Materials Science and Engineering A 512 (2009) 32–38

Contents lists available at ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

Microstructure and properties of polypropylene composites filled with co-incorporation of MCM-41(with template) and OMMT nanoparticles prepared by melt-compounding

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ARTICLE INFO

Article history:
Received 9 September 2008
Received in revised form 4 January 2009
Accepted 12 January 2009

Keywords:
Composites
Polypropylene
Mesoporous MCM-41(with template)
OMMT
Mechanical properties

ABSTRACT

Mesoporous MCM-41, whose pore channels were filled with cationic surfactant *n*-hexadecyltrimethylammonium bromide (CTAB) and poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO–PO–EO) sequence centered on a (hydrophobic) poly(propylene glycol) nucleus terminated by two primary hydroxyl groups (Pluronic F_{127}, molecular weight = 11,500) template mixture inside the pore channels and on the outer surface of the particle, was used directly as new fillers for polypropylene, together with organic-montmorillonite (O-MMT). The effects of different structured nano-materials, MCM-41(with template)/OMMT, nano-SiO_2/OMMT on the crystallization, morphology and mechanical properties of polypropylene composites were investigated. The results of PLM proved the co-incorporation of MCM-41(with template)/OMMT decreased the spherulites sizes of polypropylene and acted as efficient nucleating agents for PP crystallization. SEM revealed that the enhancement of the interface was obtained by adding MCM-41(with template)/OMMT. The results of mechanical tests showed that at same nano-material loading, the co-incorporation of O-MMT and MCM-41(with template) gave rise to much better toughness effects than co-incorporating of nano-SiO_2/OMMT due to different interfacial structure between the fillers and the matrix.

1. Introduction

Recently nano-mesoporous MCM-41(without template) has been extensively served as effective reinforcement filler to enhance the mechanical, thermal properties of polymer materials, due to its unusual characters, such as extended inorganic or inorganic–organic hybrid arrays with exceptional long-range ordering, highly tunable textural and large surface area properties, controlled pore size and shape [1–5]. It is expected that a polymer could either be introduced directly or produced by in situ polymerization of organic monomers inside the mesopores. The polymer in the nano-sized pores extending along the channels to the openings can not only enhance the miscibility through the entanglement and inter-diffusion between the matrix and the particulate, but also highly suppress the aggregation of fillers. Thus nanocomposites of polypropylene, polyethylene, epoxy resin and MCM-41(without template) with enhanced thermal stability and mechanical strength were also reported in our previous work [6–9].

But this kind of filler has some disadvantage. 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. In this paper, we will use MCM-41(with template) directly as one of nano-fillers in the polymer matrix. Before calcination, the total amount of organic template mixture of CTAB and F_{127} in the nano-sized pores and on the outer surface of the MCM-41(with template) particle is about 24 wt.% (Fig. 4). The organic template mixture of CTAB and F_{127} in the nano-sized pores extending along the channels to the openings and on the outer surface of the particle can enhance the interaction through the entanglement and inter-diffusion between the polymer matrix and the particulate though the molecular weight of the organic template mixture was lower than the polymer.

The use of inorganic layered silicates or smectite clays into the organic polymer for increasing its mechanical, thermal, barrier and fire retardant properties [10–12] has also been a hot spot

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doi:10.1016/j.msea.2009.01.027

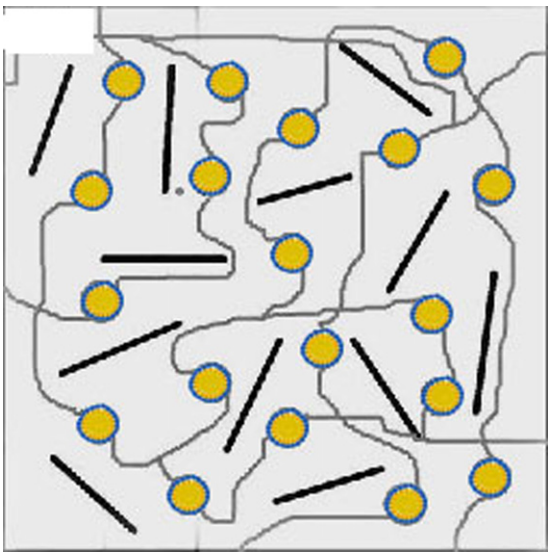

Fig. 1. Model analogy novel nanonetwork composite.

for researchers. Layered silicates are made up of several hundred thin platelets stacked in orderly particles or tactoids of the size of 8–10 μm. Each disk-shaped platelet has a very large aspect ratio about 100–1000 and is easily agglomerated due to the interlayer van der Waals force [13].

