

Polypropylene/Silica Nanocomposites *in situ* Prepared via Sol-Gel Reactions Using Porous Spherical Poly(propylene-*g*-(styrene-*alt*-maleic anhydride)) Granules as Reaction Loci*

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Abstract Using the porous polypropylene (PP) granules consisting of submicroparticles prepared by the reactor granular technology (RGT), a facile process was developed to synthesize *in situ* polypropylene/silica nanocomposites where styrene-*alt*-maleic anhydride copolymers (PSM) were firstly grafted onto both the outer- and the inner-pore surfaces of PP granules via solid-phase grafting polymerization, and then a sol-gel reaction was conducted inside these micro-pores with the carboxyl acid derived from maleic anhydride as catalyst. TEM micrographs demonstrated that the silica nanoparticles obtained by this strategy had a size around 10–20 nm in diameter and uniformly dispersed in the PSM-based nanocomposites. More importantly, the silica nanoparticles could significantly reduce the size of PP spherulites. Consequently, the PP/silica nanocomposites with high transparency and good mechanical performance were achieved.

Keywords: Nanocomposites; Solid-state polymerization; Silica.

INTRODUCTION

Polypropylene (PP) is one of the top ranking and the fastest growing polymers due to its excellent processability, chemical and thermal stability, recyclability, and relatively low cost^[1–4]. However, as a semi-crystalline polymer, the application of PP also has several drawbacks, such as relatively low impact strength and transparency. In the last few years, an effective measure to overcome the drawbacks was to prepare nanocomposites made up of silica. If their ultra-fine phase dimensions are maintained after compounding with the PP matrix, the small size of the silica nanoparticles result in a dramatic expanding in interfacial area, which will significantly improve the mechanical properties such as modulus and impact strength^[5–10]. Moreover, the silica nanoparticles reduce the dimension of spherulites and then improve transparency of the composites significantly. However, one of the most important criteria to achieve these properties is a high degree of filler dispersion in the polymer matrix. In general, simple physical mixtures of PP and silica may aggravate phase separation, resulting in poor mechanical and optical properties. Thus, many efforts have been made to overcome these drawbacks^[11–18]. Recently, the sol-gel reaction precipitating silica nanoparticles based on the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) is of particular interest to researchers. This sol-gel chemistry does not have significant side reactions with polyolefin matrices, which is beneficial to the preparation of *in situ* PP/silica nanocomposites with uniform dispersion. Donato *et al.*^[19] prepared dried xerogel silica with the existence of TEOS, ethanol, and aqueous HF

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(hydrofluoric acid). After blended with PP in a Haake torque rheometer, the silica nanoparticles still dispersed finely in PP matrix when there were coupling agents in the system. Many factors can influence the size of silica in the sol-gel process, which include the water/silane ratio, catalyst, temperature, solvent, and so forth. For that reason, Dougnac *et al.*^[20] fabricated a series of nanocomposites by melt mixing using silica particles (diameter ranging from 12 nm to 150 nm) *via* changing the ratio of ethanol and octadecylamine. They found that there was a maximum of Young's modulus when the diameter of silica nanoparticles was about 30 nm.

Nevertheless, the mixing section is usually carried out in the melting state. Due to their high specific surface energy, the silica nanoparticles usually tend to agglomerate in the polymer matrix during the mixing process. Besides, melt compounding will bring oxidation and degradation of PP *via* β -scission reaction which would take place extensively when PP is processed in molten state. Therefore, it undoubtedly will be a significant progress if the mixing can be achieved in a facile and mild way without melt state. Grafting is an effective method to improve silica nanoparticles dispersion in PP matrix. In the various strategies, solid phase grafting having the lowest reaction temperature could be an optimum one. Jain *et al.*^[21–24] grafted vinyl triethoxy silane onto PP chains and hydrolyzed with TEOS catalyzed by NH_4OH . Finally, the diameter of silica nanoparticles is in the range of 50–100 nm. Nevertheless, the solid phase grafting polymerization merely takes place on the surface of the PP powder particles, so the ratio of the grafting copolymers to PP depends greatly on the particle size of the PP powder. For this reason, we developed a versatile strategy called water-solid phase suspension grafting polymerization to prepare PP-based functional graft copolymers using porous PP granules^[25]. These porous spherical PP granules prepared by the reactor granular technology (RGT) could be expected as an appropriate approach to improve grafting percentage (GP)^[26–28]. If we make the sol-gel reaction occur inside the micropores in PP, then the silica nanoparticles could uniformly disperse in the micropores of PP particles by the confined space effect.

