

## Effect of entropy penalty on selective distribution of aluminum borate whiskers in isotactic polypropylene (iPP)/syndiotactic polypropylene (sPP) blends

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### ABSTRACT

The selective distribution of aluminum borate whisker in isotactic polypropylene (iPP)/syndiotactic polypropylene (sPP) blends was studied. For iPP/sPP/whisker composites, whiskers are distributed in iPP phase, which follow the theory of interfacial tension. When Irganox 1010 is introduced into the composites, the distribution of whiskers is changed from iPP phase to sPP phase. The results of contact angle tests indicate that the characteristics of the whisker surface are modified by Irganox 1010 and the interactions between the whisker and the matrix are dominated by van der Waals type power law. An entropy-penalty process dominates the change of distribution of whiskers in the composites. The DMA tests show that the loss modulus of composites is improved when whiskers distribute in sPP phase.

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### 1. Introduction

In the past several decades, polymer blends have been widely used instead of neat polymers. In order to further improve the physical properties of polymer blends, such as toughness, conductivity, heat distortion temperature and so on, inorganic filler was introduced into polymer blends to form ternary composites. One of the challenges in such composites is to predict how the inorganic fillers distribute in the blends, especially when these polymers are immiscible. Many thermodynamic and kinetic factors such as interfacial tension, viscosity ratio and so on, determine the morphology of composites. Up to now, several theories have been established to predict the selective distribution of fillers in polymer blends. Theory of interfacial tension [1] proposed that the fillers prefer to migrate to the phase whose interfacial tension with the filler was lower than the other phase to reduce the whole energy of composite. Most of the reports have confirmed that the selective distribution of fillers keeps to this theory [2–4]. Some other scholars [5,6] reported that when the viscosities of two polymers are incomparable, fillers will come into the phase with lower viscosity to minimize the dissipative energy of composite. Wu et al. [7] claimed that the entropy penalty might play a main role in the selective distribution of fillers in polymer blends. Theory of entropy penalty [1,7–17] points out that the polymer adsorbs better on

rough surface than on smooth and homogenous one, especially when the roughness is in the range of 1–100 nm which is just on the scale from segment size to the root-mean-square radius of gyration of a polymer. Besides, some literatures reported that blending procedure also influences the distribution of fillers [18,19]. Although these three theories cannot explain the overall phenomena about selective distribution of fillers, many technologies have been developed to control the distribution of fillers in polymer blends. Gubbels et al. [20] oxidized the surface of carbon black to change the distribution of carbon black from PE phase to PS phase. Yang et al. [21] control the migration of nano-SiO<sub>2</sub> in PP/EPDM blends by treating SiO<sub>2</sub> surface and PP matrix. Feng et al. [5] used several kinds of PMMA with different viscosities to change the migration of fillers. Dong et al. [22] used the interaction between organoclay and PEOc elastomer to retain the fillers in the elastomer phase.

To date, most of the reports of selective distribution deal with spherical fillers, such as carbon black, nano-SiO<sub>2</sub> and so on. Fibrous filler, which has been recognized as effective reinforcing additive in polymer blends, is rarely studied in this area. Unlike spherical filler, fibrous filler has larger aspect ratio which indicates that the selective distribution behavior may be different from spherical filler. Bertilsson [3] has found that when the filler is a aluminum borate whisker, the viscosity distributing factor is less important than the interfacial interactions in polymer blends.

In our opinion, the fibrous shape leads to local curvatures on the whole length of fiber and these local curvatures can be considered as a kind of roughness. If the size of fibrous filler is sufficiently small and the physical and chemical characteristics of surface are

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suitable, the main driving force of selective distribution may change from interfacial tension to entropy and the behavior of distribution is under control.

In order to confirm this point of view, the aluminum borate whisker, a kind of fibrous inorganic crystal, was chosen to determine the behaviors of selective distribution. In previous works, the polymer matrix which has been chosen for the study of selective distribution is composed of different polymer components, such as HDPE/PMMA [7], PE/PS [20], PP/EPDM [21], PP/POEc [22] and so on. It is well known that different chemical compositions lead to different chemical characteristics and interactions with filler surface. Thus, it is very important to choose suitable polymer as the matrix. Isotactic polypropylene (iPP) and syndiotactic polypropylene (sPP) were selected as the matrix blend to avoid the influence of chemical composition of polymer pair in blends. Here, both polymers are nonpolar and have the same chemical composition, which will benefit the further analysis of selective distribution. The other advantage is that the flexibility of polymer chains could be identified directly from their different conformations without other indirect method such as  $T_g$  [7]. According to the location of methyl groups, the flexibility of iPP chain is lower than that of sPP chain. Moreover, iPP/sPP blend is completely phase separated following a spinodal decomposition mechanism [23,24]. Antioxidant serves as a commonly used additive in polymer industry to prevent the degradation of polymers during the processing and has little influence on the chemical and physical characteristics of the polymer matrix. However, the antioxidant Irganox 1010 also serves as a compatibilizer in some filled polymer blends [25]. Thus, Irganox 1010 was chosen as a surface treatment agent in our study. Concerning the composite formulations, the percolation of whisker had to be considered. To minimize the influence of the filler itself whisker contents were chosen sufficiently low to avoid filler particle percolation in any of the phases. According to Bigg [26], the percolation threshold of aluminum borate whisker can be found at 7 vol.%. We used 1.5 vol.% (5 wt%) whisker loading to avoid percolation.

The purpose of this paper is to study the selective distribution and the corresponding mechanism of whiskers in iPP/sPP blends and develop a new insight to control the distribution of inorganic fillers in iPP/sPP blends.

