

# Different Effects of Silane and Carboxylated Polypropylene on Crystal Morphology of Polypropylene/Molecular Sieves Type 5A Composites

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Received 16 August 2006; accepted 21 November 2006

DOI 10.1002/app.26487

Published online 21 June 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The silane KH-550 and carboxylated polypropylene (EPP) were used as compatibilizers in this study. The effect of them on crystalline morphology of polypropylene/molecular sieves type 5A (PP/5A) composites was investigated. IR illustrated that 5A interacts with EPP by forming molecule interaction or hydrogen bonds, but interacts with silane by covalent bonds. Polarized optical microscopy (POM) and X-ray diffraction (XRD) revealed that a suitable amount of silane can promote  $\beta$ -crystal formation in PP, and the average size of spherulites in the PP/

5A/silane is smaller than that of PP. EPP interacts with 5A by molecule interaction and cocrystallizes with PP, leading to the crystal morphology of PP/5A/EPP resembles to that of pure PP. Significant difference was detected in the effect of the two compatibilizers, which attributed to the different compatibility mechanisms. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 411–416, 2007

**Key words:** compatibilization; polypropylene; composites; crystal morphology

## INTRODUCTION

Polypropylene (PP) is one of the most important commercial polymers because of its superior properties such as high melting temperature, high chemical resistance, and low density. Moreover, PP is used in combination with other inorganic particulate to improve its properties such as stiffness, flame retardancy, conductivity and to reduce cost in applications. Although fillers such as  $\text{CaCO}_3$ , talc, etc. have been widely used with PP matrices, not much work was found in the literature relating to the use of molecular sieves as filler. Molecular sieves are microporous crystalline, hydrated alumina silicates of alkaline and alkaline earth elements, extensively used as catalysts, adsorbents, and also in ion exchange because of their regular pore structures and high thermal stability.<sup>1</sup> They were also employed as an additive to impart antibacterial and flame retardant properties to polymers.<sup>2–4</sup>

Because of the inherently poor compatibility between the inorganic particulates and PP, particulate-filled PP must be continuously upgraded to meet the special requirements of various new applications. A way for the possible improvement of particulate-filled PP compatibility is the modification of interfacial interaction.<sup>5</sup> There exist three main ways to modify

interaction: (1) Surface treatment of fillers is the technique most often used to modify interactions between particulate and PP. Silanes with different functional groups have been successfully applied for the treatment of fillers.<sup>6</sup> (2) Modification in the PP matrix, inducing an improved surface wettability, are often related to the formation of polar and reactive chemical groups on the PP segment, which can be achieved by wet (acid, alkali), dry (plasma) and radiation treatments (ultraviolet radiation and laser) without affecting the bulk properties. (3) Introduction of a macromolecule compatibilizer—a graft or block copolymer which create links between the PP and filler, because macromolecule compatibilizer contains polar group and organic segment. The polar group can react with the filler, and the organic segment can be compatible with the PP matrix. Maleic-anhydride-grafted polyolefine is one of the most widely used coupling agent between fillers and polymer.<sup>7</sup>

Although content and characteristics of filler significantly influence the properties of polymer composites, any change in polymer/filler interaction also has considerable effect on these properties. Different methods have different effects on the interaction of the interface in particulate-filled polymer, and consequently represent different crystal morphology, which influence the properties of particulate-filled polymer.

In this article, a macromolecule compatibilizer-carboxylated polypropylene (EPP) and a filler surface modifier—silane coupling agent KH-550 are chosen as the compatibilizer in polypropylene/molecular

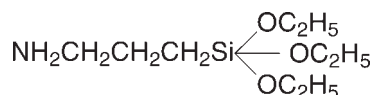
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sieves type 5A (PP/5A) composite, representing two different ways to modify interaction. The effects of them on crystal morphology of the PP/5A composites are compared. The way the compatibilizer is bonded to the filler surface and the characterization of the crystal morphology are investigated. The work provides theoretic basic for choose compatibilizer, which can be applied depending on the objective to be achieved.

