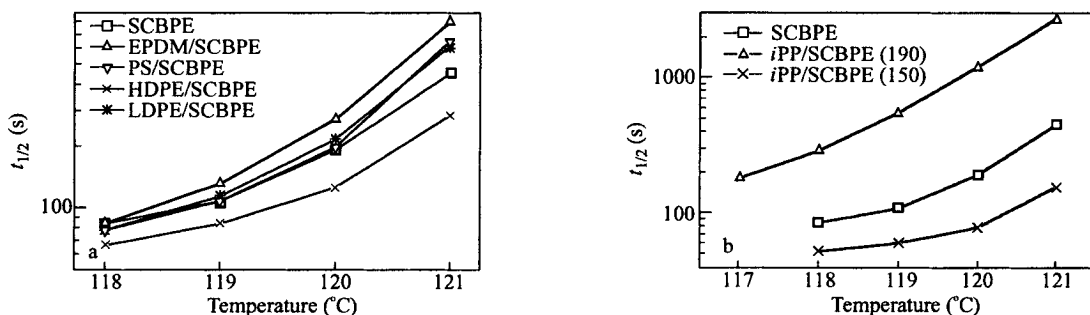


Fig. 2 Half crystallization times as a function of crystallization temperatures for (a) SCBPE and the blends except SCBPE/*i*PP and (b) SCBPE/*i*PP melted at two temperatures before crystallization

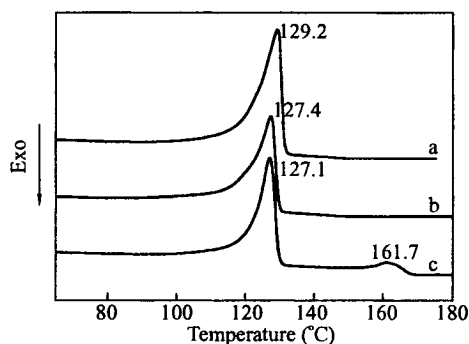


Fig. 3 DSC heating curves of (a) SCBPE/HDPE, (b) SCBPE/LDPE and (c) SCBPE/*i*PP

The same experiment has been done on SCBPE/HDPE blend, as shown in Fig. 5. Because the peak temperature of pure HDPE (112.6°C) is nearly the same as for pure SCBPE (113.0°C), the DSC curve of HDPE/SCBPE does not distinctly show two peaks, but a wide peak with a little shoulder peak for both mixed and unmixed samples. The curve of mixed sample is narrower than that of unmixed blend, indicating that the size of crystal is uniform in the mixed sample. However, the peak temperature of SCBPE is close to that of HDPE and the weight proportion of SCBPE is larger than that of HDPE, causing the merging of two crystallization peaks. One would expect that HDPE molecules should first crystallize because of their linear structure. Instead, SCBPE has a slight higher crystallization temperature than that of HDPE. This may be simply due to the effect of co-crystallization as indicated from PLM results. Due to the distribution of branching composition in SCBPE, only molecules with less branching content can co-crystallize with HDPE while molecules with high branching content cannot. That is why one can still observe two crystallization temperatures in the blend. Kwag *et al.*

reported that the phase morphology of the blend of metallocene SCBPE and HDPE appears as a homogeneous single phase, suggesting that HDPE is miscible with SCBPE. Choi *et al.* have observed that when the branch content of SCBPE is about 40 branched/1000 backbone carbon atoms, the blend of SCBPE and HDPE is phase separated in the melt^[17]. The result of Rana and his coworkers suggested that HDPE/SCBPE is thermodynamically immiscible when the branch content of SCBPE is above 40 branched/1000 backbone carbon atoms but is mechanically compatible, which has been proved by their thermal and mechanical behaviors^[18].

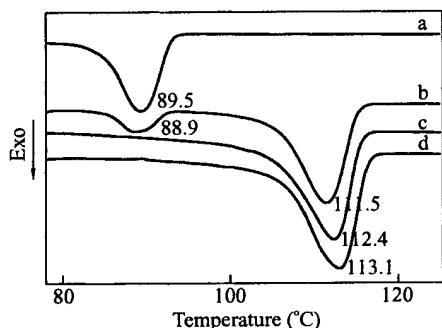


Fig. 4 DSC cooling curves of (a) LDPE, (b) SCBPE/LDPE (unmixed), (c) SCBPE/LDPE (mixed) and (d) SCBPE