## 2. Experimental

### 2.1. Materials

The iPP, F401, was supplied by Lanzhou Petrochemical (China), with the  $M_n$  of about  $11.0 \times 10^4$  g/mol. The sPP, 1751, was supplied by Total Petrochemicals (USA), with the  $M_w$  of  $2.4 \times 10^5$  and  $M_w/M_n$  of 3.5. Aluminum borate whisker ( $Al_2O_3)_9(B_2O_3)_2$ , was supplied by Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. Aluminum borate whiskers are single crystals, with a density of  $2.93$  g/cm<sup>3</sup> and a specific surface area of  $2.5$  m<sup>2</sup>/g. Irganox 1010 was supplied by Ciba Specialty Chemicals. The melting points of iPP, sPP, aluminum borate whiskers and Irganox 1010 in our research are 170 °C, 130 °C, 1440 °C and about 120 °C, respectively.

### 2.2. Sample preparation

The whisker coated with Irganox 1010 (whisker(A)) was prepared in xylene at 130 °C. The whiskers and Irganox 1010 were added into xylene and stirred for 5 min before completed coating. The product dried in vacuum for 48 h.

The composition ratio of composites was chosen as listed in Table 1. In order to avoid the thermal degradation of polypropylene, the whole processing time was limited to 6 min. Compounding of

**Table 1**

The composition ratio of blends and composites.

Sample	Ingredients	(wt/wt)
1	iPP/sPP	70/30
2	iPP/sPP/whisker	70/30/5
3	iPP/sPP/whisker/antioxidant	70/30/5/0.5
4	iPP/sPP/whisker(A)	70/30/5

the polypropylene blends and composites was done in an internal mixer at a barrel temperature of 190 °C and an apparent shear rate of 30 r/min. iPP and aluminum borate whisker were first plasticized for 3 min, then sPP with or without Irganox 1010 was added and mixed for another 3 min. Neat iPP/sPP blend was mixed by the same processing for comparison.

### 2.3. Scanning electron microscopy (SEM)

For morphology observation, the samples were fractured in liquid nitrogen. Then the fractured samples were dipped into toluene for 10 min at a temperature of 70 °C to remove sPP component from the fracture surface, washed with fresh toluene and acetone and dried in vacuum for 24 h. The samples were sputtered with gold and observed in a JEOL JSM-5900LV SEM instrument, using an acceleration voltage of 20 kV.

### 2.4. Contact angle measurements

Contact angles were measured in a sessile drop mold with KRÜSS DSA100. iPP and sPP samples were compression molded between clean silicon wafers at 190 °C while Irganox 1010 was compression molded at 130 °C. Aluminum borate whiskers were compression molded at room temperature under a certain pressure. Contact angles were measured on 3  $\mu$ l of wetting solvent at 20 °C.

### 2.5. Fourier transform-infrared spectroscopy (FT-IR)

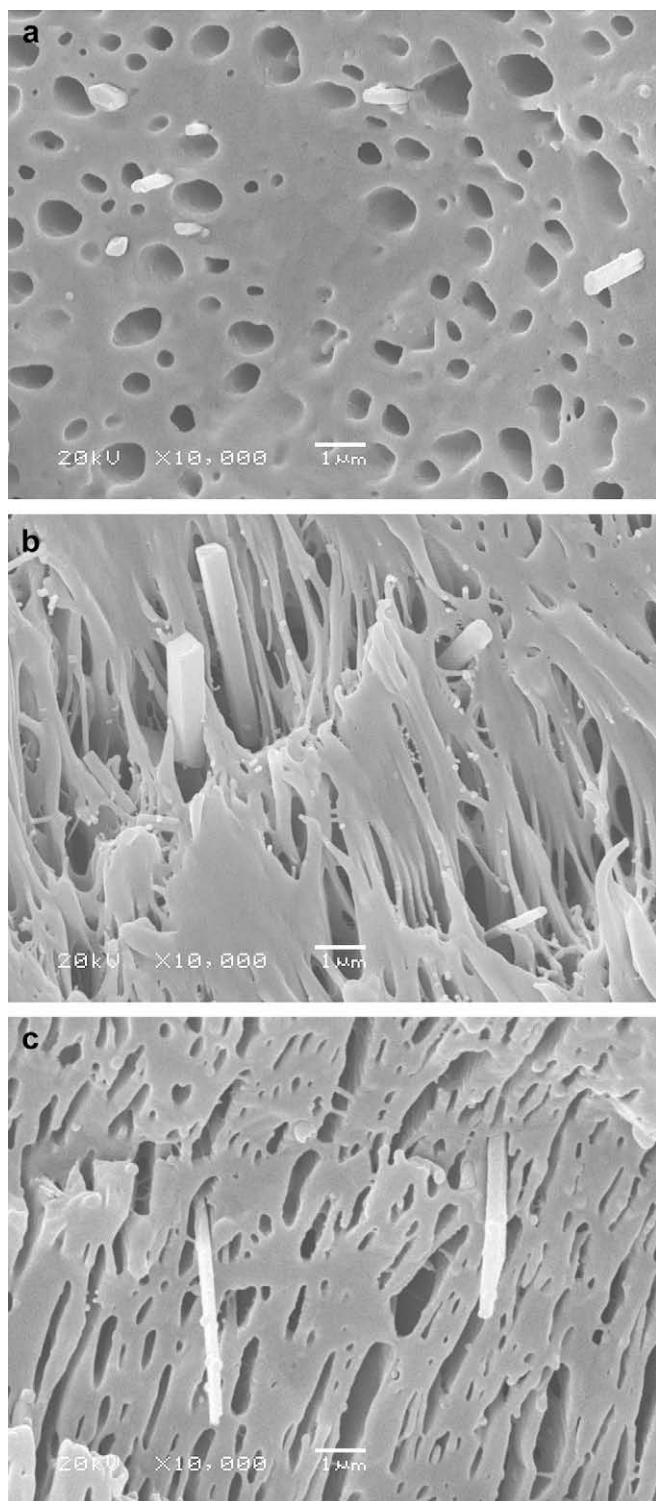
iPP, sPP and whisker samples were dried under vacuum for 6 h. PP samples were compressed into thin film between clean silicon wafers at 190 °C and the whiskers were compressed into plates at room temperature for FT-IR testing. The FT-IR spectra were recorded using a NICOLET-560 spectrophotometer.