## EXPERIMENTAL

### Materials

The PP [type T30S, density: 0.901 g/cm<sup>3</sup>] was supplied by Tianjin United Chemical (Tianjin, China). 5A was supplied by Shanghai Molecular Sieves Factory (Shanghai, China). 5A particles less than 0.074 mm in size were obtained by grinding, and sifting through 200 mesh sieve. EPP was obtained through oxidize PP by inorganic oxidant in aqueous solution as reference<sup>8,9</sup> (acid no. 0.1006 mg KOH/g). The KH-550 silane coupling agent was supplied by Beijing Shenda Fine Chemical Company (Beijing, China). Its structure is given below.



### Equipment and analysis procedures

The crystal morphologies of samples were observed by a SM-LUX-POL polar optical microscope (Leitz, Germany), magnified 40 times. The crystal structures of composites were measured by a Y-4Q X-ray diffractometer using Cu-K<sub>α</sub> radiation. The IR spectra were recorded by a VECTOR22 IR analyzer (Germany).

### Surface treatment of 5A

**EPP-modified:** EPP was dissolved in boiling xylene (EPP/xylene = 1 g/10 mL), then added 5A, cooled with stirring, filtrated, air-dried, and dried in a vacuum oven at 80°C for 10 h to get rid of xylene completely.

**Silane-modified:** The 5A and silane kneaded in a ZH-0.5 kneader at ambient temperature.

### Preparation of composites

The composites were done at 170–180°C in a two-roll mill. After PP had melted, surface treated 5A was added, and the blending was carried out for 10 min; then the composites were removed for compression molding at 180°C for 3 min; finally, the

composites were cooled to room temperature by cool pressing. After annealing at 70–80°C for 8 h, the specimen was operated on a ZHY-W almighty sample preparing machine.

### Preparation of analysis samples

#### Polarized optical microscopy

The compression-molded film sample was sandwiched between two cover glasses, was kept on the hotplate at 200°C for 10 min to melt completely, then transferred to a 200°C oven, and cooled naturally to 142°C, isothermal-crystallized at 142°C for 3 h.

#### X-ray diffraction

The composites were compression-molded at 180°C for 3 min, and then cooled to room temperature by cool pressing to prepare 1 mm thick membrane, for X-ray diffraction collection data.

### Fourier transform infrared spectrophotometry

#### 5A/EPP sample

5A modified with EPP (5A and EPP in 1 : 1.5 weight proportion) was packed with filter paper, immersed in boiling xylene, which must be repeat replacing more than five times to ensure PP and EPP extracted to liquor. The residual was dried for IR analysis.

#### 5A/silane sample

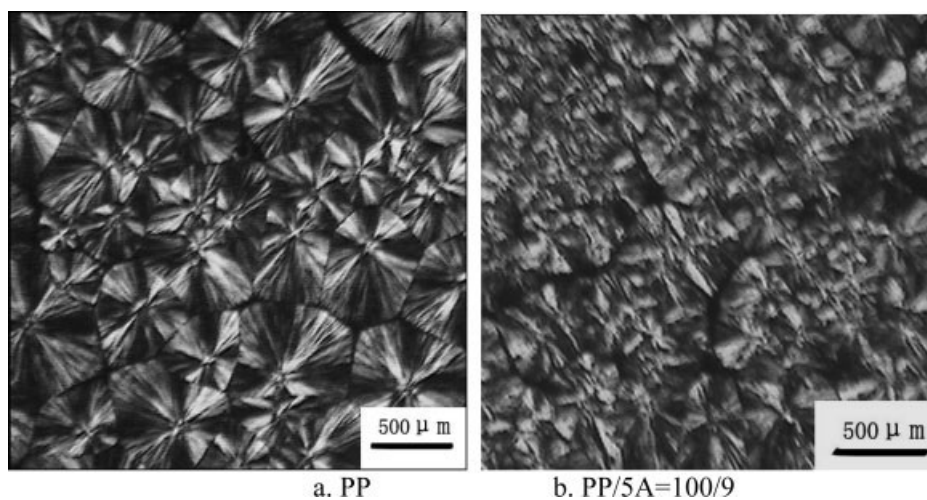
5A modified with Silane (5A and silane in 1 : 1 weight proportion) was packed with filter paper and extracted with acetone in a Soxhlet apparatus for 72 h to wash off unreacted silane, and then dried for IR analysis.

