



Kinetics-controlled compatibilization of immiscible polypropylene/polystyrene blends using nano-SiO₂ particles

Qin Zhang, Hong Yang, Qiang Fu*

Department of Polymer Science and Materials, State Key laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, P.R. China

Received 30 October 2003; received in revised form 16 January 2004; accepted 21 January 2004

Abstract

Rigid inorganic filler has been long time used as a reinforcement agent for polymer materials. Recently, more work is focused on the possibility that using filler as a compatibilizer for immiscible polymer blends. In this article, we reported our efforts on the change of phase morphology and properties of immiscible polypropylene(PP)/polystyrene(PS) blends compatibilized with nano-SiO₂ particles. The effects of filler content and mixing time on the phase morphology, crystallization behavior, rheology, and mechanical properties were investigated by SEM, DSC, ARES and mechanical test. A drastic reduction of PS phase size and a very homogeneous size distribution were observed by introducing nano-SiO₂ particles in the blends at short mixing time. However, at longer mixing time an increase of PS size was seen again, indicating a kinetics-controlled compatibilization. This conclusion was further supported by the unchanged glass transition temperature of PS and by increased viscosity in the blends after adding nano-SiO₂ particles. The compatibilization mechanism of nano-SiO₂ particles in PP/PS blends was proposed based on kinetics consideration.

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Keywords: Immiscible blends; Compatibilization; Nano-particles

1. Introduction

Blending of two polymers has become an increasingly importance not only for the development of new materials but also for practical recycling. Polymer blends, such as PP/EPR, PC/PBT, PA/EPDM and PS/PPO, have been widely used in many fields. However, as we know, most polymer blends are immiscible, that is, simply mixing these polymer pairs cannot get practically useful materials. With regard to this, improving the compatibility and controlling the phase separation and morphologies of polymer blends turn out to be one of the most key factors in polymer blending. Usually, the conventional methods for compatibilization of two polymers are: (1) changing the molecular structure to introduce reaction group between the components, (2) introducing the third part as a compatibilizer, (3) forming the interpenetrating networks, and (4) forming the crosslinking between the two polymer molecules. Among them, introducing the third part as compatibilizer is considered to be the most effective way of improving the

compatibilization of polymer blends. The function of a compatibilizer is as a dispersant, reducing the characteristic size of the heterogeneous morphology and as a coupling agent, providing significantly improved adhesion between the continuous and dispersed phase in the blend. It has been reported that compatibilizer can also lower the interfacial tension, resulting in the suppression of coalescence in the dispersed phase [1].

So far almost all the compatibilizers used have been organic materials (block copolymers or modifiers). In recent years, a new concept of compatibilization by using rigid nano-particles, which instead of the conventional organic compatibilizer, has been proposed [2–9]. This idea is of importance to the theoretical study, and possesses a profound prospect in industrial application. Zhu et al. [2] reported that in spin-cast films prepared from PS/PMMA-organoclay blends (PS is incompatible with PMMA), the presence of organoclays has resulted in a drastic reduction of the average microdomain size. Similarly, a reduction of domain sizes induced by the addition of organoclays was observed in incompatible blends of PS and poly (ethyl methacrylate) [3]. Zlata Hrnjak-Murgic and co-workers [4] studied the effects of modified nano-CaCO₃ on the

* Corresponding author. Tel.: +86-28-5460953; fax: +86-28-85405402.
E-mail address: qiangfu@scu.edu.cn (Q. Fu).

morphologies and properties of immiscible SAN/EPDM blends, eliciting that the morphology of the SAN/EPDM blends was affected by the reduction of surface energy of the filler. In our previous work [5], clay was used as compatibilizer for PP/PS blends, and great compatibilization has been achieved.

Two kinds of compatibilization, namely, equilibrium compatibilization and non-equilibrium compatibilization are possible to explain the observed phenomenon. Lipatov and co-workers have done a lot of work on the effect of filler on the phase behavior of polymer blends [10–13]. They proposed a simultaneous action of two mechanisms: by changing the thermodynamics of interaction near the surface due to selective adsorption of one of the components and by the redistribution of the blend composition according to their molecular masses between filler surface and in the bulk that may diminish the phase separation temperature, suggesting an equilibrium compatibilization. On the other hand, an increase of viscosity in the polymer–polymer–filler ternary system has also been noted, which will slow down the kinetic conditions of phase separation. In this case, sufficient experimental time is needed to reach the equilibrium state. Here the non-equilibrium compatibilization plays a role in polymer–polymer–filler system.

Polypropylene and polystyrene, which are among the plastics most widely used in the world, form the typical example of immiscible polymer blends. In this article, the effect of the introducing nano-SiO₂ particles on the phase morphology, rheology, and mechanical properties of PP/PS blends was investigated to verify further the concept of compatibilization by nano-filler. The compatibilization effect of nano-SiO₂ particles was discussed from both thermodynamic and kinetics point of view.

2. Experimental

2.1. Materials

Polypropylene (PP) and polystyrene (PS) used in our study were commercially available. Fumed nano-SiO₂ particles with a size of 10–30 nm, treated with coupling agent D-4 (octamethylcyclo tetraoxysilane) were selected. The chemical nature of filler surface is very important and essential for good dispersion of filler in polymer. In our work, the coupling agent was selected because it provides excellent hydrophobicity. The specification of these materials is listed in Table 1.

