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Microstructure and mechanical properties of polypropylene/polystyrene blend filled with as-synthesized MCM-41 prepared by melt-compounding

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Abstract Nano-sized as-synthesized MCM-41 particle, whose pore channels and outer surface full of organic CTAB template, was used as compatibilizers for immiscible polypropylene (PP)/polystyrene (PS) blends. In this paper, the solid structure SiO_2 was selected to compare with as-synthesized MCM-41 in properties of PP/PS blend. The mechanical results showed that tensile strength of the blend was increased by 32% and the impact strength was increased by 41.1% by addition low content of as-synthesized MCM-41 compared to pure PP/PS. The presence of SiO_2 in the blend cannot improve the mechanical properties obviously. SEM indicated that incorporation of as-synthesized MCM-41 into PP/PS blend can act as compatibilizer, which resulted in a decreased particle size of dispersion phase together with morphological evidence of interfacial adhesion. However, with the presence of SiO_2, 1%, 3%, in the blend, the interface did not show clear change compared with the PP/PS blend.

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Introduction

Using polymer blend is a traditional method for making new materials with enhanced mechanical properties [1, 2]. Unfortunately, because of the large interfacial strength, most of blends tend to phase separate, which results in poor mechanical properties. It is known that one of the classical routes to ensure adhesion between the phases is the use of a third component, a compatibilizer, which is compatible or miscible with both phases. Recently, nano-filler as a compatibilizer has been extensively served as effective compatibilization to enhance the adhesion of the immiscible interface [3–5]. So far, numerous researchers have studied the field of polymer blends with nano-filler, such as clay silicates, calcium carbonates, and other inorganic solid particles [6–8]. In many cases, if the surface of the filler is incompatible with the polymer, then phase separation and agglomeration of filler particles may occur [9]. As demonstrated by Albano et al. [10] and Ichazo et al. [11] who analyzed the effect of $CaCO_3$ on blends of PP/HDPE found that the addition of this blend at 30 wt% did not improve the mechanical properties of the blends. This behavior has been attributed to weakness in the interaction of these two-phase systems caused by stress concentration or discontinuity at the dispersed phase and matrix.

Mesoporous materials (mesoporous silica), i.e., dual MCM-41 (nanoparticle and nanochannel) is also used as one kind of filler [12]. Mesoporous MCM-41 can be synthesized via soft template (cetyl trimethylammonium bromide, CTAB) pathway. In water, the template molecules can have a highly ordered structure and retain the original ordered structure [13, 14]. Calcination can remove the template and obtain the ordered mesopores. But calcination process has some disadvantages. It must be calcined at 600 °C for 10 h to remove the template in the mesopores which is used in the synthesis of mesoporous MCM-41. This process is a complex procedure because of the long time and high temperature and also will pollute the atmosphere due to the great amount of organic matter. For the as-synthesized MCM-41, before calcinations, in the nano-sized pore and on the outer surface are full of organic template of CTAB. It is synthesized by our group, with uniform diameters in the order of 80–100 nm, spherical shape, mono-dispersed. The total amount of organic template of CTAB in the nano-sized pores and on the outer surface of the particle is 24 wt% [15]. We have used it in PP-based, PE-based, and epoxy resin nanocomposites in our previous studies [16–18]. The results of tensile test showed that as-synthesized MCM-41 particle could provide the matrix with strength and toughness effects simultaneously at rather low filler content. But few papers have reported as-synthesized MCM-41 particle as compatibilizer in immiscible blend.

Polypropylene (PP) and PS are among the most widely used plastics in the world and they are the typical examples of immiscible polymer blends. The aim of this paper is to investigate the fundamental question of compatibilization role of as-synthesized MCM-41 particle in the PP/PS blend. Compared to as-synthesized MCM-41 particle, the nano-particle SiO_2 was selected as compatibilizer which possessed solid structure and the same particle size with as-synthesized MCM-41 particle. The main objective of the research here is to analyze the effect of the characteristics of as-synthesized MCM-41 particle on the tensile performance and fractured surfaces in the immiscible blend.