## RESULTS AND DISCUSSION

### Polarized optical micrographs

The POM is an important way to characterize the crystal morphology of the composites directly.

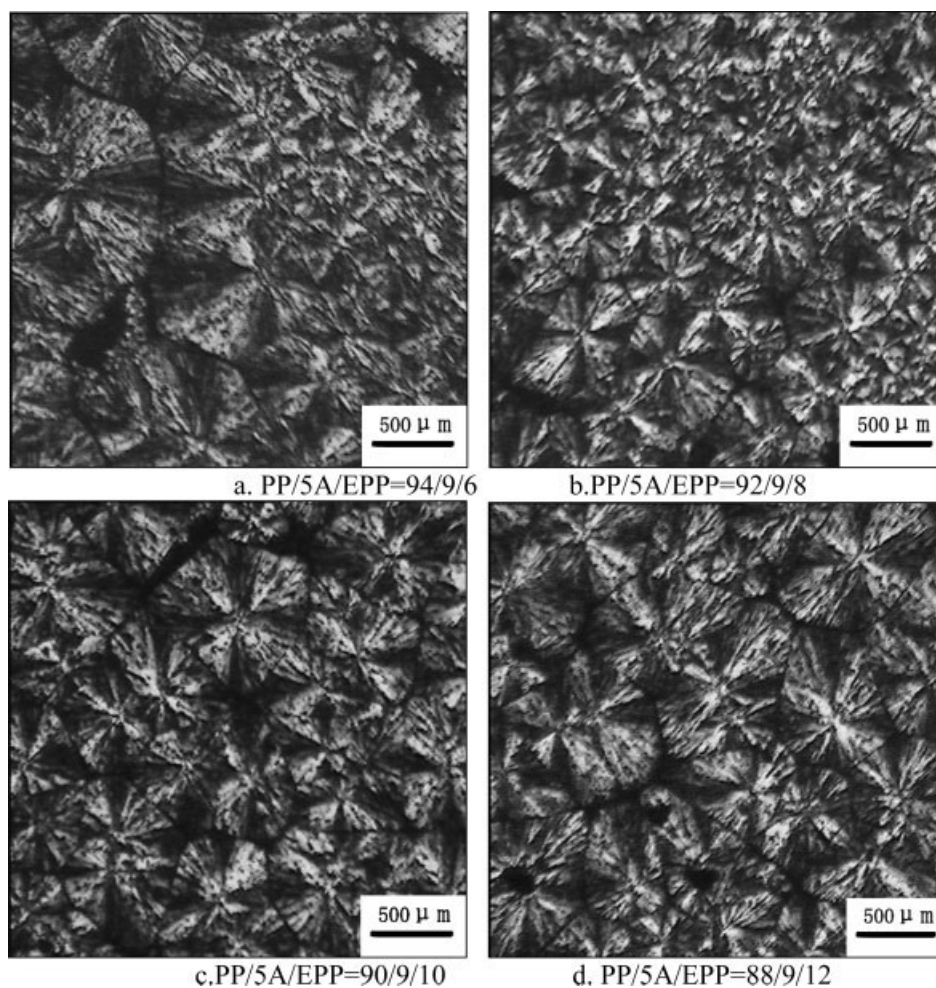
Figure 1 displays the polarized optical micrographs (POM) of pure PP and 5A-filled PP. It can be seen from Figure 1(a) that pure PP appears as complete sphere crystal with gloomy “cross” in the crystal. The composite PP/5A depicted in Figure 1(b) shows clearly that the crystal morphology of the PP is greatly affected by the addition of 5A. As 5A added, the size of the spherulites are nonuniform, and the spherulites are small in the place where 5A agglomerated, but large in the place where less or no 5A. It suggests heterogeneous nucleation effect of 5A.