Table 1
Materials

Materials	Brand	Supplier	Characteristics
PP	T30S	Du Shan ZI Petroleum Chemical, China	MFR = 2.6 g/10 min (230 °C, 2.16 kg)
PS	666D	Yan Shan Petroleum Chemical, China	MFR = 4.6 g/10 min (190 °C, 5 kg)
Nano-SiO ₂	JT-SQ	Chendu Today chemical Co., Ltd	Particle size: 10–30 nm $S_{(BET)} = 200 \text{ m}^2/\text{g}$

2.2. Specimen preparation

Melting blending of PP/PS at fixed ratio (70:30 wt/wt) with different SiO₂ contents was conducted using a Haake internal mixer set at a barrel temperature of 190 °C, and the rotor speed was 50 r/min. Melting blending time varying from 1 to 30 min was selected under the same processing parameters to see the change of morphology with time.

To obtain enough materials for mechanical property test, melting blending was also conducted by using a twin-screw extruder (TSSJ-25 co-rotating twin-screw extruder). In the extruding step, barrel temperatures were set at 140/160/190/210/210/195 °C and a screw speed of 120 rpm was used (the mixing time is less than 3 min). The *L/D* ratio of the screws was 32, and *D* = 25 mm. The filaments obtained upon extrusion were immediately quenched in water, and then cut into pellets by a pelletizer. After compounding, the blends were injection moulded into standard rectangular bars and dumbbell shaped specimen by using a PS40E5ASE injection-moulding machine. The temperature was chosen as 210/210/190/175 °C from die to hopper. The temperature of the mold was kept at room temperature. The standard rectangular bars and dumbbell shaped specimen were used to test the impact strength and yield tensile strength or flexural strength, respectively.

2.3. Characterization

2.3.1. Scanning electron microscopy (SEM)

SEM images were taken to study the morphology of PP/PS blends with or without SiO₂ particles. The samples were cryogenically fractured in liquid nitrogen. The fracture surfaces were immersed in dimethylbenzene at room temperature for 2 h. The PS phase was preferentially etched by the solvent. The fractured surfaces of the etched samples were then sputter-coated with a thin layer, and investigated in a SEM instrument, JSM-5900LV, operating at 20 kV.

2.3.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry spectra were recorded on a Perkin–Elmer DSC Pyris-I differential scanning calorimeter calibrated the temperature with indium, and then crystallization behavior can be obtained. All DSC were performed under nitrogen atmosphere. In this experiment, about five milligrams of dried sample was first hold in 50 °C for 0.5 min, then heated quickly from 50 to 200 °C at 40 °C/min and hold for 5 min after reached 200 °C in order to eliminate the influence of thermal history. After that, the

samples were cooled from 200 to 50 °C (at -10 °C/min) and kept at 50 °C for 1 min. At last, a heating scanning from 50 up to 200 °C (at 10 °C/min) was carried out. The melting temperature of PP and glass transition temperature (T_g) of PS were obtained by heating curves. The degree of crystallinity was calculated from heat of fusion using 209 J/g as the heat of fusion of 100% crystalline iPP [14].

2.3.3. Advanced rheometric expansion system analyzer (ARES)

Rheology property was carried out on an advanced rheometric expansion system analyzer (ARES). The test temperature was kept at 190 °C and the frequency varied from 0.25 to 100 s^{-1} . Specimen dimensions were 22×2 cm.

2.3.4. Mechanical tests

2.3.4.1. Notched izod impact test. The Izod impact tests of notched specimens were carried out using a VJ-40 impact test machine, according to GB/T 1834-1996 standard. The impact strength was calculated by dividing the absorbed energy by the initial cross-section area behind the notch (around 32 mm^2). All measurements were carried out in ten-fold.

2.3.4.2. Yield tensile strength, flexural strength and modulus test. Standard tensile tests were conducted on dumbbell shaped specimens using an AG-10TA tensile testing machine at room temperature. Test speed was kept at 50 mm/min, according to GB/T 1040-92 standard. The flexural strength and flexural modulus were measured using an AG-10TA flexural testing machine with a speed of 2 mm/min according to GB 9341-88 standard. Both of these tests were carried out in five folds.

3. Results

3.1. SEM results

The change of phase morphology of PP/PS blends at fixed composition (70/30) and mixing time (10 min) as function of nano-SiO₂ content was investigated by SEM, and the result is shown in Fig. 1. The black domains represent the position of the etched PS dispersed phase in the PP matrix. Both the interparticle distance and the size of the dispersed PS phase are found to decrease with the increase of nano-SiO₂ content. The PS particle size is decreased from 1 to 5.5 μm (Fig. 1(a)) to 0.68–3.64 μm upon the addition of 1 wt% nano-SiO₂ (Fig. 1(b)). The addition of 3 wt% A-SiO₂ causes a further decrease of PS particle size to 0.45–1.59 μm (Fig. 2(b)). When SiO₂ content increases to 5 and 10 wt%, the PS particle size is, respectively, decreased to 0.15–1.25 μm and 0.14–1.0 μm together with a very homogeneous size distribution

(Fig. 1(c) and (d)). SEM result indeed suggests a remarkable compatibilization of immiscible PP/PS blends by using nano-SiO₂.

In order to investigate the mixing time dependence of phase morphology, the samples at different mixing time were examined. SEM images of samples at fixed nano-SiO₂ content but prepared at different mixing time (1, 5, 15, 20 and 30 min) are shown in Fig. 2. The influence of mixing time is obvious. An increase in mixing time from 1 to 15 min leads to a significant decrease in the particle size of PS dispersed phase and a simultaneous improvement in size distribution (Fig. 2(a)–(c)). However, with further increasing of the mixing time, the PS particles tend to coalesce and a worse distribution is observed (Fig. 2(d) and (e)). This result indicates that the phase morphology shown in Fig. 1 may represents a non-equilibrium state, thus suggests a kinetic-controlled compatibilization. Of course, another possibility may also exist that may cause an increase of PP size after longer mixing due to the degradation of PP or PS chain. This will result in a change of viscosity ratio between PP and PS thus an increased PS size. This later case has been ruled out by checking the stability of PP and PS at experimental temperature for different time. Only slight decrease of melt flow index for both PP and PS was seen after mixing at 190 °C for 30 min.