Experimental

Materials

Tetraethylorthosilicate and CTAB were supplied by shenyang Xinxi Chemical Co. Ltd. and Beijing Zhonglian Chemical Co. Ltd., respectively. PP and PS were commercial products from Liao-Yang Petrochemical Co., China (PP, F401, MFI = 2.5 g/10 min; PS 666D, MFI = 4.3 g/10 min at 190 °C). SiO_2 particles with uniform diameter (ca. 80–100 nm) were provided by Harbin Engineering University.

Synthesis of the mesoporous as-synthesized MCM-41 particle

The as-synthesized MCM-41 particles were prepared by sol–gel method, which was reported in our previous study [15].

Preparation of blend

The blend was prepared by melting the polymers first, and then mixing as-synthesized MCM-41 particle for 15 min in a Thermohaakemixer at 180 °C and a rotor speed of 50 rpm. The blends were then compression molded using a laboratory press at 180 °C for 6 min into sheets of 1.0 mm thick, and then cooled at room temperature. In order to compare with PP/PS/as-synthesized MCM-41 particle blend, PP/PS/SiO_2 blend was prepared by the same way.

In blends, the nano-filler loading was 0, 0.5, 1, 3, and 5 wt%. For PP and PS, the weight ratio was 80:20.

Characterization of the blend

Test specimens for the tensile measurements were prepared from 1.0-mm-thick plates, which were cut from the molded sheets with a die cutter. The tensile strength was measured in a tensile Instron1211 testing machine at the strain rate of 10 mm/min at room temperature. The impact strength properties of PP/PS blend measured according to the Chinese Standard GB527-83. The measurement was repeated five times for each type of sample and the average value was calculated. All of the mechanical properties were listed in Fig. 4, results showed that the correlation coefficient was more than 0.890.

A supra 35 scanning electron microscope (SEM) with an accelerating voltage of 15 kV was employed to observe the morphology of the tensile fractured surfaces. A thin layer of gold was sputtered on the surface of the specimens for electrical conductivity.

FT-IR measurements were performed on Nicolet MNGNA-IR 560 with 4 cm^{-1} resolution.

Results and discussion

Characterization of as-synthesized MCM-41 particle

Figure 1 shows IR of as-synthesized MCM-41 nano-particle. The as-synthesized samples exhibit the absorption bands around 2921, 2850, and 1490 cm^{-1}, respectively, which correspond to *n*-C–H and *d*-C–H vibrations of the surfactant molecules [16]. The broad bands at 3500 cm^{-1} may be attributed to the surface silanols and adsorbed water molecules. The adsorption bands at 1620–1640 cm^{-1} are caused by the deformation vibrations of adsorbed water molecules [16]. The absorption bands at 1050 and 1221 cm^{-1} are due to the asymmetric stretching vibrations of Si–O–Si bridges [19].

Figure 2 shows the XRD patterns of as-synthesized MCM-41 particle. The MCM-41 possesses hexagonal symmetry before or after calcinations. As-synthesized