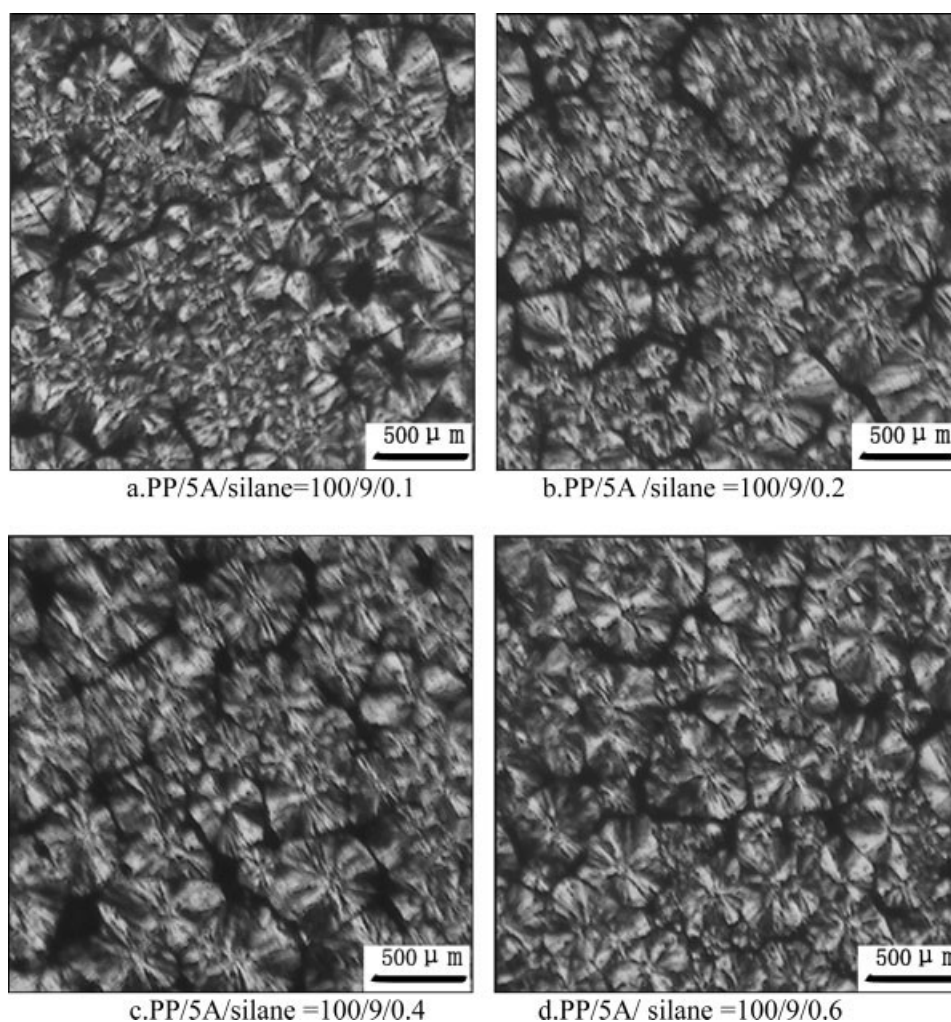
**Figure 1** The POM of the pure PP and composite PP/5A.

The crystal morphology of PP/5A/EPP composites can be observed in Figure 2. The size distribution of the spherulites becomes narrow, and the average size becomes bigger with the EPP content

increased, particularly when the EPP content more than 10% [Fig. 2(c,d)], the size of the spherulites are uniform, and the crystal morphology resembles to that of pure PP.