In this paper, we proposed a new strategy to prepare PP/silica nanocomposites as a successful extension of our previous work^[25]. The first step is to introduce maleic anhydride (MAH) groups onto the inner surface of the porous PP particles by the surface solid-phase grafting copolymerization with MAH and styrene (St) as comonomers. Subsequently, TEOS absorbs into the micropores of styrene-*alt*-maleic anhydride copolymer (PSM) and generates silica nanoparticles *via in situ* sol-gel reaction. During the sol-gel reaction, PSM plays the role of not only compatibilizer between PP and silica but also catalyst (carboxyl acid groups). With this method, PP/silica nanocomposites with ultra-fine phase dimension structure are produced. Moreover, transparency, impact strength, and tensile modulus are improved remarkably. As a comparison, PP/silica nanocomposites using routine PP were also performed.

EXPERIMENTAL

Materials

PP granules were provided by Beijing Research Institute of Chemical Industry, Sinopec. The melt flow index (MFI) is 7.84 g/10 min. Maleic anhydride, styrene and tetraethyl orthosilicate were analytical grade reagents and bought from Sinopharm Chemical Reagent Co., Ltd. Divinylbenzene (DVB) was purchased from J&K Chemical Ltd. Benzoyl peroxide (BPO), purchased from Sinopharm Chemical Reagent Co., Ltd, was purified by recrystallization in methanol before use. Ethanol was analytical grade reagents bought from Beijing Modern Eastern Fine Chemicals Co., Ltd.

Procedures of Solid-phase Grafting Polymerization

Before the grafting polymerization, PP granules (200 g) were put into a flask, vacuum degassing for 5 min. Per the formula, a certain amount of BPO (0.07 g), MAH (3 g), St (3.5 mL) and DVB (0.07 mL) were dissolved in acetone, after that the solutions were injected into the flask in vacuum. The grafting polymerization was preceded at 100 °C for 4 h. After polymerization the reactants were extracted with acetone in a Soxhlet extractor for 24 h and dried to the constant weight in vacuo at 40 °C.

Procedures of Sol-Gel Reaction

First, TEOS and extracted PSM were put into a beaker, shaken up for a while in order to make sure TEOS was soaked into the micropores of PSM. After that, deionized water and ethanol were added into the beaker, and then the beaker was sealed. The ratio of reactants was determined by the formula (see Table 1). The beaker filled with the above reactants was settled in an oven at a constant temperature of 50 °C for 24 h. After the reaction, the product was washed with DI water and acetone under ultrasonification in order to remove the small molecule substances and free SiO₂.

Table 1. Data of sol-gel reaction using PSM as matrix (PSM = 5 g, C₂H₅OH = 10 mL)

Run	TEOS (g)	H ₂ O (mL)	SiO ₂ (wt%)	<i>T</i> _{cp} (°C)	<i>T</i> _{co} (°C)	ΔH_m (J·g ⁻¹)	<i>T</i> _m (°C)
PP				92.78	116.07	79.45	144.34
PSM				100.55	120.00	83.70	148.52
PSM-1	0.934	0.4	1.94	97.37	116.21	78.30	145.10
PSM-2	1.401	0.6	1.24				
PSM-3	1.868	0.8	2.64				
PSM-4	2.335	1.0	4.39	100.15	121.54	78.46	145.85
PSM-5	2.802	1.2	4.80				
PSM-6	3.736	1.6	9.84				

Characterization

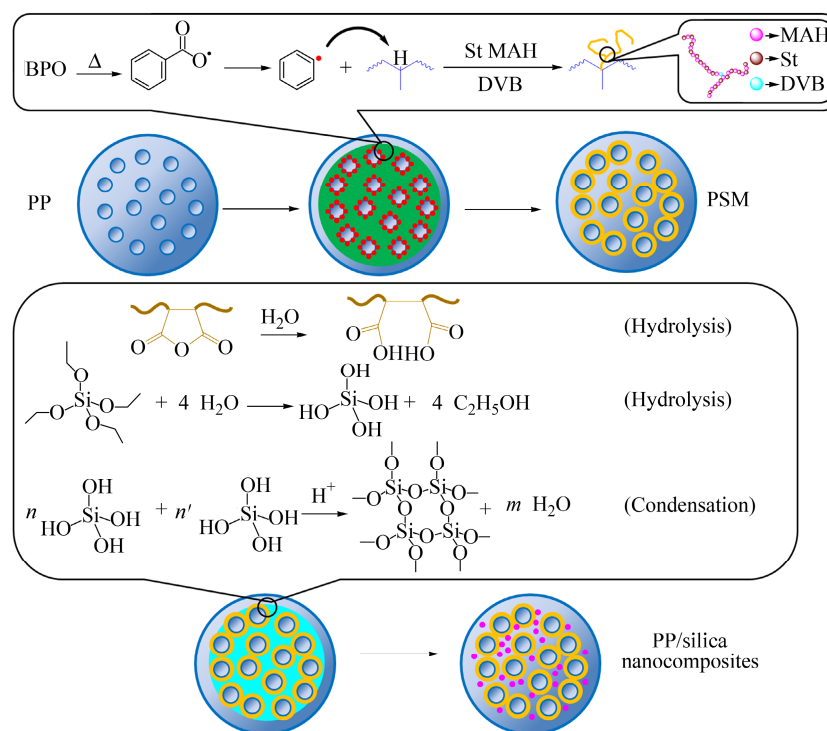
The Fourier transform infrared (FTIR) spectra were recorded with a Nicolet NEXUS 670 FT-IR spectrometer. The content of SiO₂ in nanocomposites was measured using a TA Instruments TGAQ50 thermogravimetric analyzer. Scanning electron micrographs were obtained using a Hitachi S-4700 SEM instrument. TEM observations were performed with a Hitachi H-800 transmission electron microscope. The crystalline morphology of PP/Silica nanocomposites was investigated by using an Olympus BX51 polarized optical microscope (POM). Thermal analysis was performed with a Q100 Differential Scanning Calorimeter (DSC) of TA Instruments, USA. X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX 2500 VB2+/PC diffractometer. The optical transmittance of visible light (380–700 nm) was determined by UV-Vis scanning spectrophotometer (CENTRA 20, GBC Scientific Equipment Pte Ltd., Australia). Charpy V-notch impact tests were carried out on notched specimens using a CEAST Resil Impactor 6957 pendulum. The tensile strength and modulus of the samples were measured with a universal testing machine (Instron-1185, England) at room temperature as well as 50% humidity^[29–31].