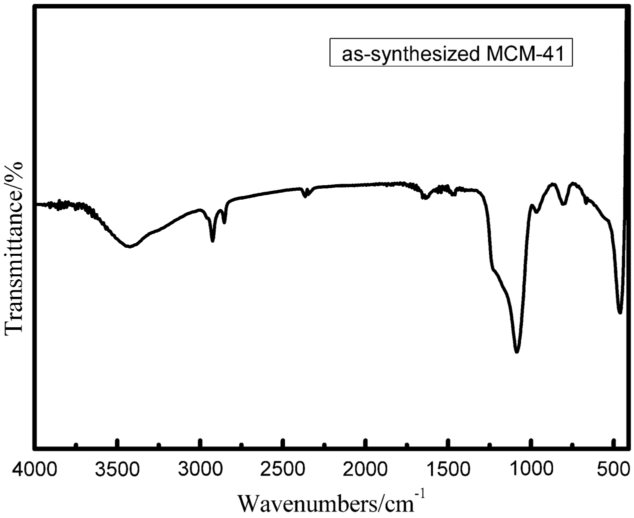

Fig. 1 FTIR spectra of as-synthesized MCM-41 particle

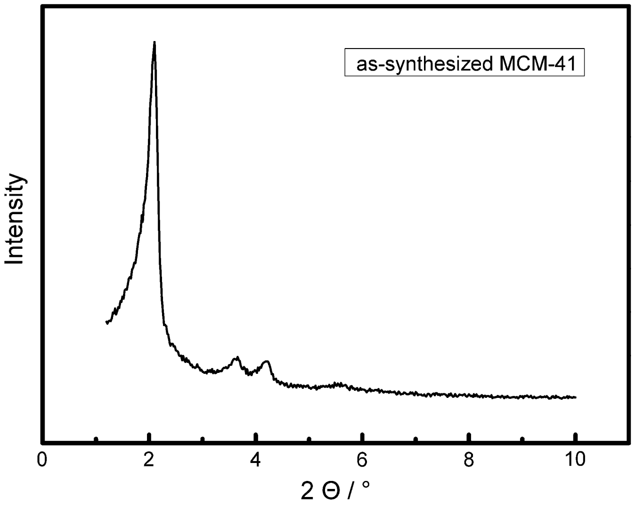

Fig. 2 XRD of as-synthesized MCM-41 particle

MCM-41 particle exhibits one intense (100) diffraction peak and two additional small reflection (110) and (200) at low reflection angles, with the characteristics of well aligned hexagonal ordering [13, 14, 20].

Nano-sized mesoporous MCM-41 particles with uniform diameters in the order of 80–100 nm, spherical shape, mono-dispersed, are synthesized by our roup to exclude the size and shape effects of fillers on composites (Fig. 3).

Mechanical properties

Tensile strengths

Figure 4a gives the tensile strength of the blends versus the content of two fillers. It is well known that the mechanical properties of two incompatible polymers are usually increased in the case of great adhesion at the immiscible interface of them [21]. It can be seen that addition of as-synthesized MCM-41 particle improves the strength obviously. The tensile strength is increased by 32% at the 3 wt% nano-filler loading compared to pure PP/PS. On one hand, the extremely high surface area is one of the most attractive characteristics of as-synthesized MCM-41 particle because it facilitates creating a great amount of interphases in blend, which can reduce the interface strain. The result indicates that as-synthesized MCM-41 particle could improve the adhesion between the phases. On the other hand, the total amount of organic template of CTAB in the nano-sized pores and on the outer surface of the particle is 24 wt% [15]. These suggest that the CTAB chains on the external surface of the particle and inside the pore channel extending to the opens can give physical entanglement with two polymeric molecules, like a bridge to link the PP and PS molecules. The model like this is shown in Fig. 5. When the content of as-synthesized MCM-41 exceeds 3 wt%, the tensile strength of the blends decreases. Maybe the low molecular weight of the organic template CTAB ($C_{19}H_{42}BrN$, 364.46) in the nano-sized pores and on the outer surface of the particle dominates the interfacial interaction in the blend.

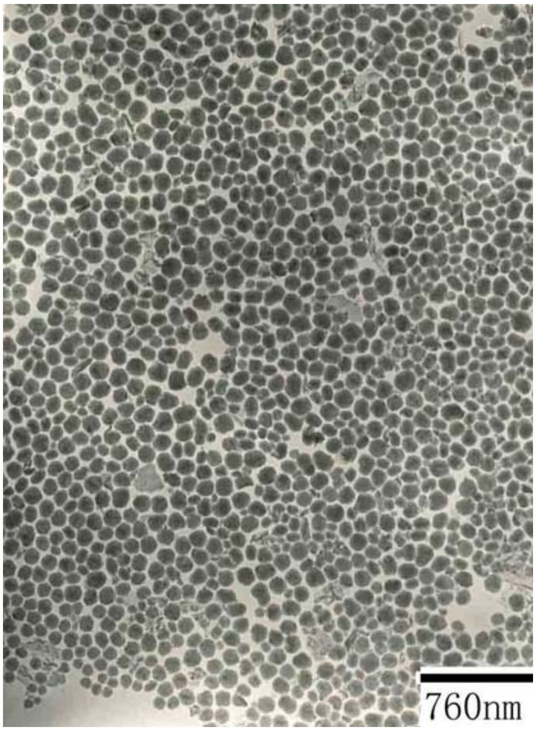

Fig. 3 TEM images of as-synthesized MCM-41 particle

In contrast, an approximately linear blend dependence of tensile strength is perceived in the blend filled with SiO_2.