**Figure 2** The POM of the composites PP/5A/EPP.



**Figure 3** The POM of the composites PP/5A/silane.

The POM of PP/5A/silane composites (Fig. 3), clearly demonstrated that the size distribution of the spherulites becomes narrow and uniform with addition of silane. Especially in Figure 3(b), the size of spherulites is much smaller, and well dispersed, due to 5A uniformly distribution throughout the matrix. It indicates that a suitable amount of silane can activate the heterogeneous nucleation centers on the filler surface, and improve the compatibility of 5A with PP. However, 5A modified with excess of silane [Fig. 3(c,d)], the average size of spherulites is smaller than that of composites modified with EPP (Fig. 2), and the crystal morphology is unlike that of pure PP.

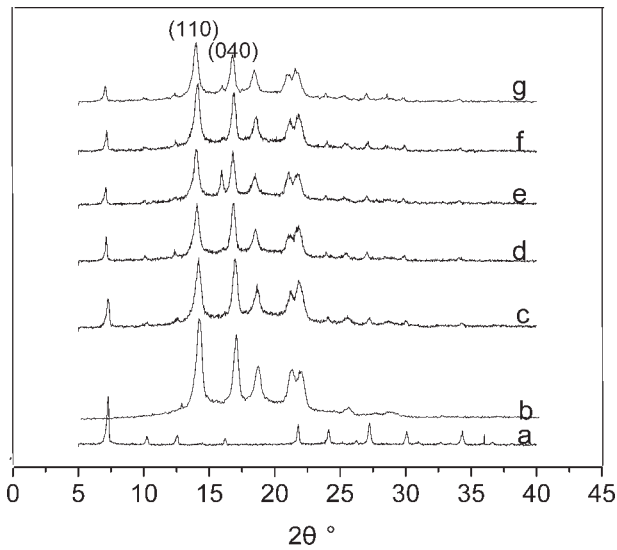
The POM of the composites clearly indicates that the differences on crystal morphology of the PP/5A composite are significant with different compatibilizer.

### X-ray diffraction

Figures 4 and 5 show the XRD pattern for the composites. Curves (a–c) in Figure 4 correspond to 5A,

pure PP, and PP/5A composite respectively. As shown in the curve (b), pure PP shows five prominent peaks in the  $2\theta$  range of  $10\text{--}30^\circ$ , which corresponds to monoclinic  $\alpha$  crystalline phase. In PP/5A composite [curve (c)], same number of peaks is observed in the range of  $2\theta$ , which suggests that these also contain mainly  $\alpha$ -phase. However, the difference lies in the relative intensities of the peaks, especially the intensity of the  $\alpha$  (0 4 0) plane of PP, which decreases considerably in the presence of 5A, due to the heterogeneous nucleation effect of 5A.

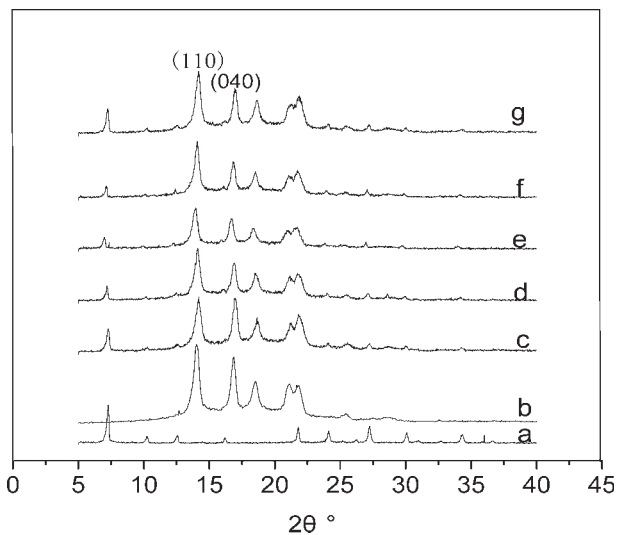
Curves (d–g) in Figure 4 correspond to PP/5A/silane composites with different silane content. As shown in the Figure, a diffraction peak at  $2\theta = 16.2^\circ$  corresponds to the  $\beta$  (3 0 0) plane is appeared. This indicates that 5A modified with silane affects the crystal structure of the PP matrix. The intensity of this peak first increases and then decreases with the increase of silane, and it exhibits the maximum value in curve (e) in Figure 5, implying that a suitable amount of silane can activate the heterogeneous