RESULTS AND DISCUSSION

Synthesis of PSM and SiO₂

Scheme 1 demonstrates the solid-phase grafting polymerization and the sol-gel reaction processes. Pristine PP granules were firstly soaked in reagents/acetone solution. After acetone evaporated, BPO and monomers were coated onto the surface of PP granules especially the interior surface of the subparticles. Under heating, two primary free radicals (*i.e.*, benzoyl free radical and subsequent phenyl radical) were generated by BPO^[32]. According to our experimental setup, BPO was mainly located on the outer surface of PP and the inner-pore surface or the interface between the PP and monomer. The environment surrounding BPO was quite different from when it was surrounded by a solution. Therefore it had enough time for benzoyl free radicals to take a further decomposition into phenyl radicals because of space limitation. Maleic anhydride-styrene is a typical system taking the alternating copolymerization. In the reason of that, styrene was chosen to improve the content of anhydride groups in the final grafting product. After grafting polymerization, the reactants were extracted with acetone to remove the homopolymer and small molecules, and the GP was 2.9 wt% measured by titration^[33]. Figure 1 is the SEM pictures of the interior of the pristine PP and PSM granules. According to the photos, micron-size pores could be seen in both PP and PSM granules. Thus there is enough space in PSM granules for the sol-gel reaction. In the micropores of PSM, Si-Sol solution was formed by the hydrolyzing of TEOS in the

presence of carboxylic acid catalyst (provided by maleic anhydride hydrolysis of PSM). In this step, ethoxy groups in TEOS transformed into silanols. As the reaction ongoing these highly reactive silanols would form linear polymer firstly and then cross-link to result in the —Si—O—Si— network.



Scheme 1 Mechanism of sol-gel reaction using PSM granules as precursor

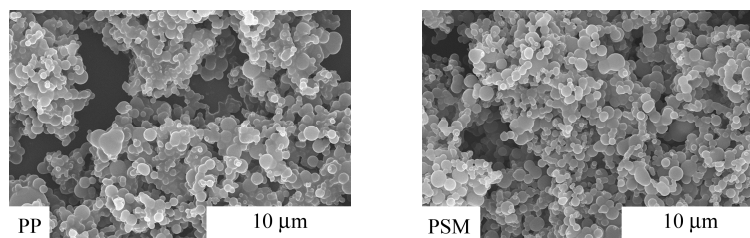


Fig. 1 SEM micrographs of the interior of the pristine PP and PSM granules

Figure 2 shows the FTIR spectra of pristine PP and the products. The existence of anhydride groups in PSM was demonstrated by FTIR. Compared to the spectrum of pristine PP, there are strong absorption bands at 1780 cm^{-1} and 1885 cm^{-1} (assigned to symmetric and asymmetric C=O stretching vibration of anhydride groups respectively) in grafting products^[34]. Considering the homopolymer of poly(St-*alt*-MAH) has been removed by extraction it indicates the samples are the PSM. According to the FTIR spectrum, the strong absorption bands at 1080 cm^{-1} is assigned to the stretching vibration of Si—O—Si of the as-prepared nanocomposites. Taking into account that the free SiO_2 has been removed by ultrasonification, it could be concluded that SiO_2 was successfully introduced into PP matrix.