### 2.6. Dynamic mechanical analysis (DMA)

The DMA was carried out using a TA Instruments Q800 DMA. Dimensions of specimen were  $40 \times 10 \times 4$  mm<sup>3</sup>. All the samples were measured over the temperature range of  $-50$  °C to 150 °C at a heating rate of 3 °C/min and at a frequency of 10 Hz.

## 3. Results and discussion

The morphology of iPP/sPP/whiskers was observed by SEM and the different distributions of whiskers in iPP/sPP blends are shown in Fig. 1 (the dark holes represent the etched sPP phase). As seen in Fig. 1(a), almost all whiskers were distributed in the continuous phase (iPP phase) or nearby the interfaces between continuous phase and disperse sPP phase. While when the Irganox 1010 was introduced into blends, even though whiskers were mixed with iPP first, the whiskers change their locations from iPP phase to sPP phase (seen in Fig. 1(b)). The same phenomenon of selective distribution also could be seen in iPP/sPP/whisker(A) composites. Thus, in iPP/sPP blends, whiskers preferred to distribute in iPP phase rather than sPP phase. When the Irganox 1010 was



**Fig. 1.** SEM images of ternary blends: (a) iPP/sPP/whisker; (b) iPP/sPP/whisker/1010; (c) iPP/sPP/whisker(A).

introduced into blends, whether added into the blends directly or covered the whiskers first, both processes could change the distribution of whisker from iPP phase to sPP phase.

In order to understand the mechanism of selective distribution of whiskers in the blends, some thermodynamic and kinetic factors should be taken into account. Interfacial tension is considered first. The value of contact angles with water and diiodomethane, the

surface tension and polarity calculated by Eqs. (1), (2) [1,21] and (3) [27] are listed in Table 2. Where the number behind materials is the mixing time (min) and sPP(A) is the blend of sPP and 0.5 wt% Irganox 1010.

$$(1 + \cos \theta_{\text{H}_2\text{O}})\gamma_{\text{H}_2\text{O}} = 4 \left( \frac{\gamma^{\text{d}}_{\text{H}_2\text{O}}\gamma^{\text{d}}}{\gamma^{\text{d}}_{\text{H}_2\text{O}} + \gamma^{\text{d}}} + \frac{\gamma^{\text{p}}_{\text{H}_2\text{O}}\gamma^{\text{p}}}{\gamma^{\text{p}}_{\text{H}_2\text{O}} + \gamma^{\text{p}}} \right) \quad (1)$$

$$(1 + \cos \theta_{\text{CH}_2\text{I}_2})\gamma_{\text{CH}_2\text{I}_2} = 4 \left( \frac{\gamma^{\text{d}}_{\text{CH}_2\text{I}_2}\gamma^{\text{d}}}{\gamma^{\text{d}}_{\text{CH}_2\text{I}_2} + \gamma^{\text{d}}} + \frac{\gamma^{\text{p}}_{\text{CH}_2\text{I}_2}\gamma^{\text{p}}}{\gamma^{\text{p}}_{\text{CH}_2\text{I}_2} + \gamma^{\text{p}}} \right) \quad (2)$$

$$\text{Polarity} = \frac{\gamma^{\text{p}}}{\gamma} \times 100\% \quad (3)$$

where  $\gamma$  is the surface tension,  $\gamma^{\text{d}}$  is the dispersion component,  $\gamma^{\text{p}}$  is the polar component and  $\theta$  is the contact angle with water or diiodomethane.

The interfacial tensions were calculated by the equation of Wu [1] (Eq. (4)) and Owens–Wendt equation [28] (Eq. (5)), where  $\gamma_{12}$  is the interfacial tension between materials 1 and 2,  $\gamma_1$  and  $\gamma_2$  are the surface tensions of the two contacting components in the composites. The iPP–sPP blend is a nonpolar–nonpolar system which is suitable for Wu’s equation, while Owens–Wendt equation is valid to calculate the interfacial tension of nonpolar–polar system, such as PP–whisker, Irganox 1010–whisker and Irganox 1010–PP. The calculated results are listed in Table 3.

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left( \frac{\gamma_1^{\text{d}}\gamma_2^{\text{d}}}{\gamma_1^{\text{d}} + \gamma_2^{\text{d}}} + \frac{\gamma_1^{\text{p}}\gamma_2^{\text{p}}}{\gamma_1^{\text{p}} + \gamma_2^{\text{p}}} \right) \quad (4)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^{\text{d}}\gamma_2^{\text{d}}} - 2\sqrt{\gamma_1^{\text{p}}\gamma_2^{\text{p}}} \quad (5)$$

It is well known that the lower level of total energy the composites have, the more stable morphology of composites will form. In order to identify the variation of surface tension of neat polymer in the processing of the composites, the surface tension of iPP or sPP at critical mixing time was measured. As seen in Table 2, due to the syndiotactic locations of methyl on sPP main chain which average the adsorption of electron clouds, the surface tension and polarity of sPP are slightly lower than that of iPP. Aluminum borate whisker has a high-energy surface which attracts the polymer with the highest energy in order to minimize the total interfacial energy of the multi-phase blends.