3.2. Mechanical properties

Fine control of the phase morphology of multi phase polymer blends is the key approach to impart desired mechanical properties to these materials. Increased compatibility between PP and PS should be reflected in mechanical properties. Impact strength, tensile strength, flexural strength, and modulus of PP/PS blends with different A-SiO₂ contents are all summarized in Table 2. One observes indeed somewhat increase of tensile strength, flexural strength and modulus of PP/PS blends by introducing only small amount of SiO₂ particles (less than 3 wt%). This can be considered as due to the enhanced compatibilization. Since the samples for mechanical properties were obtained by a twin-screw extruder, instead of obtained by a Haake internal mixer, the mixing time is quite short (less than 3 min). From the mixing time dependent experiment, only limited compatibilization is expected. The corresponding decrease of impact strength with the addition of nano-SiO₂ particles may be due to the stress concentration effect. That

Table 2
Mechanical properties of PP/PS (70:30) blends with different A-SiO₂ contents

A-SiO ₂ content (wt%)	0	1	3	5	10
Impact strength (kJ/m ² , 20 °C)	2.6	2.1	1.2	1.5	1.5
Tensile strength (MPa)	36.9	38.9	37.6	35.8	35.8
Flexural strength (MPa)	44.5	48.3	50.6	50.8	49.0
Flexural modulus (GPa)	1.43	1.63	1.77	1.82	1.74

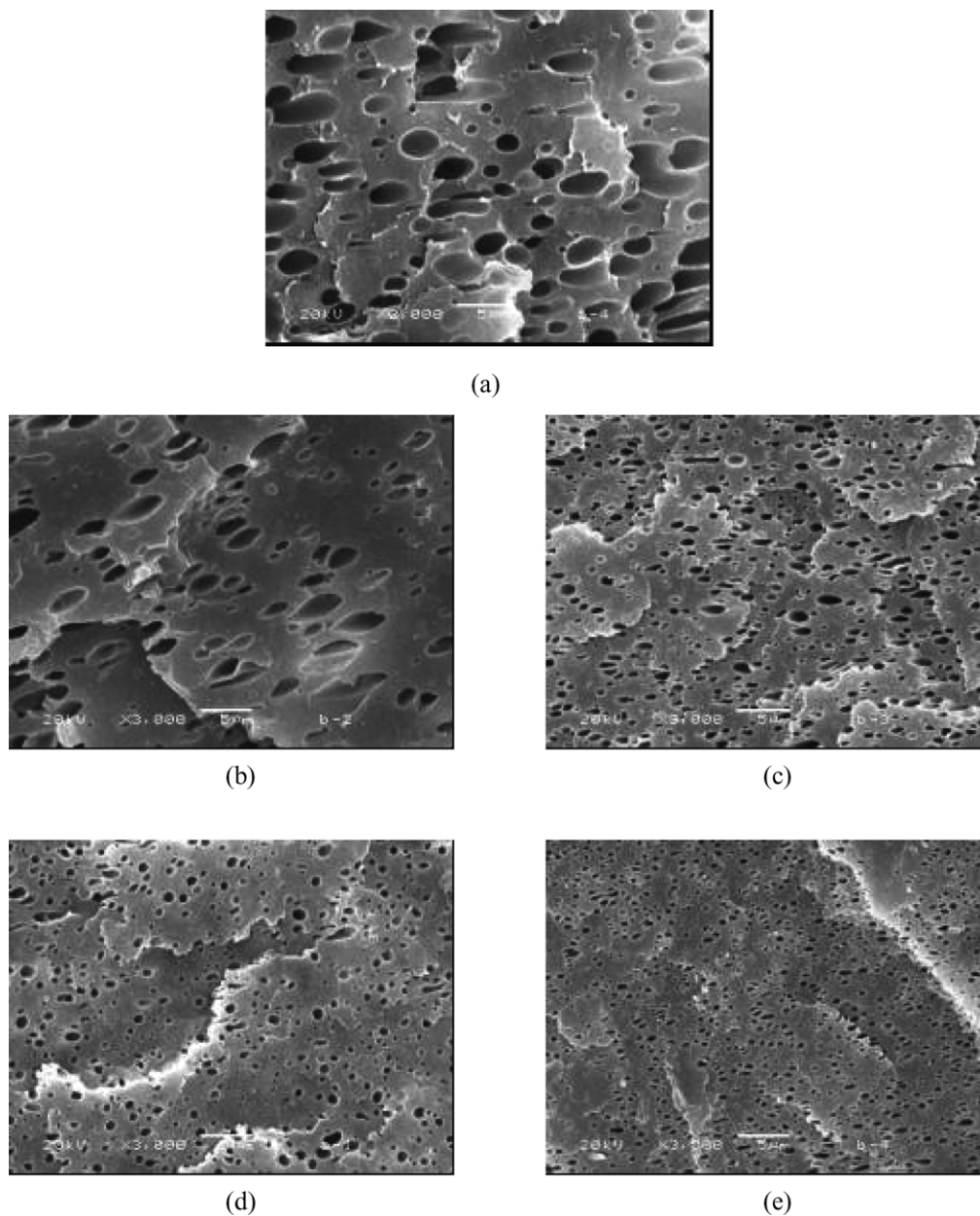


Fig. 1. SEM images of PP/PS/(70/30) blends with varying nano-SiO₂ contents: (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, (e) 10 wt%.

is because the rigid nano-SiO₂ particles, which act as stress concentration, cannot transfer the stress from dispersed phase to the polymer matrix when suffered from sudden impact energy.