Filler dispersion and adhesion with the polymer matrix are of great importance for improving the mechanical behavior of the composites. Figure 3 is the TEM photos of PSM-based nanocomposites and PP-based nanocomposites. From these micrographs we can conclude that silica particles are dispersed much better in PSM-based nanocomposites than in PP-based ones. In the PSM situation, individual silica nanoparticles with

an average particle diameter of around 10–20 nm can be observed in PP. Ashori^[35] and Qian^[36] reported the preparation of PP/silica nanocomposites by using non-porous PP, PP-g-(maleic anhydride) and 10–30 nm silica nanoparticles. The former got some aggregations of nanosilica, and the latter achieved the silica particles in the diameter of 200 nm, which implied that the system of porous PP granules, MAH, and TEOS was beneficial to reducing the size of silica particles. Moreover, obvious aggregates in the size of several hundred nanometers can be seen easily in all samples of raw PP situation. Furthermore, there is no nanoparticle with clear boundary in the visual field. Bikiaris *et al.*^[37] found that large agglomerates can be broken up into finer ones with the addition of PP-g-MAH. When there is PSM in the system, the silica nanoparticles could chemically bond on the PP chain, leading to the prevention of their agglomeration. Also, polar interactions such as those due to hydrogen bonds are more favorable to take place between the carboxyl groups of PSM and the surface hydroxyl groups of the silica nanoparticles. Regarding the interaction between the polymer chains and silica nanoparticles, bridging and confinement effects of PSM will be much stronger than that of neat PP as matrix.

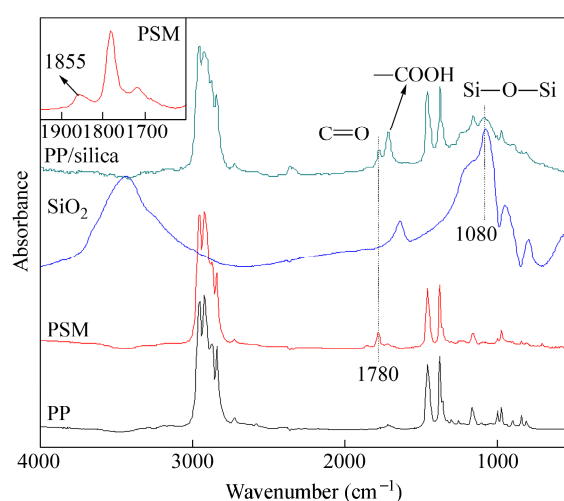


Fig. 2 FTIR spectra of pristine PP and the products

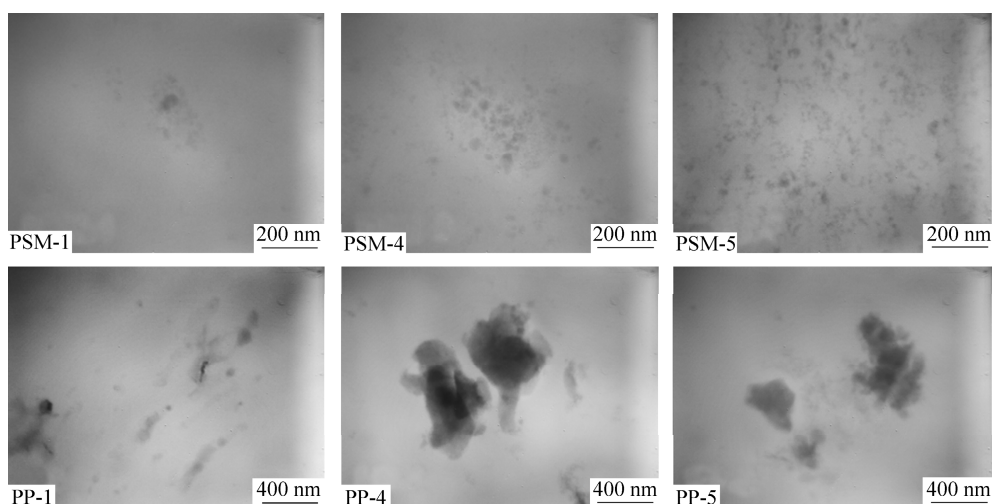


Fig. 3 TEM micrographs of the nanocomposites with different TEOS contents using PSM and raw PP as matrix

The content of SiO₂ in PP/silica nanocomposites is an important factor that influences the composites' properties. Figure 4 shows the effect of TEOS concentration on SiO₂ content in PSM matrix, which is also

displayed in Table 1. In these series of experiments, the concentration of TEOS varied from 18.68 wt% to 74.72 wt% of PSM. According to the figure, silica residue raised with the concentration of TEOS on the overall trend. The value could be 1.24 wt% as a minimum to 9.84 wt% as a maximum of PSM. There are four ethoxy groups in a single TEOS molecule, so the residue of silica in PP/Silica nanocomposites will not reach as high as the concentration of TEOS. Quite apart from this, the generation of free SiO_2 particles was inevitable in the reaction mixture. So it is necessary to investigate the efficiency of silica incorporation into PSM. The value of “ $\text{SiO}_2/\text{SiO}_2$ in TEOS” in the right Y axis in Fig. 4 reflects the ratio of SiO_2 finally diffused into the micropores of PSM and total amount generated by sol-gel reaction. When the concentration of TEOS was relatively low (18.68 wt%), most TEOS could diffuse into the micropores of PSM that was why the first datum was so high. However, the quantity of micropores in PSM was limited. So with increasing concentration of TEOS, some TEOS spilled over the pores would become considerable and resulted in the decrease of $\text{SiO}_2/\text{SiO}_2$ in TEOS. During the sol-gel reaction, TEOS adsorbed on the outside of the PSM granules could diffuse into the micropores driven by the volume shrinkage of the generation of silica nanoparticles and concentration difference. In spite of the first datum, $\text{SiO}_2/\text{SiO}_2$ in TEOS increased with the concentration of TEOS and finally reached a maximum of 45.66%. That means more TEOS in the system will promote the diffusion of silica into the micropores of PSM.