Based on the theory of interfacial tension, in all of possible component pairs in Table 3, although the interfacial tension of iPP–whisker increases with increased mixing time, iPP–whisker has lower interfacial tension compared with sPP–whisker during the mixing time, i.e.,  $\gamma_{\text{iPP-whisker}} < \gamma_{\text{sPP-whisker}}$ . It implied that the whiskers prefer to distribute in iPP phase as shown in iPP/sPP/whisker

**Table 2**  
Contact angle, surface tension and polarity of the composites.

Sample	Contact angle (°)		Surface tension (mN/m)			Polarity (%)
	Water	Diiodomethane	$\gamma$	$\gamma^{\text{d}}$	$\gamma^{\text{p}}$	
iPP0	98.7	47.8	36.89	34.77	2.12	5.75
iPP3	99.5	49.9	35.81	33.79	2.02	5.64
iPP6	99.9	48.6	36.31	34.53	1.78	4.90
sPP0	100.8	52.4	34.46	32.71	1.75	5.08
sPP(A)3	103.5	63.1	29.36	27.48	1.88	6.40
Whisker	20.4	17.9	79.38	44.86	34.52	43.49
1010	85.2	21.9	50.15	44.48	5.68	11.33

**Table 3**  
The values of the interfacial tension of the composites.

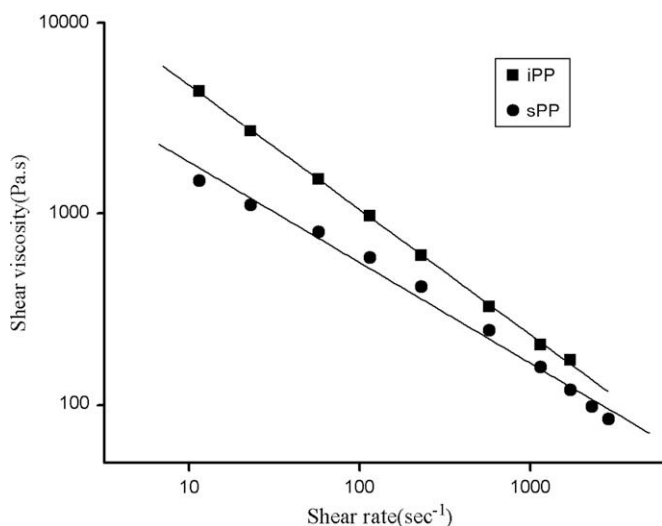
Possible pairs	Interfacial tension (mN/m)
iPP3-sPPO	0.04
iPP0-whisker	20.17
iPP3-whisker	20.62
iPP6-whisker	21.29
sPPO-whisker	21.69
sPP(A)3-whisker	22.41
1010-iPP	1.44
1010-sPP	2.02

composite (Fig. 1(a)). However, this theory cannot explain the distribution of whiskers in the iPP/sPP/whisker/1010 composite. The surface tension of whisker(A) (coated with Irganox 1010) was determined by Irganox 1010 but the interfacial tension of 1010-iPP was still lower than that of 1010-sPP. It means that whisker(A) has the similar behavior of distribution with the whiskers without coating. In fact, the distribution of whisker(A) is contrary to the prediction of the theory, as seen in Fig. 1(c). Considering that the Irganox 1010 was incorporated into sPP, these small molecules would increase the polarity of sPP and meanwhile decrease the surface tension [1], which could be confirmed by contact angle, that is, polarity of sPP increases from 5.08% to 6.40% while the surface tension decrease from 34.46 mN/m to 29.36 mN/m. It means that the interfacial tension of sPP-whisker increases from 21.69 mN/m to 22.41 mN/m. As a result, the whiskers should be retained in iPP phase which is still contrary to the result of SEM observation (Fig. 1(b)). Moreover, as seen in Table 3, the interfacial energy between different pairs of components has increased as the processing time goes forward. It is possible that the interfacial tension of iPP-whisker may maintain the increasing trend and exceed that of sPP-whisker at some time, but in our research (processing time from 0 min to 3 min) this reversion has not occurred. Thus, the change of interfacial tension is not the reason which forces the whiskers to migrate from iPP phase to sPP phase.

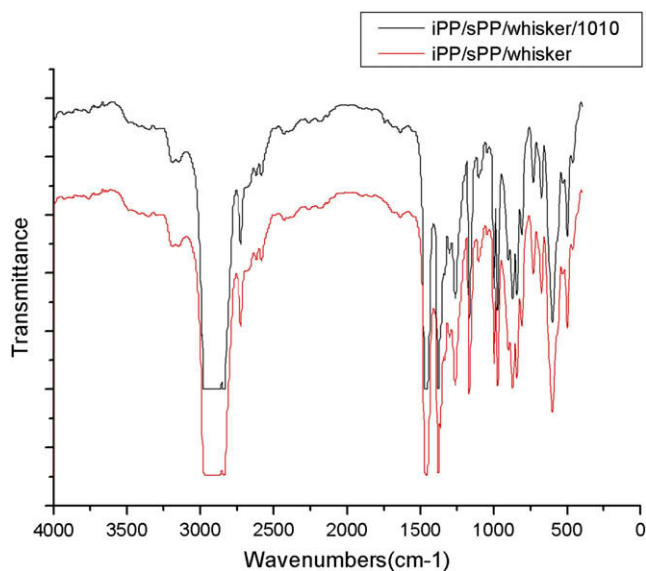
Then let us examine the influence of viscosity. As seen in Fig. 2, the viscosity of iPP is higher than sPP and the viscosity ratio of iPP and sPP is changed from 2.9 to 1.4 within the shear rates from  $11.52 \text{ s}^{-1}$  to  $1728 \text{ s}^{-1}$ , but the difference is not very large. So the interfacial tension controls the distribution of whisker as seen in SEM photo of iPP/sPP/whisker composite which keeps to the Bertilsson's work [3]. Although whiskers selectively distribute in sPP