3.3. DSC result

The DSC experiments were carried out to study the crystallization behavior and glass transition temperature of PP/PS blends after compatibilized by nano-SiO₂ particles. Fig. 3 depicts the DSC crystallization traces of samples recorded during cooling from the isotropic melt with a cooling rate of 10 °/min. And Fig. 4 shows the DSC heating

Table 3
The various crystallization parameter of the samples (PP/PS/A-SiO₂)

A-SiO ₂ content (%)	T _g (°C)	T _c (°C)	T _m (°C)	ΔH _f (J/g)	X _c (%)
0	105.5	115.0	161.4	47.8	32.7
1	105.0	119.3	163.7	34.7	24.1
3	104.5	118.0	162.4	35.5	25.3
5	105.0	116.9	162.5	31.2	23.0
10	105.2	116.9	163.2	28.2	22.4

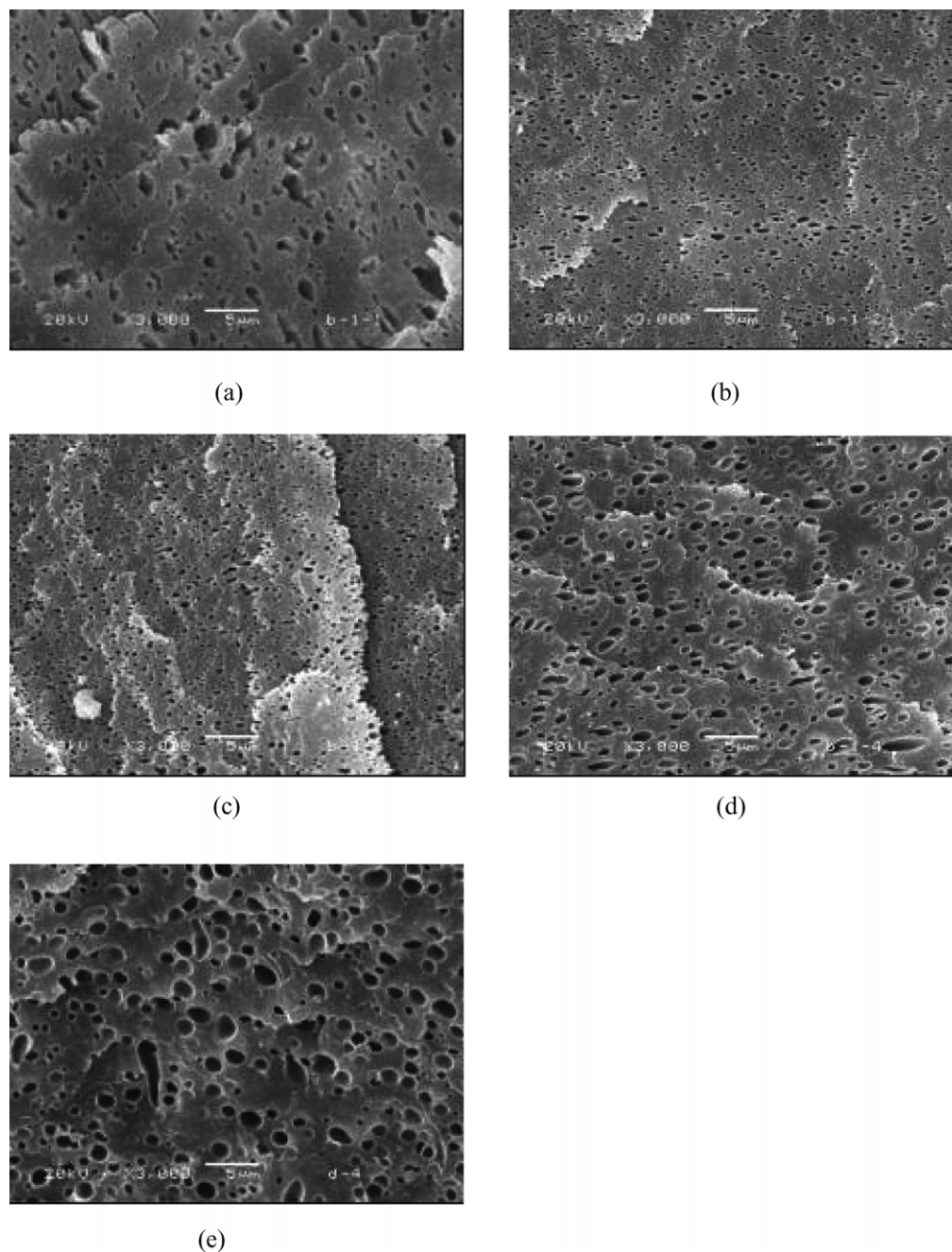


Fig. 2. SEM images of PP/PS/nano-SiO₂ blends (70/30/5) at different mixing times: (a) 1 min, (b) 5 min, (c) 15 min, (d) 20 min, (e) 30 min.

curve of the samples after cooling. All data obtained from two curves, which include the glass transition temperature (T_g) of PS, crystallization temperature (T_c), melting temperature (T_m), heat of fusion (ΔH_f) of PP, as well as the crystallinity calculated from the heat of fusion for all the samples are listed in Table 3.