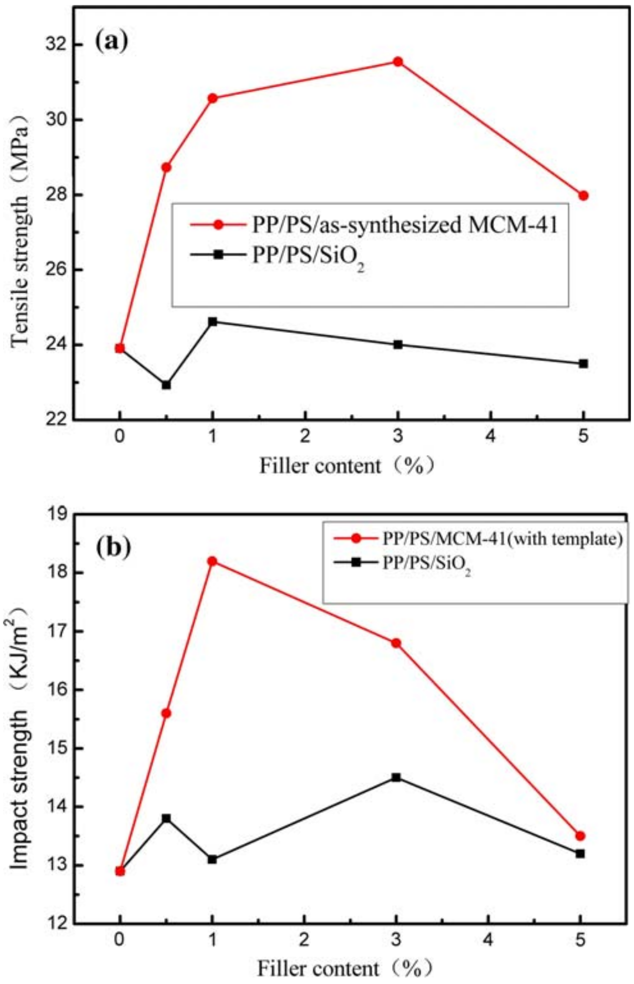

Fig. 4 Effect of as-synthesized MCM-41 particle and SiO_2 content on mechanical properties of PP/PS (80/20) (**a** tensile, **b** impact)

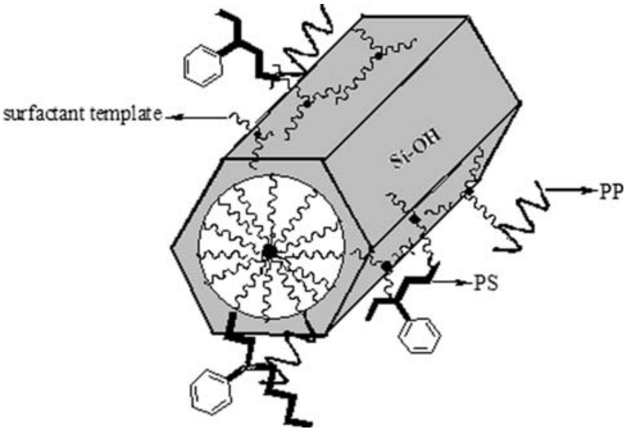

Fig. 5 Model analogy PP/PS/as-synthesized MCM-41 particle blend

This can be interpreted as the absence of a rigid interphase and the appearance of larger agglomerates of SiO_2 at the interface as a result of poor adhesion.