phase with lower viscosity when the Irganox 1010 was introduced into the composites, the content of Irganox 1010 mixed with sPP is insufficient to act as plasticizer to decrease the viscosity of sPP in the composites within 3 min. In fact, the Irganox 1010 molecules prefer to cover the whiskers rather than distributing inside of any polymer phase in the composites and the reason will be discussed later. Thus, even though the whiskers were distributed in sPP phase with low viscosity, the influence of viscosity has nothing to do with the selective distribution of fillers in our composites.

The chemical interactions also determine the distribution of inorganic fillers in polymer blends. In fact, chemical interaction is stronger than physical influence. Based on this point, the processing time was limited in 3 min (6 min for iPP) to decrease the possibility of thermal degradation on PP chains during the processing. Because if the thermal degradation occurred during the processing, some oxygenated functional groups would generate on PP molecules. These groups might have chemical interactions with the surface of the whiskers. In order to confirm it, iPP and sPP with different mixing times and their composites with whiskers were tested by FT-IR. As seen in Fig. 3, around the wavenumbers of  $1700 \text{ cm}^{-1}$  which relate to the existence of oxygenated functional groups, the adsorption peaks could not be found in iPP/sPP/whisker composite. It means that thermal degradation did not occur during the processing. In iPP/sPP/whisker/1010 composite, a small adsorption peak could be found at  $1743 \text{ cm}^{-1}$ , but it was not originated from PP molecular. Irganox 1010 molecule contains carboxyl groups and its structure is shown in Fig. 4 [29]. The small adsorption peak at  $1743 \text{ cm}^{-1}$  may originate from Irganox 1010 and this point can be confirmed in FT-IR results of sPP. The FT-IR curves of sPP with the mixing time of 0 min and 3 min are shown in Fig. 5 and both of the curves are nearly the same and no adsorption peaks can be found around  $1700 \text{ cm}^{-1}$ . Interestingly, a small peak at  $1743 \text{ cm}^{-1}$  was found in sPP with Irganox 1010 after 3 min mixing. Compared with sPP3 and sPP(A)3, we could confirm that the small peak at  $1743 \text{ cm}^{-1}$  related to Irganox 1010. The FT-IR curves of iPP with the mixing time of 0 min and 6 min were tested and shown in Fig. 6. The adsorption peaks of oxygenated functional groups cannot be found in both curves too. According to the results of FT-IR, the thermal degradation has not occurred during the process, so the influence of thermal degradation was excluded.



**Fig. 2.** Shear viscosity as a function of shear rate of neat iPP and neat sPP.



**Fig. 3.** FT-IR of iPP/sPP/whisker and iPP/sPP/whisker/1010 composite.

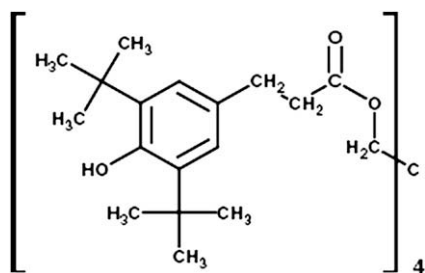


Fig. 4. Molecule structure of Irganox 1010.

It is well known that increasing entropy can lead a system to achieve a more stable state in thermodynamics. In filled polymer blends, the polymer chains are adsorbed on filler surface which decrease the value of entropy. If the loss of entropy is minimized, the stable state of the composite can be obtained. In other words, polymer adsorption takes place only when the enthalpic contribution of attractive polymer surface contacts overcomes the loss of configurational and/or conformational entropy arising from confinement to the surface [7]. When the entropy factor dominates the selective distribution of fillers in composites, the final morphology of the composites maybe no longer determined by the interfacial tension or viscosity but depends on the flexibility of polymer chain, since a flexible chain needs a low entropy cost. However, some problems about this theory should be clarified before being introduced into our study.

First, the essential difference between a rough surface and a smooth one should be considered. Due to the work of Ball et al. [30], when van der Waals type power law dominates the interactions between the surface and monomers, the potential interaction between the monomers and the surface is dependent on the local curvatures. Monomers are preferentially adsorbed in the concave of scraggly surface, so-called 'valleys' which have high local curvatures. It indicates that if the surface has suitable curvatures, even though it is smooth and homogeneous, polymer chains still adsorb onto the surface. In other words, the critical curvature is the key adsorbent factor of a certain surface. Aluminum borate whisker, a kind of fibrous filler, has the whole curvatures through whole