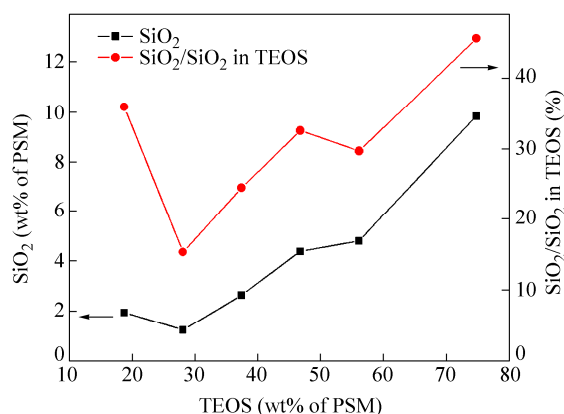


Fig. 4 Effect of TEOS concentration on SiO_2 residue

Thermal Performance

Differential scanning calorimetry is an effective method to investigate the non-isothermal crystallization. Figure 5(a) shows the cooling exotherms of PP, PSM and PP/silica nanocomposites with a cooling rate of $-10 \text{ K} \cdot \text{min}^{-1}$. The crystallization onset temperatures (T_{co}) and crystallization peak temperatures (T_{cp}) are given in Table 1. T_{oc} and T_{cp} of PSM (120.00 °C and 100.55 °C, respectively) shifted to the right significantly in comparison with those for the ungrafted PP (116.07 °C and 92.78 °C, respectively), which may be the result of the nucleation effect of the grafted maleic anhydride^[38]. As a polar polymer, poly(maleic anhydride) enhanced the interactions between the grafted PP molecules, which improved the polymer crystallinity accordingly. T_{oc} and T_{cp} of PP also shifted to the right in the case of that there were silica nanoparticles in the system (PSM-1 and PSM-4). According to Fig. 5(a), T_{cp} occurred earlier if there were silica nanoparticles in the system. The crystallization of polymers, including the nucleation and the crystal growth, is a complicated process^[39]. In raw PP, the spherulite nucleation is mainly a homogeneous nucleation process for the formation of nuclei is difficult. Then the crystallization is followed by nucleation-controlled spherulite growth. While in the composites, a large number of nuclei would be produced for the existence of silica nanoparticles. The speed of heterogeneous nucleation is extremely fast.