Compared with the crystallization temperature (T_c) of pure PP/PS blends (115.0 °C), a dominant exothermic peak (T_c) for all the samples is visible, which shifts to higher temperatures for PP/PS/ SiO₂ blends. This suggests a nucleation effect of nano-SiO₂ particles. The melting peak

(T_m) for PP/PS blends with different content of nano-SiO₂ particles is nearly constant at 162.0 °C. The glass transition temperature (T_g) of PS is also constant at 105 °C with the addition of nano-SiO₂ particles. One should expect a change of glass transition temperature of PS if the compatibilization is caused by an emulsifying effect of nano-SiO₂, as in the case by using block polymer as a compatibilizer. However, in agreement with time dependent SEM result, DSC result indicates that the improved compatibilization results from rather a kinetics reason than thermodynamic one. A remarkable decrease of crystallinity is seen after introducing

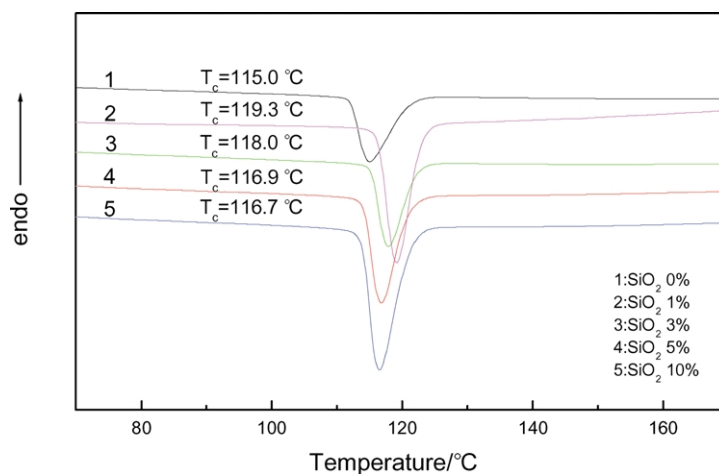


Fig. 3. The DSC cooling thermograms of PP/PS blends (70/30) compatibilized by nano-SiO₂ particles.

nano-SiO₂ in PP/PS blends. This can be understood as a result of decreased PP chain mobility due to the increasing of viscosity in the blends (see below). In other word, the decrease in the crystallinity of PP is a result of the enhanced compatibility and increased viscosity of PP/PS blends by nano-SiO₂ particles.

3.4. ARES results

To verify the change of rheology properties of PP/PS blends by nano-SiO₂ particles, ARES experiment was carried out. Fig. 5 shows the change of storage modulus of PP or PS by adding nano-SiO₂ particles (5 wt%). PP or PS shows an obvious decrease of storage modulus (G') after adding one and another, but only slight decrease by adding nano-SiO₂ particles. This result indicates a highly phase separated structure between PP and PS, but somewhat adhesion between PP and nano-SiO₂ particles, or between PS and nano-SiO₂ particles. It seems that

nano-SiO₂ particles disperse easier in PS than in PP, because nano-SiO₂ particles cause somewhat storage modulus decrease of PP, but almost no effect on PS storage modulus. The corresponding change of viscosity (η') is shown in Fig. 6. The similar trend is also found for viscosity change. The change of storage modulus and viscosity of PP/PS blends by adding different nano-SiO₂ content is shown in Fig. 7. An increase of storage modulus (Fig. 7(a)) and viscosity (Fig. 7(b)) is seen with increasing of nano-SiO₂ content. Even solid like behavior is observed at low frequency for PP/PS blends with nano-SiO₂ particles. It is interesting that PP/PS or PP/nano-SiO₂ blends show a decrease of storage modulus and viscosity of PP, but PP/PS/nano-SiO₂ ternary system shows in a much higher storage modulus and viscosity compared with that of PP/PS or PP/nano-SiO₂ blends. This once again suggests an increased compatibilization between PP and PS in the PP/PS/filler system.

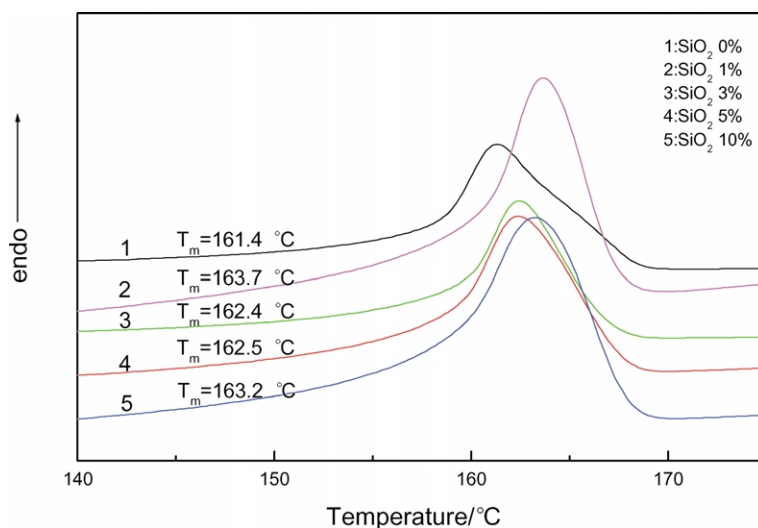
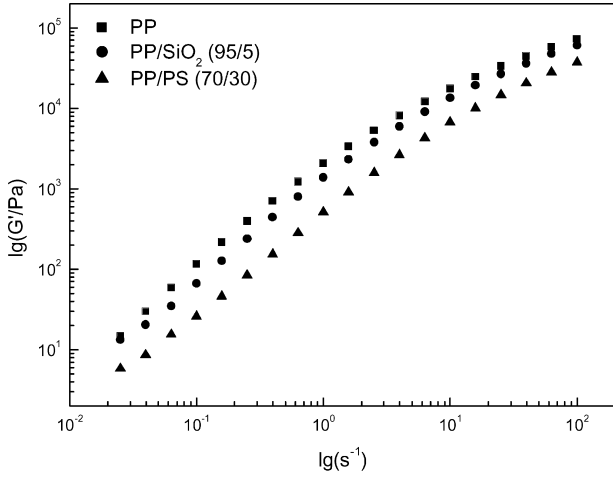
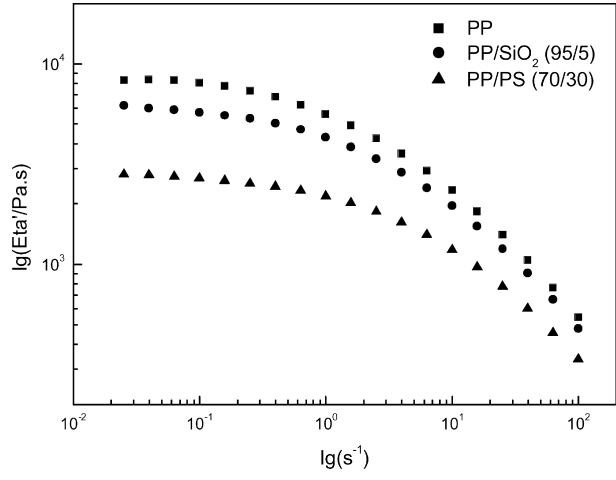