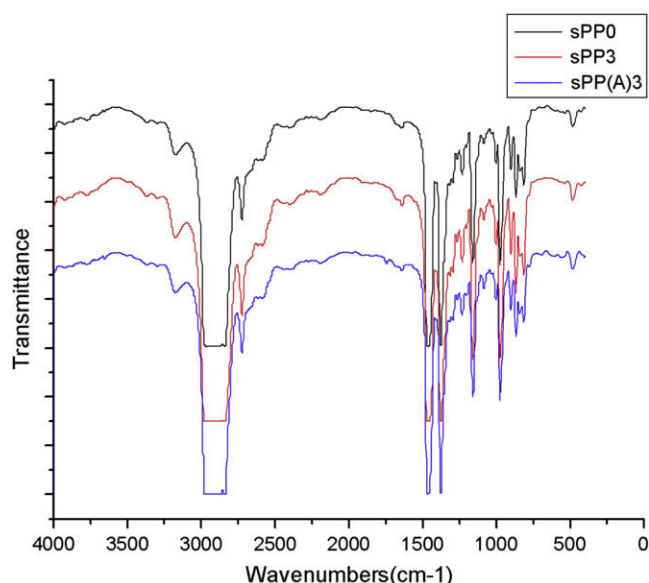


Fig. 5. FT-IR of sPP0, sPP6 and sPP(A)3.

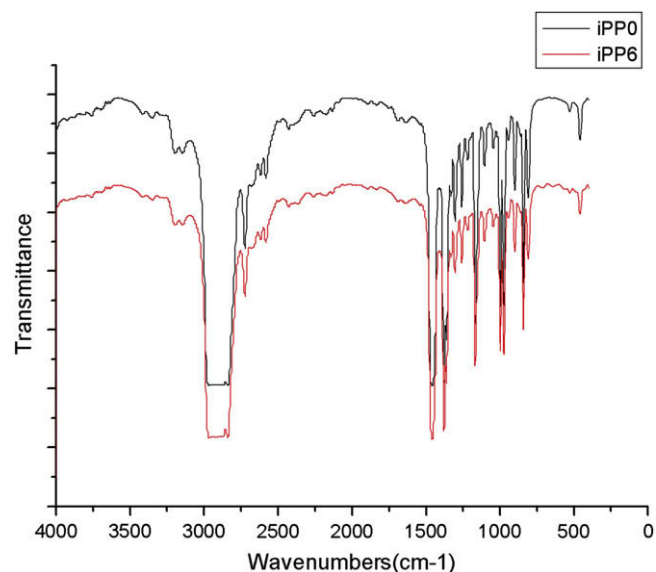


Fig. 6. FT-IR of iPP0 and iPP6.

length of whisker body, which means that whiskers can serve as an effective surface, regardless of its smooth surface.

Secondly, the influence of the polymer environment on this process cannot be neglected. The model of entropy penalty was found in polymer solution which ignored the interaction between polymer chains, thus the curvature is related to the size of a single polymer chain. While in polymer melt it cannot be neglected and in fact, the polymer chains always entangle with each other to form polymer coil rather than single chain. In this case, correspondingly larger curvature of the surface is required. Li et al. [31] reported that in PE/*p*-xylene suspension, PE single crystals have been successfully grown on the surface of carbon nanotubes and 'nanohybrid shish-kebabs' (NHSK) were formed in the secondary nucleation of PE. It means that carbon nanotubes with diameter of tens of nanometer have been considered as rigid macromolecules and polymer chain prefers to align along the tube axis regardless of the lattice matching. Interestingly, the same phenomenon had been found on the surface of SiO<sub>2</sub>-MgO-CaO whiskers (with the diameters of 200–500 nm) when they were mixed with PE melt [32]. From these reports, the critical size of fibrous particle which can be considered as 'rigid macromolecules' depends on the polymer environment. In our study, the diameters of aluminum borate whisker (100–500 nm) are close to that of SiO<sub>2</sub>-MgO-CaO whiskers and then the larger critical curvatures which make the adsorption become valid is required in iPP/sPP blends. Furthermore, during adsorption of one polymer chain onto the surface, a second chain may initiate its own adsorption in a contiguous region, and different chains maybe incorporated in the same surface area [33]. Although the tangled polymer chains decrease the number of conformation of a single chain in coil, the fraction of adsorbent repeat units of polymer coil is lower than that of each single chain when they were adsorbed onto surface, as seen in Fig. 7. It means that the less adsorbent repeat units, the fewer limits to the change of conformations of polymer chain; as a result, the entropy penalty is further decreased.

Thirdly, the chemical property of the whisker surface can also influence the distribution behavior. The roughness of the surface can arise from physical or chemical origins. As mentioned above, the local curvature was considered as physical roughness, and the chemical roughness could be induced by chemical impurities on the surface [9]. Before discussing the function of Irganox 1010 in the selective distribution of whiskers, one point should be cleared. The PP resin



Fig. 7. Adsorption of polymer on whisker.

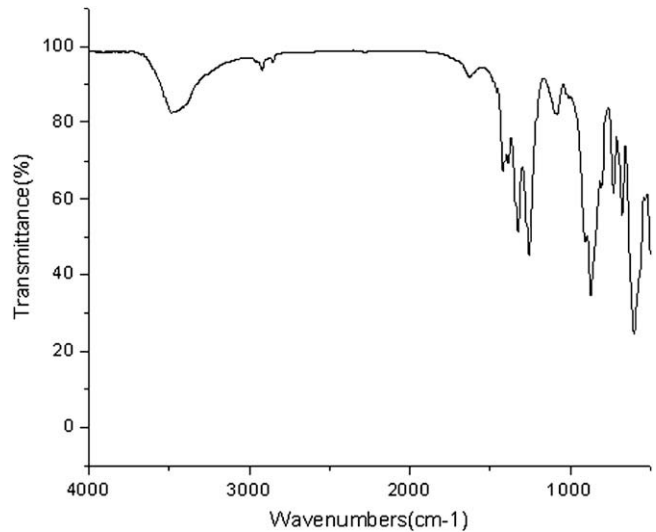


Fig. 8. FT-IR of aluminum borate whisker.