Impact strengths

In Fig. 4b, the impact strength is increased by 41.1% with 1 wt% as-synthesized MCM-41 particle, as compared to that of pure blend. Then, when the loading of the filler is increased (e.g. >1 wt%), the impact strength is decreased.

This behavior is attributed to its particular structure. Under the low filler content level, the extremely effective improvement of impact strength of the blend should result from the entanglement between the two polymer molecular chains and the template of the stiffness filler. The interfacial adhesion is strong enough to ensure stress transfer between phases during fracture. With a rise in filler content, the increase of organic template is dominated, leading to a drop in impact strength of the blend. That is, the organic template mixture of CTAB ($C_{19}H_{42}BrN$, 364.46) in the nano-sized pores has a low molecular weight, the disadvantages contribution made by the CTAB provide soft layer between the filler and matrix under a rather high nano-filler loading.

By comparing as-synthesized MCM-41 particle with the same loading of nano-SiO_2, a disorderly variation in the strength with SiO_2 content is detected. The nano-SiO_2 is only rigid filler with high surface area. The more particles are exposed to the blend, the more possibly agglomerates and dispersion inhomogeneous can be generated. So, the nano-SiO_2 structure would certainly be detrimental to the stress transfer.

SEM patterns

The typical morphologies of blends are shown in Fig. 6, which shows the tensile fracture surface of pure blend and the blend with as-synthesized MCM-41 particle and nano-SiO_2 at the same content. The pure blend has a relatively smooth continuous phase in association with PS particles dispersion within the PP matrix (Fig. 6a). The particle size of the dispersed phase (PS) is 8 μm. It should be stressed here, the holes where the PS particles are removed from the PP matrix during extraction show poor adhesion between the phases. This indicated that the interphase adhesion of PS with PP is too weak to sustain the stress at fracture. In the case of SiO_2 adding into blend, at the content of 1 wt%, the fractured surface becomes rougher but the trace of plastic deformation does not appear (Fig. 6b). Many PS particles are dispersed in the matrix and the particle size is not decreasing obviously. These demonstrate the poor adhesion capability of the blend. For as-synthesized MCM-41 particle, the fractured surfaces are full of extensive matrix fibrils (Fig. 6c). Moreover, the dispersed particle size of PS is decreased from 8 to 5 μm, where a clear decrease in particle size is obtained. The compatibilization engenders the desired blend by controlling the size of the