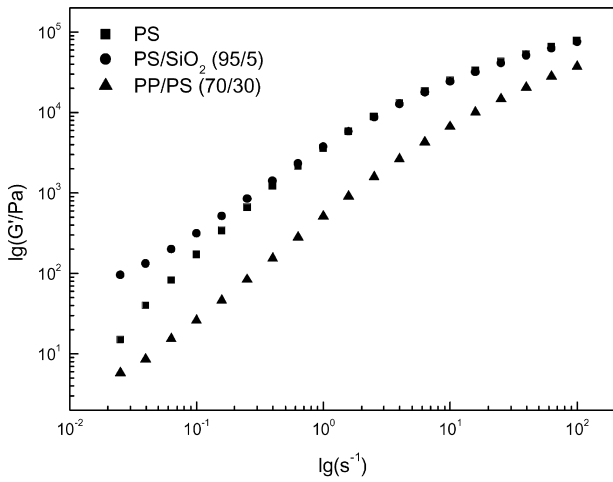
Fig. 4. The DSC heating thermograms of PP/PS (70/30) blends compatibilized by nano-SiO₂ particles.



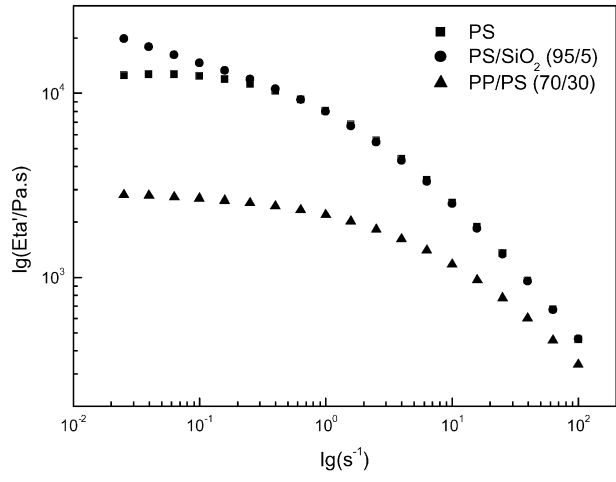
(a)



(a)



(b)



(b)

Fig. 5. (a) Storage modulus of PP, PP/PS(70/30) and PP/nano-SiO₂ (95/5) and (b) Storage modulus of PS, PP/PS(70/30) and PS/nano-SiO₂ (95/5), as a function of frequency.

Fig. 6. (a) Storage viscosity of PP, PP/PS(70/30) and PP/nano-SiO₂ (95/5) and (b) storage viscosity of PS, PP/PS(70/30) and PS/nano-SiO₂ (95/5) as a function of frequency.

4. Discussions

From the framework of the Flory–Huggins theory, one can describe the compatibilization effect of two immiscible polymers by adding the third component. The change in the free energy of mixing three components (per unit volume) is expressed as

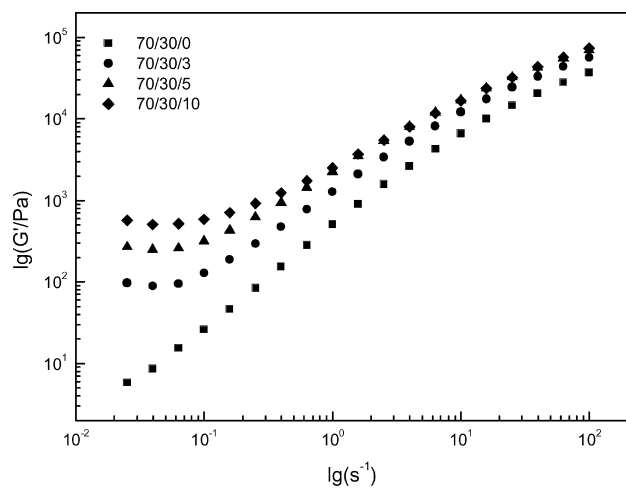
$$\Delta G_{\text{mix}} = RTV(\chi_{AB}\varphi_A\varphi_B + \chi_{AC}\varphi_A\varphi_C + \chi_{BC}\varphi_B\varphi_C) \quad (1)$$

where V is the mixture volume, χ_{ij} is the interaction parameter between components i and j , which determines the sign and value of the heat of mixing. And φ_i is the volume fraction of component i . The terms in brackets may be expressed through the thermodynamic interaction