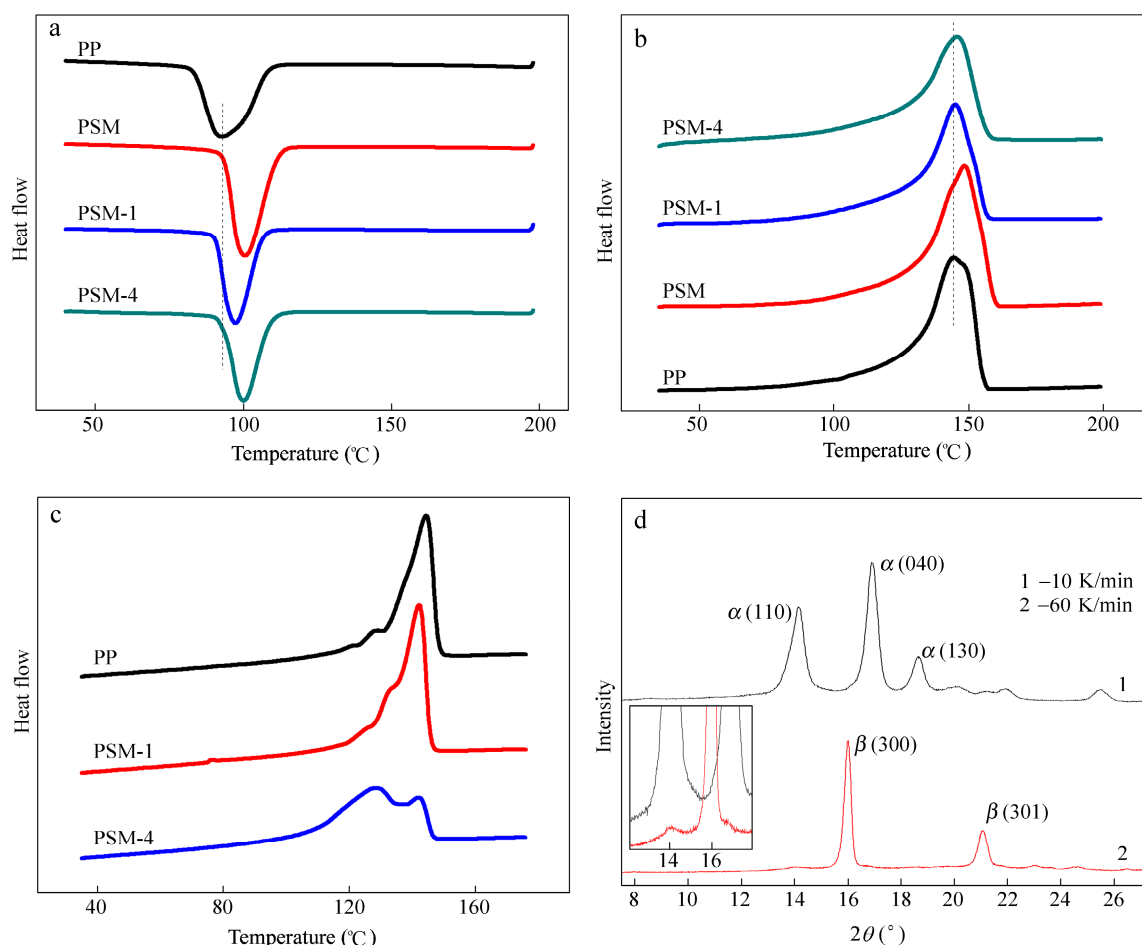


Fig. 5 DSC and XRD results of PP and PP/silica nanocomposites: (a) Cooling exotherms observed by DSC with the rate of $-10\text{ K}\cdot\text{min}^{-1}$; (b) Melting behavior observed by DSC after cooling rate of $-10\text{ K}\cdot\text{min}^{-1}$; (c) Melting behavior observed by DSC after cooling rate of $-60\text{ K}\cdot\text{min}^{-1}$ and (d) XRD patterns of PP/silica nanocomposites with different cooling rates

Figure 5(b) shows the melting behavior of PP, PSM and PP/silica nanocomposites. ΔH_m and melting temperature (T_m) are given in Table 1. Compared with pure PP, PSM has higher ΔH_m and T_m which indicate a higher crystallinity and more perfect crystallization morphology. In the case of PP/silica nanocomposites, T_m increased slightly compared with PP. Figure 5(c) is the second fusion scan with a quick cooling rate of $-60\text{ K}\cdot\text{min}^{-1}$ (Cooling 2), which indicates a quite different phenomenon compared with that of $-10\text{ K}\cdot\text{min}^{-1}$ (Cooling 1). The introduction of silica nanoparticles led to the development of an endothermic melting shoulder at a temperature lower than the main melting peak (PSM-1, Silica 1.94 wt%) or two melting peaks (PSM-4, Silica 4.39 wt%), and one imperceptible endothermic melting shoulder was also seen in pure PP. Many different explanations have been given for the presence of multiple melting peaks in the DSC thermograms^[40–44]. Explanations vary based on the polymer chain structure and the crystallization conditions. One explanation is attributed to the different crystalline polymorphs (α -, β -forms), which have different T_m . Usually the T_m of α -form crystalline PP is much higher than that of β -form. There is a conversion of β -form to the α -form which strongly depends on the thermal history of the sample. Jones *et al.*^[44, 45] found that the conversion takes place above 130°C ; hence a rapid quench of the polymer from the melt to below 130°C is required to produce the β -form. Another explanation for the two melting peaks is a melting-recrystallization process that occurs during heating after crystallization. Petraccone *et al.*^[46] hold that the melting peak on the lower temperature side (or the

shoulder) may be attributed to the fusion of original crystals, its position being determined by the competition of melting and recrystallization processes. The melting peak on the higher temperature side may be attributed to the fusion of crystals generated by the recrystallization processes occurring during the scan. The melting of samples is a complex process consisting of three partially overlapping processes (β -melting, recrystallization into the α -form, and α -melting). During cooling, the rapid quench results in the production of β -form and finally leads to a melting-recrystallization-melting process along with heating. To verify our presumption, the XRD patterns with two different thermal histories were followed by crystallizing the PSM-4 sample of Cooling 1 and Cooling 2, respectively. After a mild cooling, three diffraction peaks with high intensity located at 14.1° , 16.9° and 18.6° corresponding to the three crystalline planes of $\alpha(110)$, $\alpha(040)$ and $\alpha(130)$ of polypropylene (see Fig. 5d1). After a rapid quench, two peaks at 16.0° and 21.1° corresponded to $\beta(300)$ and $\beta(301)$ planes of the β -form PP crystallites (see Fig. 5d2). Meanwhile, a partial enlargement of the samples demonstrated that there were also a spot of $\alpha(110)$ crystalline plane after a rapid cooling. Comparing with PSM-1 and PSM-4, it could be concluded that the quantity of silica in nanocomposites has a strong influence on the generation of β -form under a rapid quench.