In the literature, combining two nano-materials with different shapes may generate more effectively enhanced effect due to the expected synergistic effect [14]. In our recent research, PP composite showed better mechanical properties filled with co-incorporation of MCM-41(without template)/OMMT filler, compared with single OMMT filler or MCM-41(without template) filler. In this study, polypropylene nanocomposites reinforced by MCM-41(with template) and OMMT were prepared by melt-compounding method. This novel nanonetwork composite with the fully exfoliated OMMT and dispersed MCM-41(with template) is seen in Fig. 1. The purpose of this paper is to study the reinforcing and toughening effect of co-incorporation two different kinds of nano-materials with different forms, layers (OMMT) and particles (MCM-41(with template)), compared with nano-SiO_2/OMMT filler, into the polymer matrix on morphology and mechanical properties of resultant composites which have not been reported in our previous papers.

2. Experimental

2.1. Materials

Tetraethylorthosilicate and cetyl trimethylammonium bromide (CTAB) were supplied by shenyang Xinxi Chemical Co. Ltd. and Beijing Zhonglian Chemical Co. Ltd., respectively. OMMT was supplied by zhejiang fenghong Co. Ltd. Nano-SiO_2 was supplied by Shenyang chemical factory, the size and the shape of the particle was the same with MCM-41(with template). PP homo-polymer was provided by Liao-Yang Petrochemical Co. (China).

2.2. Synthesis of the mesoporous MCM-41

The nano-sized mesoporous MCM-41 particles were prepared in an aqueous phase by sol–gel method. A triblock copolymer (Pluronic F_{127}, molecular weight = 11,500) was added as an assistant surfactant and dispersant to prevent the agglomeration of the particles [8]. The as-synthesized particle was named as the MCM-41(with template) nano-filler.

2.3. Preparation of PP nanocomposites

Before use, the MCM-41(with template), OMMT and SiO_2 powder were all treated in the oven at 180 °C to exclude the physisorbed water on the particle surface. In order to study the effect of different filler on morphology and mechanical properties of resultant composites, the composite was prepared by taking desired quantity of two types of filler (MCM-41(with template)/OMMT, SiO_2/OMMT) with respect to PP powder using a twin screw extruder. The temperature of the extruder was maintained at 150, 190, 190, 200, 200 and 190 °C from hopper to die, and the screw speed was 110 rpm. Pure PP was also passed through extruder under the same conditions to serve as a reference. The pelletized granules were dried for 20 h under 80 °C and then injection molded under the temperature of 200 °C.

In all composites, the total nano-material loading was 1, 2 and 4 wt.%. For PP composite, the weight ratio of MCM-41(with template) or nano-SiO_2 to OMMT was 1:1.

2.4. Characterization of the composites

The particle size (PS) and particle size distribution (PSD) of each sample was determined using a laser particle size analyzer (Rise-2008, Shandong, China). Approximately 5 mg microparticles were suspended in the sample cell filled with distilled water. Before measurement, the suspension was dispersed by ultrasonic waves with power 100 W for 1 min. Next, the rotative pump started at 1250 rpm to circulate the sample's suspension. Analytic software was automatically used to assay the particle size and PSD.

The shape and dispersion of the nanoparticles were determined by a Philips EM420 transmission electron micrograph (TEM). To prepare the nanoparticle sample for TEM examination, the MCM-41 nanoparticles were dispersed in ethanol by an ultrasonic bath for 10 min.

The template content of the mesoporous MCM-41 nanoparticles was measured using a thermogravimetic analyzer (NETCH STA449C). The measurement was carried out under N_2 at a heating rate of 10 °C/min.

The identification of MCM-41, OMMT, and the PP composites was carried out by X-ray diffraction (D/max-2500PC, using Cu Kα radiation at 50 kV and 200 mA with a scanning rate of 1°/min and scan step of 0.01).

Spherulitic growth was observed by hot-stage optical microscopy (XP-201, Shanghai LW Scientific Co., Ltd.). PP and PP composites was placed between two glass slides on a hot stage kept at 210 ± 2 °C for 10 min to allow the sample to melt completely and remove thermal memory, then squeezed on the top slide to form a film. It was then quenched to 120 ± 1 °C (for nanocomposite samples) at a rate of 50 °C/min and maintained at that temperature until the spherulitic growth ceased. The micrographs were captured with the help of a camera attached to the microscope.

Tensile tests were carried out on Instron1211 testing machine. One-millimeter thick dumbbell specimens were cut from the molded sheets with a die cutter. A cross-head speed of 50 mm/min was used and the tests were performed at room temperature. Notched Izod impact strength tests were conducted according to ASTM D 256-97 at room temperature. The measurement was repeated five times for each type of sample and the average value was calculated.

A supra 35 scanning electron microscope 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.