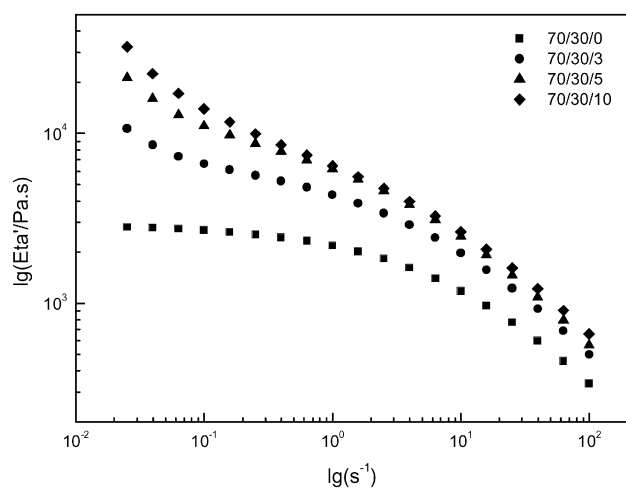
parameter for the ternary mixture

$$\chi_{A+B+C} \approx \chi_{AB}\varphi_A\varphi_B + \chi_{AC}\varphi_A\varphi_C + \chi_{BC}\varphi_B\varphi_C \quad (2)$$

A positive value of the parameter χ_{A+B+C} corresponds to an immiscible system whereas a negative value is indicative of miscibility. Nesterov et al. [10] found that if both polymeric components of the blend are strongly adsorbed onto the filler surface, the interaction parameters of a polymer A and B with the functional groups on surface S are negative (χ_{AB} and χ_{AB}). In this case, for both miscible and immiscible polymer pairs, the introduction of a filler that strongly interacts with polymer A and B will decrease the value χ_{A+B+C} and enhance the thermodynamic stability of the system. For immiscible PP/PS blends in our study, which χ_{AB} value is positive, if the introduction of nano-SiO₂



(a)



(b)

Fig. 7. Storage modulus (a) and storage viscosity (b) of PP/PS/nano-SiO₂ (70/30/5) blends obtained at different mixing time.

particles makes a large number of PP and PS molecules adsorbed onto the surface of them, the ΔG_{mix} value will be negative and the PP/PS blends becomes more stable thermodynamically. However, if nano-SiO₂ particles are not located at the interface between PP and PS, a truly compatibilization will not be achieved.

To investigate the location of nano-particles in the blends, SEM at higher magnification on the dispersion of A-SiO₂ particles was also carried out. The morphologies shown in Fig. 8 indicate a fine dispersion of nano-SiO₂ particles (bright beads) and no large aggregates are present (about 50–80 nm). After mixing for a short time (1 min), nano-SiO₂ particles mainly exist in PP matrix (Fig. 8(a)). With the further increasing of the mixing time, a large number of nano-SiO₂ particles gradually migrate from PP matrix to the interface of PP and PS (Fig. 8(b) and (c)),

which corresponds to the better dispersion of PS in PP matrix, as shown in Fig. 2(b) and (c). However, the location of nano-SiO₂ at the interface seems not stable. After a longer mixing time, most of nano-SiO₂ particles go back to PP matrix (Fig. 8(d)), correspondingly one observes a deteriorated dispersion of PS in PP matrix, as shown in Fig. 2(d) and (e). So it can be concluded that the location of nano-SiO₂ particles on the interface between PP and PS is necessary for good compatibilization, and the compatibilization achieved is not stable thermodynamically.

Consequently, there are three possible explanations for the decrease in PS particle size of PP/PS blends containing nano-SiO₂ particles: (1) enhanced the compatibility caused by the adsorption of both PP and PS molecules onto the surface of nano-SiO₂ particles which possess very large specific surface area and lots of active spots, (2) increased viscosity ratio caused by the introduction of nano-SiO₂ particles, leading to a retardation of coalescence of the dispersed PS particles, (3) enhancing the bending energy of the interface due to the stiff nano-SiO₂ particles migrating to the interface of PP/PS blends, thus slowing down the rate of phase separation. In a word, the addition of nano-SiO₂ particles causes the increase in the viscosity of PP/PS blends, retarding the coalescence of PS droplets and slowing down the rate of phase separation. With the increase of mixing time, however, the polymer system tends to reach the equilibrium state. So, the average size of the dispersed PS phase initially decreases and then increases. Our result suggests that the compatibilization in PP/PS blends by nano-SiO₂ particles is a process controlled by kinetics rather than by thermodynamic.

Combined with previous results, the development of phase morphologies in immiscible PP/PS blends can be described as follows: (1) formation of large droplets of the dispersed PS phase in the PP matrix at the melting state, (2) deformation of PS particles under the shear force, (3) breaking up of the deformed PS particles to result in the formation of small droplets, and finally (4) coalescence of the droplets. However, the introducing of nano-SiO₂ particles, which migrate to the interface between PP and PS, leads to the increase in viscosity of PP/PS blends and retarding the coalescence of PS droplets. The schematic of the development of the phase morphologies is shown in Fig. 9.

