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Preparation and properties of POSS grafted polypropylene by reactive blending

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ABSTRACT

The octavinyl polyhedral oligomeric silsesquioxane (POSS) grafted polypropylene (PP) was first prepared by reactive blending. The structure and properties of physical blending and reactive blending composites of PP/POSS were investigated by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA). WAXD analysis shows that the POSS in the reactive blending composites has better compatibility with PP than in the physical blending composites. The β-form crystalline hence disappears even the non-reactive POSS can act as an effective β-nucleating agents. DSC analysis shows the reactive blending composites have higher crystalline temperature while POSS in the physical blending composites have little effect on the crystalline temperature. The modulus of reactive blending composites increases in the presence of POSS, while that of the physical blending composites decreases with increasing POSS content.

1. Introduction

In the recent years, the area of polymer nanocomposites has invoked much interest. Polyhedral oligomeric silsesquioxane (POSS) (The schematic drawing of POSS is shown in Fig. 1) based materials, both as organic–inorganic hybrids and as polymer nanocomposites have been studied widely. POSS can be effectively incorporated into polymers by copolymerization, grafting or even blending through traditional processing methods. POSS and its derivatives have been reported as candidates in modifying a wide range of thermoplastics such as polyolefin [1–4], polystyrene [5], poly(methyl methacrylate) [6], polycarbonate [7], poly(ethylene terephthalate) [8], polyamide [9], polycaprolactone and polylactide [10] and a few thermoset systems [11–14]. The incorporation of POSS or its derivatives into polymers can lead to some dramatically improved properties, such as the increase in use temperature, oxidation resistance, surface hardening and improved mechanical properties, as well as reductions in flammability, heat evolution and viscosity during processing, etc. [15].

When POSS is copolymerized or grafted to the backbone of polymer chains, they can cause significant performance enhancements [1,6,7]. However, POSS-containing hybrid polymers reported in most the literature are made from one-pot copolymerization method, where POSS monomers and organic monomers are mixed together prior to the polymerization process. There are little reports about the POSS directly grafted to polymers chains. While the activity for copolymerizations of POSS macromonomers is quite low due to its steric bulkiness [16,17]. The presence of POSS in monomers can dramatically affect the rate of polymerization. Therefore, any changes in POSS monomer structure and/or initial feed ratios can result in different degrees of polymerization for each copolymer [18]. Fu and Lee et al. [18,19] had synthesized and characterized a series of tri-block polystyrene–butadiene–polystyrene (SBS) containing grafted POSS by the hydrosilation method in toluene solution. Unlike typical free radical copolymerizations commonly used for many other POSS incorpora-

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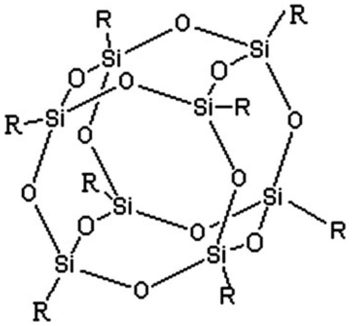

Fig. 1. Structure of polyhedral oligomeric silsesquioxane.

tions investigated, this synthesis method has advantages of making a series of polymers with varying amounts of POSS without any change to the overall degree of polymerization or structure of the main SBS backbone. This method can only be used for polymers containing C=C bonds or Si—H group [20] and much solvent need to be removed. Reactive blending has proven to be a key technology in the polymer industry and is regarded as an efficient method for the continuous polymerization of monomers and for the chemical modification of existing polymers in the absence of solvents. In this paper, octavinyl POSS was successfully grafted to isotactic polypropylene (PP) chains by reactive blending of PP and POSS in the presence of dicumyl peroxide (DCP). Compared with the physical blending composites of PP/POSS, reactive blending composites had better mechanical and thermal properties. The morphology structure, crystallization and melt behaviors were also changed because of the graft reaction. To the best of our knowledge, this is the first time that polymer POSS copolymer is prepared by reactive blending method. This gives us a simple and effective approach to prepare POSS grafted polymers without rigorous reaction environment and limitation of polymers.

2. Experimental

2.1. Materials

PP, F401 was produced by Liaoning Panjin Petrochemical Co., Ltd., China, with a melt flow index (MFI) of 2.3 g/10 min (230 °C, 2.16 kg). The octavinyl POSS, OL1160 was purchased from Hybrid Plastic Co., USA. Dicumyl peroxide (DCP) was analytical grade and used as received.

2.2. Samples preparation

Before blending, PP and POSS were dried at 70 °C under vacuum for about 12 h. PP, POSS and DCP (0.1 wt% to the total weight) were reactively blended in the mixing chamber of a Haake Rheometer RC90 at 180 °C and 60 rpm for 8 min. The composite was removed out and compression molded in a press at 190 °C for 20 min (preheat 15 min and then mold for 5 min), then cold pressed to get samples for testing. Physical blending composites of PP and POSS (without DCP) were also underwent similar processes for comparison. Hereafter the reactive blending and physical blending composites were referred as RBx and PBx, respectively, and the number x means the weight content of POSS. The reactive blending composites were resolved in refluxing xylene, precipitated and washed by acetone, the precipitate was resolved and precipitated at least three times and dried at 80 °C for 12 h and thought as POSS grafted PP (POSS-g-PP) (hereinafter referred as POSS-g-PPx).

2.3. Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis was obtained using an FTIR spectrometer (Paragon 1000 from Perkin-Elmer Co., USA). The scan range was from 4400 to 400 cm^{-1} with a resolution of 4 cm^{-1}. Samples of POSS-g-PP were pressed to thin films for testing.

2.4. POSS content in POSS-g-PP and gel determination

The molded reactive blending composites were cut into small pieces, weighted and packed with filter paper, respectively, and then were Soxhlet extracted in boiling acetone at least 72 h, dried and weight until the weight didn't changed, the left samples were thought as POSS-g-PP and used to determine POSS content in POSS-g-PP. The samples were further Soxhlet extracted in boiling xylene for 48 h, dried and weight to determine gel content. No gel was observed for all the samples.

2.5. Si content measurement

The Si element content in POSS-g-PP was measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (VISTA-AX from Varian Co., USA).

2.6. Scanning electron microscopy (SEM)

The morphology of PP/POSS composites was observed by field emission scanning electron microscopy (FESEM) (JSM-7401F, JEOL Co., Japan). The samples were fractured under cryogenic condition with liquid nitrogen. The fracture surfaces were coated with thin layers of gold of about 10 nm.

2.7. Wide-angle X-ray diffraction (WAXD)

A sample with the thickness of 1 mm was scanned at a speed of 4 °C/min at ambient temperature using an X-ray diffractometer (SA-HF3, Rigaku Corp., Japan) with CuK_α radiation($\lambda = 0.154$ nm) at a generator voltage of 40 kV and a current of 40 mA. The data were collected from 5° to 35° intervals.

2.8. Differential scanning calorimetry (DSC) analysis

Thermal analysis of samples ware performed using a Perkin-Elmer DSC. All tests were performed in a nitrogen atmosphere with a sample weight of about 4 mg. All samples were first heated to 200 °C at 20 °C/min and kept for 3 min to eliminate prior thermal history. The specimen