(84.31 mN/m) and Irganox 1010-sPP (82.60 mN/m). Thus, the antioxidant Irganox 1010 tends to cover the surface of whiskers when the composite is mixed in the internal mixer.

$$W_{12} = 2\sqrt{\gamma_1^d \gamma_2^d} + 2\sqrt{\gamma_1^p \gamma_2^p} \quad (6)$$

Additionally, the tips of fibrous filler have the highest local curvature and some physical or chemical deficiency may be exposed here, which can adsorb polymer chains more easily than the other parts of the fibers. To observe the situation of coating location, we coated sPP onto the whisker(A) surface in toluene and the SEM result is shown in Fig. 9. It could be observed that the sPP covered not only the tips of the whisker but also the whole length of the whisker, to form an interesting covered structure, which can be called 'Tomatoes on sticks', regardless of the different parts of the whiskers. This phenomenon confirms that the adsorption is possible on every part of the whisker surface along the axial direction.

According to the discussion above, when the whiskers were added into blends without Irganox 1010, the large difference of polarity between the whisker and polypropylene matrix leads to

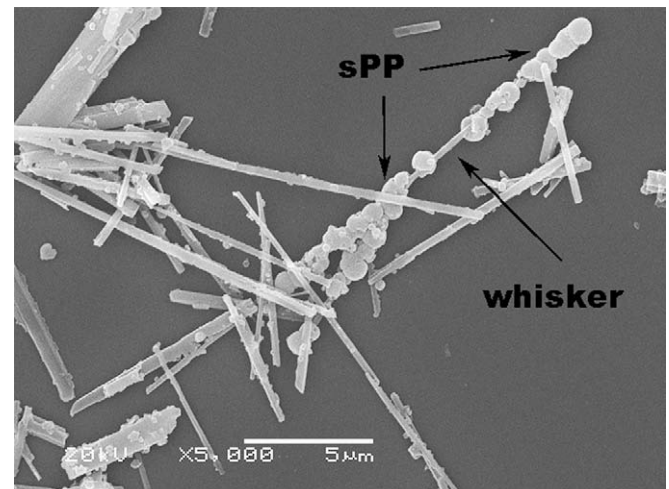


Fig. 9. SEM images of sPP coated with whisker in solution.

we used in this study was commercial brands which may contain small amount of additives. Considering the other additives in starting polymer would make the discussion complex and unreasonable. But this influence could be excluded by the SEM results of iPP/sPP/whisker composite. In this composite, the whiskers located in iPP phase rather than sPP phase. It indicated that the amount of additives that have existed in polypropylene before our experiments was too limited to influence the distribution of whiskers. When more Irganox 1010 was introduced into composite, the whiskers changed their locations from iPP phase to sPP phase. Thus, the role of Irganox 1010 in selective distribution of whiskers in iPP/sPP blends is obvious and determines the distribution of the antioxidant Irganox 1010 in the composites is important. On one hand, Irganox 1010 perhaps has special interaction with inorganic filler surface in the composites [25]. In our study, although the surface of the whisker has been regarded as chemical inert surface, strong absorption peak of hydroxyl ( $3500 \text{ cm}^{-1}$ ) also can be seen in the FT-IR spectroscopy (Fig. 8). As a result, the Irganox 1010 may have some interactions with the functional groups on the whisker surface. On the other hand, small polar molecules prefer to migrate to the surface of materials to decrease the surface tension [1,34]. In multi-phase system, small molecules tend to distribute in interface to decrease interfacial tension. Due to the principle of polar attraction, the interface of whisker-PP has more priority to attract the Irganox 1010 than the iPP-sPP interface. To illustrate this, the thermodynamic work of adhesion ( $W_{12}$ ) was calculated. The higher value of  $W_{12}$  reflects a stronger interaction between the two components, which will result in a relatively more stable interface under the shear forces during mixing [1,21]. According to Eq. (6), the  $W_{12}$  of Irganox 1010-whisker is 117.34 mN/m, higher than that of Irganox 1010-iPP

poor compatibility. In this case, polar repulsion limits the interaction between the surface of whisker and polypropylene chain. According to the work of Sumita [7], when the conditions cannot meet the requirement of adsorption with entropy-penalty type, interfacial tension will serve as the main driving force to determine where the fillers would be. In iPP/sPP blends, the whiskers were selectively distributed in iPP phase, which could decrease the total interfacial energy of the composites.

When the Irganox 1010 was introduced into the iPP/sPP/whisker composites, it covered the whisker surface and lowered down the polarity of the surface. The polarity of Irganox 1010 is close to polypropylene relatively, thus the polarity difference is decreased and the adsorption of the polymer chains onto the surface of whisker becomes feasible. In other words, the whisker can be regarded as a 'rigid macromolecule'. In this case, the adsorption of the flexible sPP chains onto the whiskers decreased the entropy penalty to achieve a more stable state. Moreover, the complete coating of the whisker surface with Irganox 1010 is unnecessary, because the Irganox 1010 here just provides effective adsorbent point for the polymer chains. If the surface was covered incompletely, the friction of repeat units in the polymer coils which adsorbed on the surface would decrease and the number of possible conformations of polymer coils would increase, which benefits the process of adsorption.