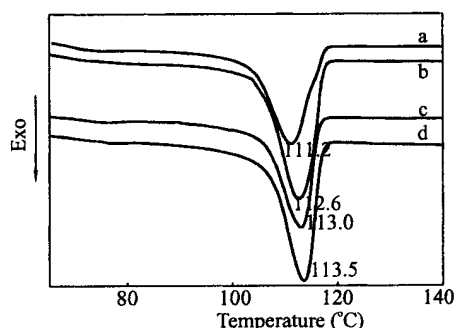


Fig. 5 DSC cooling curves of (a) SCBPE/HDPE (unmixed), (b) HDPE, (c) SCBPE and (d) SCBPE/HDPE (mixed)

Figure 6 shows the DSC result of SCBPE/*i*PP blends. The crystallization peak of SCBPE is 10°C higher than that of *i*PP. Not only the crystallization of SCBPE/*i*PP (unmixed) but also that of SCBPE/*i*PP (mixed) shows one crystallization peak and almost has the same crystallization peak temperature. We know that phase separation should happen in the unmixed blend of *i*PP/SCBPE, but still there is only one peak observed. So one must be very careful when dealing with the DSC crystallization curves, and the appearance of a single peak does not necessarily mean the blend is miscible. Other instrumental analyses are needed to determine the phase behavior. The crystallization enthalpy, X-ray analysis and TEM (or AFM) are needed to further determine the phase behavior.

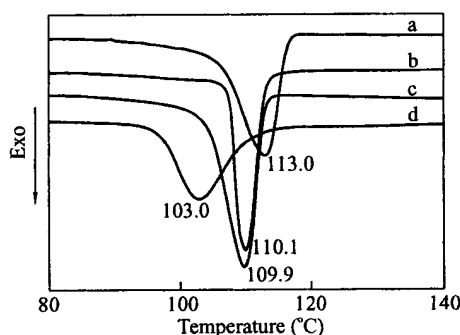


Fig. 6 DSC cooling curves of (a) SCBPE, (b) SCBPE/*i*PP (mixed), (c) SCBPE/*i*PP (unmixed) and (d) *i*PP

Mechanical Properties

Figure 7 shows the frequency dependence of tensile storage modulus E' of the blends at three fixed temperatures (50°C, 80°C and 100°C). E' of all the samples is increased with increasing frequency for all the three temperatures, as we know that increasing frequency is analogous to decreasing temperature. SCBPE/PS has the highest modulus while SCBPE/EPDM has the lowest modulus, and others lay in-between. It has been known that PS has the highest modulus and EPDM has the lowest modulus among the materials used. This result indicates that the tensile modulus of blends is neither related with phase behavior (miscible or immiscible) nor

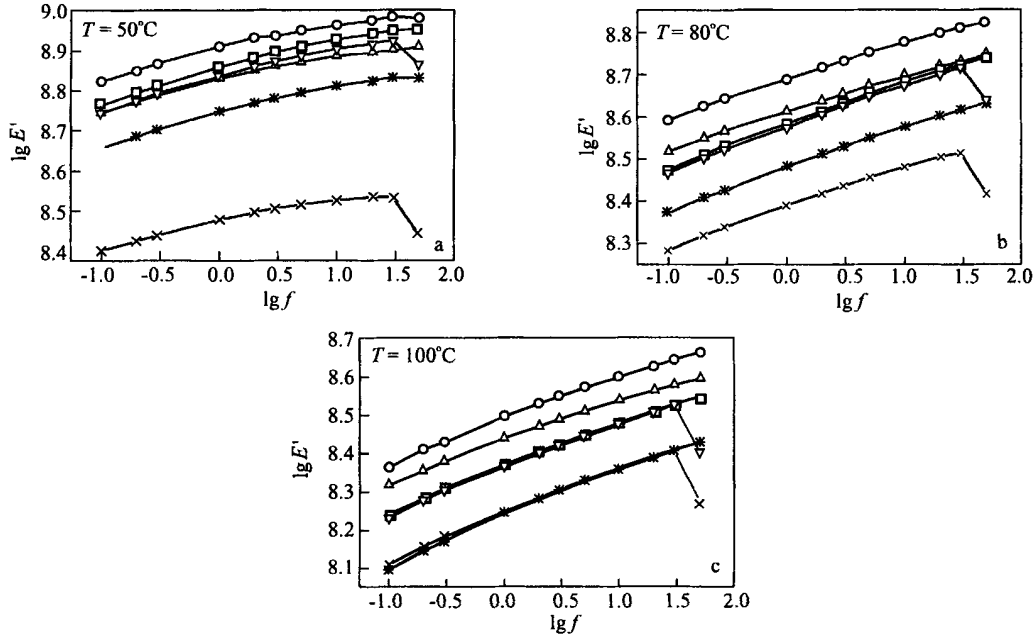


Fig. 7 Plot of the tensile storage modulus of SCBPE and the blends versus frequency at different temperature (T)
a) $T = 50^\circ\text{C}$, b) $T = 80^\circ\text{C}$, c) $T = 100^\circ\text{C}$