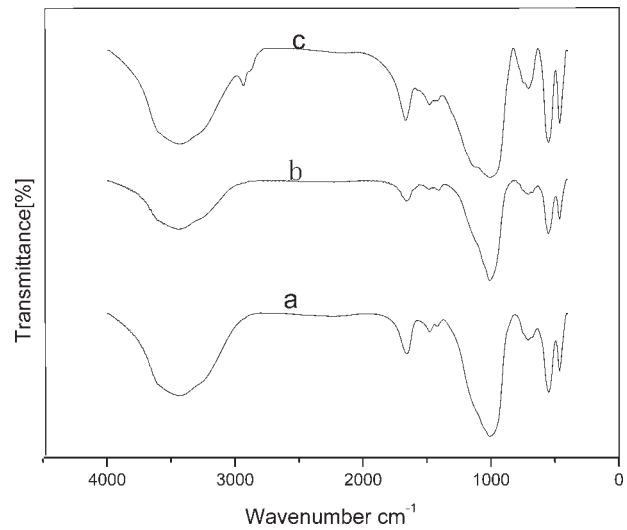
**Figure 4** X-ray diffraction pattern of PP/5A/silane. (a) 5A, (b) PP, (c) PP/5A = 100/9, (d) PP/5A/silane = 100/9/0.1, (e) PP/5A/silane = 100/9/0.2, (f) PP/5A/silane = 100/9/0.4, (g) PP/5A/silane = 100/9/0.6.

nucleation centers on the filler surface, and promote  $\beta$ -crystal formation in PP.<sup>10</sup>

Curves (d–g) in Figure 5 correspond to PP/5A/EPP composites with different EPP content, in which no new peak appears, suggests that PP/5A/EPP composites contain mainly  $\alpha$ -phase as well. This result is consistent with that of the POM. It is interesting to note that the peaks relative intensity becomes similar to that of pure PP with the increase of EPP content.



**Figure 5** X-ray diffraction patterns of PP/5A/EPP. (a) 5A, (b) PP, (c) PP/5A = 100/9, (d) PP/5A/EPP = 96/9/4, (e) PP/5A/EPP = 94/9/6, (f) PP/5A/EPP = 92/9/8, (g) PP/5A/EPP = 90/9/10.