Crystalline Morphology and Transparency

Polarized optical micrographs of pure PP, PSM and PP/silica nanocomposites with different concentrations of TEOS crystallized under isothermal conditions are shown in Fig. 6. The spherulites with a diameter of more than $80\ \mu\text{m}$ can be seen for raw PP and PSM (Fig. 6a and Fig. 6b). The incorporation of silica nanoparticles greatly decreases the spherulite size to about $40\ \mu\text{m}$ even if its content is low (PSM-1, silica 1.94 wt%), however, it is still possible to observe the presence of spherulites (Fig. 6c). When the content of silica increased to 4.39 wt% (PSM-4), the clear spherulitic structure could not be observed and the crystalline size decreased further (Fig. 6d), which became much smaller than that of pure PP. In raw PP and PSM, the spherulite growth is mainly a homogeneous nucleation process because the formation of nuclei is difficult. The nucleus is sparse, hence the spherulite of PP can become very large till it contact with the other ones. While in the composites, a large number of nuclei would be produced for the existence of silica nanoparticles. Because of the existence of a great deal of nuclei, the spherulites cannot grow large enough, so the size of spherulites in PP/silica nanocomposites would be much smaller than that of PP.

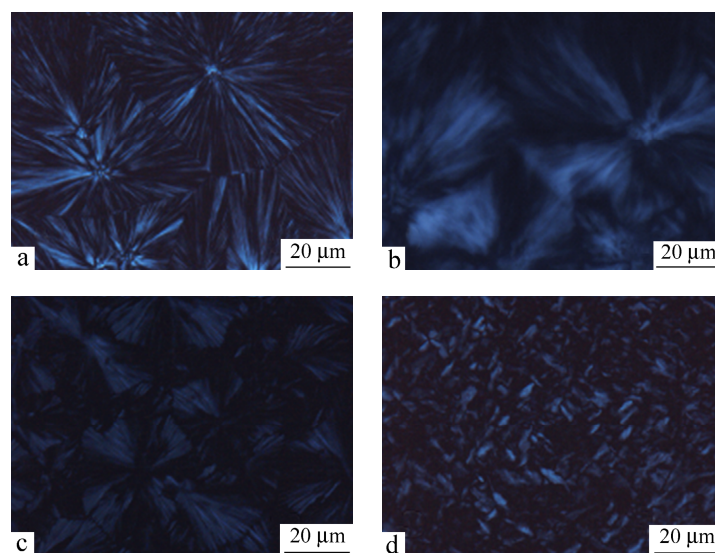


Fig. 6 POM micrographs of pristine PP and the products: (a) PP, (b) PSM, (c) PSM-1 and (d) PSM-4

The transmittance (T) of PP, PSM, and PP/silica nanocomposites films in the range of wavelength from 380 nm to 700 nm is displayed in Fig. 7. T of all samples increased when the light varied from blue to red. However, the wavelength has less influence on the transmittance of PSM-3 and PSM-4. The transmittance of PSM is much lower compared with that of pure PP. However, T will raise in the case of a little amount of silica nanoparticles in PP (PSM-1, silica 1.94 wt%, PSM-2, silica 1.24 wt%). When the residues is 4.39 wt% and 9.84 wt%, T of PP/silica nanocomposites was as high as 87.5%–90%. For the diameter of silica nanoparticles is much smaller than the wavelength of the visible light, T is mainly determined by the crystal morphology of the samples. Contrasted with POM pictures, the residues of silica nanoparticles has a remarkable strongly influence on the crystal morphology of the PP/silica nanocomposites. For the semi-crystalline polymers, light would be scattered on the different units of their structure which makes the products opaque^[47]. In PP the incident light is scattered on the crystallites, spherulites, and crystal-amorphous interface having different refractive indices. Large and complete spherulites of pure PP is large enough to interfere with visible light and will results in haze of the products. Hence reducing the size of spherulites is an essential criteria to achieve fabulous optical properties. According to the POM picture the silica nanoparticles create microspherulitic structure and the size of spherulites decreases with increasing silica content. At the large concentration applied (PSM-4, 4.39 wt%), spherulites are small enough to result in reasonable transparency and little haze, so a larger content of silica would not lead to a further improvement of optical properties.