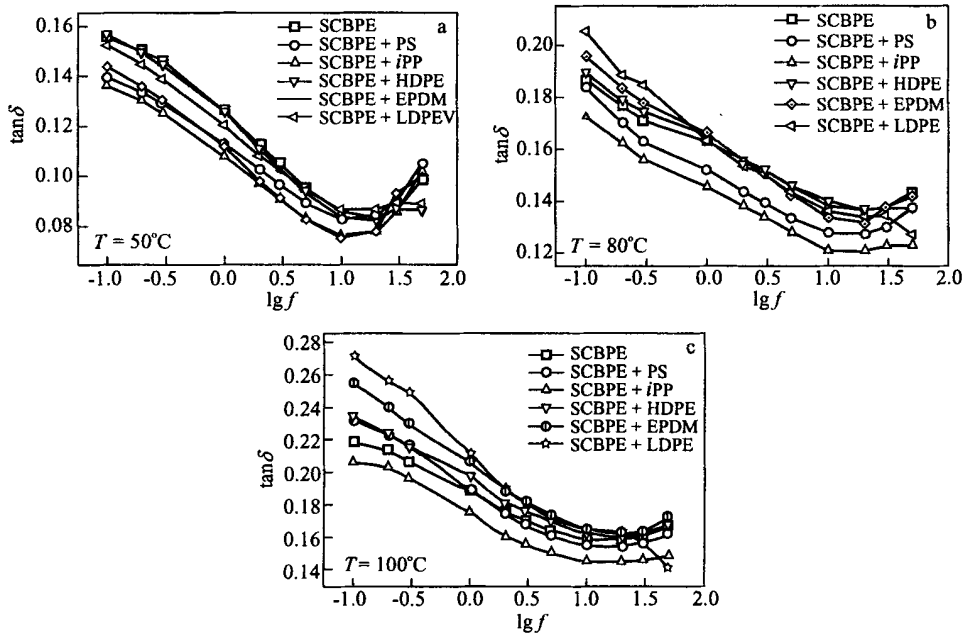


Fig. 8 Plot of $\tan\delta$ of SCBPE and the blends versus frequency at different temperature (T)
a) $T = 50^\circ\text{C}$, b) $T = 80^\circ\text{C}$, c) $T = 100^\circ\text{C}$

with crystal morphology, but it only depends on the modulus of the second component. On increasing the temperature, the modulus difference between SCBPE and the blends becomes smaller due to partial melting of SCBPE. The only exception is SCBPE/PS, which shows more rigidity than the pure SCBPE as temperature is increased. This is probably due to the fact that the glass transition temperature of polystyrene is about 100°C and

PS retains its rigidity below the glass transition temperature (T_g). Figure 8 shows the $\tan\delta$ of the blends changes with increasing frequency, at three fixed temperatures. A decrease of $\tan\delta$ with frequency was observed first for all materials, and a minimum appeared around 10 Hz. The curves overlap at lower temperature (50°C, 80°C), and the difference between the $\tan\delta$ becomes more obvious at higher temperature (100°C). The value of $\tan\delta$ for SCBPE/*i*PP is always the lowest among other samples at three temperatures. Compared with the storage modulus, the change of $\tan\delta$ of SCBPE on adding second a component is much more complicated, and worthy of further investigation. It must be related to both the phase morphology and the crystal morphology. It should be also noted that no transition peak can be seen for any of the samples, so apparent molecular relaxation does not occur during the experiment.

CONCLUSION

In summary, the crystallization and mechanical properties of SCBPE are greatly affected by the incorporation of second polyolefins, in a different way, depending on the phase behavior and the modulus of the second components. SCBPE may be phase miscible in the melt with HDPE, LDPE and EPDM and can co-crystallize together with HDPE or LDPE during cooling. There exists a big change of crystal morphology and crystallization kinetics of SCBPE/*i*PP blends, and it needs to be further studied since the unmixed samples shows a similar crystallization behavior to mixed samples. DMA results show the E' values of all the blends decrease with increasing temperature at the fixed frequency, and the tensile modulus of the blends is not related with phase behavior, but only depends on the modulus of the second component. Compared with E' , the change of $\tan\delta$ is much more complicated, and the lowest $\tan\delta$ is obtained for the SCBPE/*i*PP system.

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