5. Conclusions

The compatibility of PP/PS blends can be dramatically improved with the addition of nano-SiO₂ particles, which possess excellent hydrophobicity and contain a large number of alkyls in their surface. The SiO₂ content and mixing time also has profound effects on the compatibility of PP/PS blends. The crystallization of PP is changed with the introduction of SiO₂ particles. The increase of the compatibility of PP/PS blends impedes the motion of PP

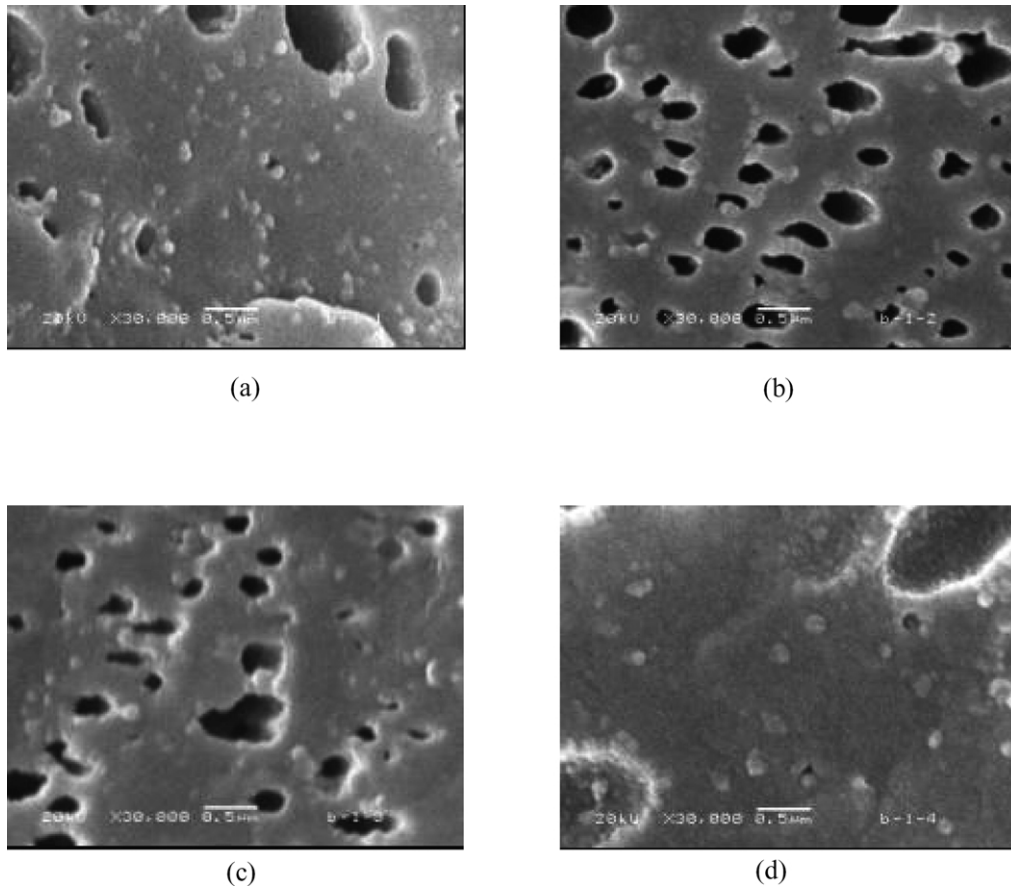


Fig. 8. SEM images of PP/PS/nano-SiO₂ blends (70/30/5) at different mixing times: Highlight the location of the filler. (a) 1 min, (b) 5 min, (c) 15 min, (d) 20 min.

molecules during the crystallization, thus decrease the crystallinity of PP. Flexural strength and modulus of PP/PS/A-SiO₂ composite are all improved, which is also resulted from the compatibilization after introducing SiO₂ particles. The compatibilization of nano-SiO₂ particles in PP/PS blends is a kinetic controlled process. An increase of viscosity in this system has been observed, which will slow

down the kinetic conditions of phase separation. After sufficient experimental time the phase morphology will reach to the equilibrium state. The idea of using rigid inorganic nano-particles to improve the compatibility of immiscible polymer blends is new and unique. However, further work is needed to better understand the mechanism of the compatibilization.

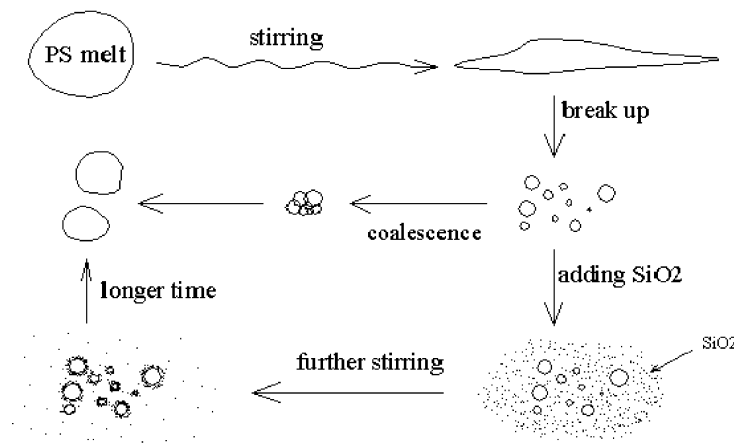


Fig. 9. The schematic drawing of the development of phase morphologies of PP/PS blends compatibilized by nano-SiO₂ particles.

Acknowledgements

We would like to express our great thanks to the China National Distinguished Young Investigator Fund (29925413) and National Natural Science Foundation of China (20274028) for Financial Support. This work is also partly supported by Ministry of Education of China for Doctoral Degree Program (20020610004).

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