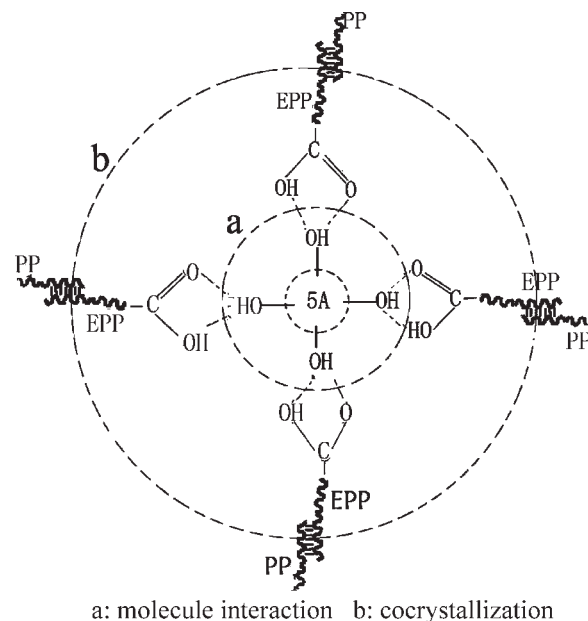


**Figure 6** IR spectra of 5A and modified 5A.

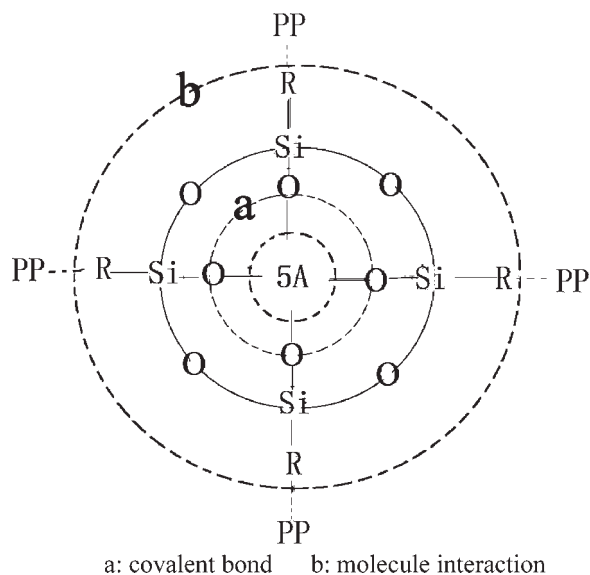
### Mechanism of compatibility

Figure 6 shows IR spectra of 5A and modified 5A. It can be seen from curves (a,b) in Figure 6 that no chemical reaction took place between EPP and 5A. The enhancement of the interface can be explained by the forming molecule interaction or hydrogen bonds between 5A and EPP.

Curve (c) in Figure 6 shows the IR spectra of silane modified 5A. Silane grafts on the surface of 5A is proved by the appearing of C–H stretch absorption at  $2935\text{ cm}^{-1}$ . In addition, this result is further supported by the fact that the absorption band at  $1100\text{ cm}^{-1}$  broadens, which is assigned to Si–O–Si



**Figure 7** The mechanism of EPP as compatibilizer in PP/5A.



**Figure 8** The mechanism of silane as compatibilizer in PP/5A.

linkage formed by reaction of silane with 5A or self-condensation of silane.

Significant differences of the PP/5A composite with different compatibilizer were detected by POM and XRD, which attributed to the different compatibility mechanisms.

The mechanism of EPP as compatibilizer in PP/5A composite can be speculated that the structure of 5A as a core, PP as a shell, and EPP as a bridge is formed, illustrated in Figure 7. EPP covers on the surface of 5A, blocking the heterogeneous nucleation effect of 5A, and cocrystallize with PP, leading to the crystal morphology resembles to that of pure PP, as shown in XRD and POM.

The mechanism of the silane as compatibilizer in PP/5A can be speculated by the simplified illustration in Figure 8. The composites modified with silane shows a chemical mechanism of adhesion, with the formation of covalent bonds. A suitable amount of silane can decrease the surface energy of 5A,<sup>11</sup> and consequently promote the  $\beta$  crystal forming on the surface of 5A. This fact is particularly reflected

in the POM, in which the average size of spherulites is smaller than that of composites modified with EPP. However, the 5A particles modified with a larger excess of silane, forms crosslinked encapsulating silane layer on the surface of 5A particles, blocking the direct contact of 5A and PP, leading to PP crystallize on the surface of crosslinked encapsulating layer.

## CONCLUSIONS

EPP covers on the surface of 5A by molecule interaction, and cocrystallize with PP, leading to the crystal morphology of PP/5A/EPP resembles to that of pure PP.

Silane grafts on the surface of 5A formed cross-linked encapsulating layer on the surface of filler particles, decreases the surface energy of 5A, promoting  $\beta$  crystal nucleation of 5A.

Different compatibility mechanisms lead to different crystal morphology, and may be consequently influence the properties of particulate-filled polymer.

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