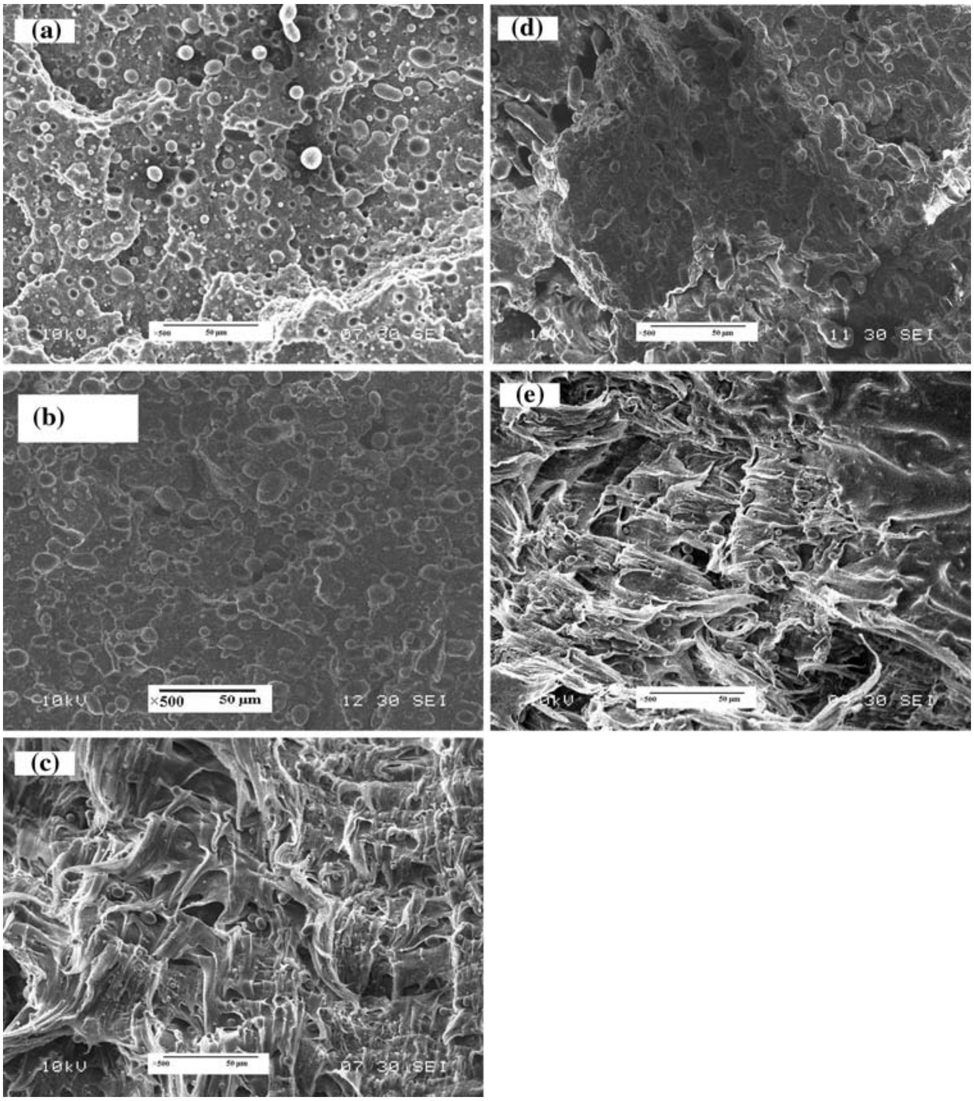

Fig. 6 SEM images of fracture surfaces of (80/20) PP/PS blends with as-synthesized MCM-41 particle and SiO_2 [**a** PP/PS, **b** PP/PS/SiO_2 (1 wt%), **c** PP/PS/MCM-41 (1 wt%), **d** PP/PS/SiO_2 (3 wt%), **e** PP/PS/MCM-41 (3 wt%)]

dispersed droplets of the minor phase [22]. It can be evidenced that by adding low as-synthesized MCM-41 particle, the interfacial interaction could be enhanced [23]. This could be coincided with our "Impact strengths" section results.

When the content of nano-SiO_2 approaches 3 wt% (Fig. 6d), a number of PS particles are also dispersed in the matrix without clear sign of stretching of the surrounding matrix. The size of the PS particles is decreased lightly. An increased content of nano-SiO_2 would lead to agglomerates and hence greater probability of debonding due to the poor interfacial adhesion. When as-synthesized MCM-41 particle is incorporated (Fig. 6e), the matrix surrounding the PS particles has turned into plastically drawn fibrils. Besides, the PS particle size decreases from about 5 µm in PP/PS with 1% as-synthesized MCM-41 particle to about 2.5 µm with 3 wt%. The PS particle is settled or linked by the fiber of PP. This may be attributed to the organic template of CTAB in the mesopores and on the outer surface of the particle, which enhances the interaction through the physical entanglement between the matrix and the template.

Conclusion

Compared with nano-SiO_2 particle, the addition of as-synthesized MCM-41 particle caused significant change in the tensile properties and morphology of PP/PS blend. It simultaneously improved the tensile and impact strength by adding low content of as-synthesized MCM-41 particle.

(1) The tensile strength was increased by 32% by adding 3 wt% as-synthesized MCM-41 particle compared to pure PP/PS blend.

(2) The impact strength was improved by 41.1% by adding 1 wt% as-synthesized MCM-41 particle compared to pure blend.

(3) The SEM showed that the presence of as-synthesized MCM-41 particle in PP/PS blend not only reduced the particle size of the dispersed phase (PS) but also changed the matrix into plastically drawn fibrils. Moreover, as-synthesized MCM-41 particle was played as compatibilizer that can improve adhesion in the immiscible blends.

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