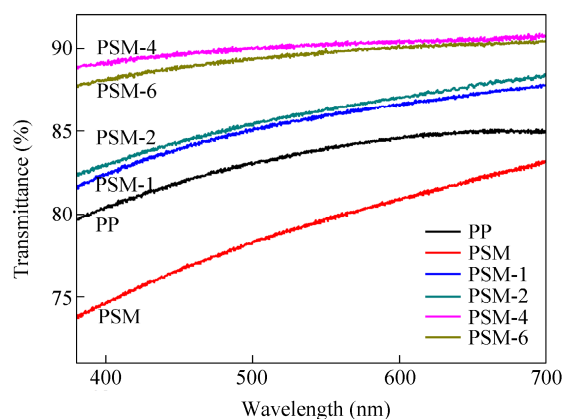


Fig. 7 Transmittance of visible light through the film of PP and PP/silica nanocomposites

Mechanical Properties

In order to evaluate the reinforcing effect of silica nanoparticles on the PP matrix, mechanical properties of the nanocomposites were measured, the results are presented in Fig. 8. The tensile strength of PSM (34.88 MPa) was a little higher than that of neat PP (32.81 MPa). However the tensile strength decreased to the range of 26.10 MPa to 30.22 MPa while there were silica nanoparticles in the matrix and had a maximum at the silica content of 1.94 wt%. Rong^[26] holds that low filler content must be beneficial to the dispersion of the nanoparticles. With increasing filler content, the interfacial area should be expanded if the particles are well dispersed. On the contrary, however, there would be more nanoparticle agglomerates in the composites at higher filler contents. When the positive effect driven by the increase of particle concentration cannot counteract the negative effect, these two opposite effects have eventually made the tensile strength decreased. The tensile modulus raised from 464.32 MPa to 589.74 MPa in the case of PSM furthermore obviously rose to 1132.50 MPa along with the addition of silica nanoparticles. The tensile modulus is an indication of the relative stiffness of the material. Usually the capability of composite interface to transfer elastic deformation depends to a great extent upon the interfacial stiffness and static adhesion strength. A high interfacial stiffness corresponds to a high composite modulus^[26]. In the composites, the PP chains were endowed with a high interfacial stiffness by the hydrogen bonds between the carboxyl groups of PSM and the surface hydroxyl groups of the silica

nanoparticles. That is why the tensile modulus of the composites increases with the silica content, and this is in agreement with Bikiaris' work^[37]. Thus the neat PP could produce greater strain and finally have a relatively low tensile modulus. In comparison with neat PP ($14.23 \text{ kJ}\cdot\text{m}^{-2}$), the impact strength has an obvious improvement in both PSM and nanocomposites. However, the incorporation of MAH ($17.59 \text{ kJ}\cdot\text{m}^{-2}$) seems to have a relatively insignificant influence compared with that of silica nanoparticles ($23.89\text{--}27.87 \text{ kJ}\cdot\text{m}^{-2}$) on PP. It has been known that grafting of PP with MAH is able to toughen PP and finally improve impact strength with the GP increased^[38, 48, 49]. The impact properties of PP/silica nanocomposites depend to a large extent on the spherulite size of PP, and a larger spherulite size usually results in a decrease of impact strength. According to the POM photos, the introduction of the silica nanoparticles strongly affected the spherulite size of PP matrix and finally improved the impact properties of PP. However, when the silica content was over 1.94 wt%, the impact strength tended to decrease slightly. This phenomenon may result from that the silica nanoparticles were too close with the filler content growing. Some minority crazes generated around the silica nanoparticles under the impact would connect to each other and become a new oversized one, and which may cause the macroscopic cracks of composites. In conclusion, the bulk mechanical properties of PP/silica nanocomposites were improved by the grafting of maleic anhydride and silica nanoparticles.

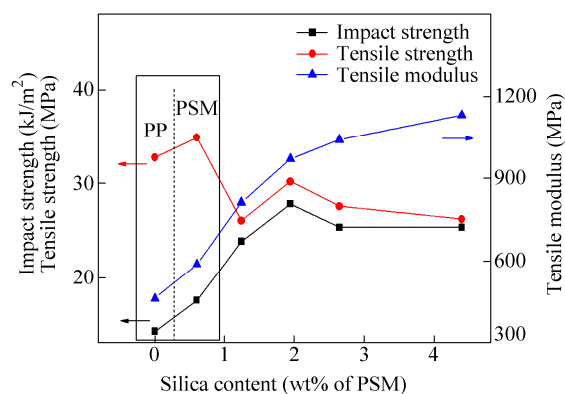


Fig. 8 Mechanical properties of PP/silica nanocomposites

CONCLUSIONS

Polypropylene/silica nanocomposites were synthesized *via in situ* sol-gel reactions in the micropores of PSM. The comparison of the TEM photos of PSM-based nanocomposites and PP-based ones denoted that PSM could break up the large agglomerates (approx. 500 nm) into finer ones (10–20 nm). The size of PP spherulites was significantly reduced by the silica nanoparticles. In the reason of that, the transparency and mechanical performance of the polypropylene/silica nanocomposites were enhanced notably. Generally, the preparation of *in situ* polypropylene/silica nanocomposites *via* sol-gel reactions using PSM as reaction loci is a valid approach to produce PP/silica nanocomposites with fine silica dispersion and various properties.

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