The different distributions of whiskers in iPP/sPP blends result in different dynamical mechanical properties of the composites. The DMA results showed that only one glass transition temperature ( $T_g$ ) can be distinguished in the composite as a result of the close  $T_g$  of iPP and sPP [35]. Furthermore, the  $T_g$  of iPP/sPP blends is 13.6 °C and the  $T_g$  decreases to 10.3 °C when the whiskers were introduced into blends. According to the free volume theory, the volume of composites consists of two different parts: one is total volume of all molecules in the composites, often called the occupied volume  $V_o$ , and the other one is the so-called free volume  $V_f$  which corresponds to the volume of all empty spaces between molecules [36]. When the whiskers were added into the blends, they came into the space between polypropylene chains to increase the  $V_f$  and improve the mobility of molecule chain, resulting in the decrease of the  $T_g$ .

Loss modulus ( $E''$ ), the imaginary part of modulus which defines the dissipation of energy, is out of phase with the strain [37].  $E''$  relates to the heat dissipation by filler–polymer and filler–filler friction [38]. Fig. 10 shows the  $E''$  of the iPP/sPP/whisker composites

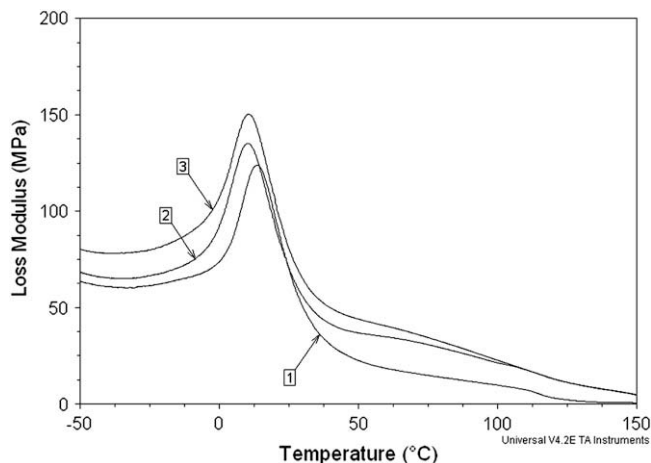


Fig. 10. Loss modulus versus the temperature for the blends: (1) iPP/sPP; (2) iPP/sPP/whisker; (3) iPP/sPP/whiske/1010.

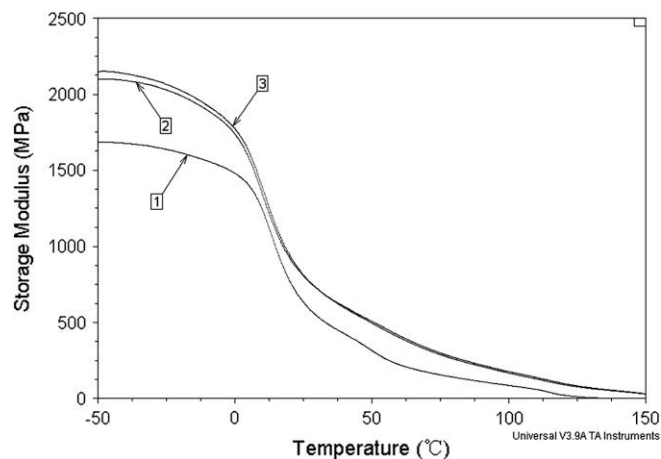


Fig. 11. Storage modulus versus the temperature for the blends: (1) iPP/sPP; (2) iPP/sPP/whisker; (3) iPP/sPP/whiske/1010.

as a function of temperature. The loss modulus of iPP/sPP/whisker composites is higher than that of the iPP/sPP blends. As discussed above, whiskers distributed in polymer matrix to form extra-interface in the composite, thus the friction between the surface of whiskers and polypropylene matrix contributes mainly to increase the loss modulus in a dynamical environment. Sample 3 has the highest loss modulus in all of the blends. It means that when the distribution of whiskers is changed from iPP phase to sPP phase the loss modulus of the composite was increased. As has been reported, the friction coefficient of polypropylene decreases with increased crystallinity [39]. In our composites, the crystallinity of sPP, which shows a thermoplastic elastomeric behavior [40–43], is lower than that of iPP [44]. Thus, sPP has higher friction coefficient than iPP, and the heat dissipation by friction between whisker and sPP is higher than that between whisker and iPP. In other words, the loss modulus of sPP-whisker composite is higher than that of iPP-whisker composite. However, the addition of whisker increased the storage modulus of composite, but the selective distribution of whisker had little influence on it, as seen in Fig. 11.

#### 4. Conclusions

The selective distribution of aluminum borate whiskers in iPP/sPP blends was clearly observed. Due to the local curvatures, the whiskers with nanometer scale can serve as valid adsorbent surface, even though their surface is smooth. When Irganox 1010 was introduced into composites, whiskers changed their distribution from iPP phase to sPP phase. In this process, Irganox 1010 covered the whisker surface and made van der Waals force domain the interaction between whiskers and polymer chains. With the explanation of entropy penalty, the flexible sPP chains adsorb the whiskers instead of iPP chain to achieve the stable state in thermodynamics. The composites with aluminum borate whiskers located in sPP phase have higher loss modulus than that located in iPP phase, while the storage modulus of both composites is almost the same.

The theory of entropy penalty could work on the fibrous surface, even though it is smooth. That means a rough solid surface no longer serves as the prerequisite of the theory of entropy penalty. A suitable surface structure with local curvature may adsorb the flexible chains in polymer matrix, and it will be helpful to targeted migration, especially when chemical reaction is unavailable or undesired.

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