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In situ preparation of $Mg(OH)_2$/polystyrene nanocomposite via soapless emulsion polymerization

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Summary

Magnesium hydroxide nanoneedles modified by oleic acid [OA–$Mg(OH)_2$] were synthesized via alkaline injection into magnesium chloride solution in the presence of oleic acid (OA). The magnesium hydroxide/polystyrene nanocomposite [$Mg(OH)_2$/PS] was then prepared by soapless emulsion polymerization technique in an aqueous suspension. The Fourier transform infrared (FT–IR) analysis shows that the polystyrene was covalently grafted onto the surfaces of the $Mg(OH)_2$ nanoneedles [OA–$Mg(OH)_2$]. The dispersion of $Mg(OH)_2$ nanoneedles in polystyrene is uniform as observed by transmission electron microscope (TEM). The grafting percentage was determined by means of elemental analysis (EA). The thermal behavior determined by the differential scanning calorimetry (DSC) indicated that $Mg(OH)_2$/PS had a higher glass transition temperature than PS matrix, and it can be concluded that $Mg(OH)_2$ could retard the degradation of PS based on the data of thermal gravimetric analysis (TGA) and differential thermoanalysis (DTA).

Introduction

Inorganic/polymer nanocomposites are of great interest because of their combined properties of both inorganic nanoparticles and organic molecules [1]. Several methods have been used to prepare polymer nanocomposites such as sol-gel reactions [2-4], intercalative polymerization [5-7], melt-processing [8-10], and in situ polymerization [11,12], depending on the nature of nanoparticles and synthesis/ processing of polymeric matrices. The most important factors in the preparation of nanomaterials with enhanced performance include obtaining uniform distribution of inorganic nanoparticles within the polymer matrix and promoting strong interface adhesion between matrices and nanofillers. The soapless emulsion polymerization has been considered as a promising and preponderant approach of nanocomposites preparation [13,14], because organic components on the surface of inorganic particles can be synthesized according to their application and inorganic particles can be well dispersed into polymer matrices. Moreover, due to lack of surfactants, the application arena of composite particles is getting wider as compared with products of emulsion polymerization.

Inorganic compound magnesium hydroxide [$Mg(OH)_2$] as a smoking- and toxic-free additive has been extensively used in polymeric halogen-free flame-retardant materials. However, its fatal disadvantage is its low flame-retardant efficiency and thus it needs very large usage amount of $Mg(OH)_2$, which gives rise to a sharp decrease of mechanical properties of flame-retardant polymeric materials due to the poor compatibility between the high energy hydrophilic surface of inorganic part and the low-energy surface of hydrophobic polymers especially when it is employed in a polyolefin matrix such as polyethylene (PE) or polypropylene (PP), because of their low polarity [15,16].

In the present work, a $Mg(OH)_2$/polystyrene nanocomposite was prepared via soapless emulsion polymerization for the first time. The product was characterized by TEM, FT–IR, EA, DSC, and TGA/DTA. The results indicate that $Mg(OH)_2$ can disperse in the composite with nanometer sizes and the $Mg(OH)_2$/PS nanocomposite exhibits better thermal stability than PS itself.

Experimental

Materials

Analytical grade magnesium chloride ($MgCl_2 \cdot 6H_2O$), sodium hydroxide (NaOH), potassium persulfate (KPS) and oleic acid (OA) were purchased from Tianjin Chemicals Co. Ltd. (Tianjin, China) and used without further purification. Styrene (St) obtained from Lanzhou Chemical Co. Ltd. (Lanzhou, China) was treated with 1 M NaOH aqueous solution to remove the inhibitor and distilled under reduced pressure in nitrogen atmosphere.

Synthesis of magnesium hydroxide nano-needles modified by oleic acid [OA–Mg(OH)$_2$]

10.0 g of magnesium chloride was dissolved in 50 ml of distilled water in a 250 ml flask. The flask was placed in an ice bath, and 50 ml of mixture solution containing 0.3 ml of oleic acid and 4.2 g of sodium hydroxide was added in dropwise at a flow rate of 0.3 ml/min at a temperature below 4°C with vigorous stiring. After all mixture solution was added, the product, oleic acid modified magnesium hydroxide nanoneedles [OA–$Mg(OH)_2$] was filtered, and washed five times with alcohol to remove excess oleic acid and the by-products like magnesium oleate.

Preparation of modified magnesium hydroxide/polystyrene nanocomposite via in situ soapless emulsion polymerization

2.7 g of modified magnesium hydroxide nanoneedles [OA–$Mg(OH)_2$] was dispersed in 100 ml water by agitation and sonicated for 0.5 h. The OA–$Mg(OH)_2$ slurry was then placed in a 250 ml three-necked round-bottom flask fitted with a condenser and a thermometer. After the slurry was heated to 85°C, 0.03 g KPS in 5 ml of water was added in dropwise with bubbling of nitrogen (N_2), and then 3.0 ml of styrene was added dropwise within 1 h. The mixture was maintained at this temperature for 12 h with continuous bubbling of N_2. The esultant suspension was filtered after it cooled down to room temperature. The solid was washed with water for several times and dried at 60°C to obtain the magnesium hydroxide/polystyrene nanocomposite [$Mg(OH)_2$/PS].

To obtain magnesium hydroxide grafted by polystyrene [PS–$Mg(OH)_2$], free polystyrene (PS) was removed by Soxhlet extraction with toluene until no PS can be detected in the extraction solvent [17].

Characterization

The morphology of the $Mg(OH)_2$/PS nanocomposite was obsevered on a H-600 transmission electron microscope (TEM). The $Mg(OH)_2$/PS nanocomposite was deposited on a copper grid covered with a perforated carbon film after it was dispersed in toluene with aid of sonication for 15 min. FT–IR spectra were recorded on a Nicolet AVATAR 360 spectrophotometer using KBr pellets. Elemental analysis of carbon, hydrogen and nitrogen was performed using an Elementar vario EL instrument. The thermal properties of the composites were measured by differential scanning calorimetry (DSC) on a Perkin-Elmer Sapphire DSC6200 with a heating rate of 10ºC/min under pure nitrogen flow of 50 ml/min. Thermal gravimetric analysis (TGA) was performed on an instrument with same heating rate under air atmosphere.

Results and discussion

The FT–IR spectra of pure $Mg(OH)_2$, OA–$Mg(OH)_2$ and PS–$Mg(OH)_2$ are shown in Fig. 1. In Fig. 1b, two absorptions bands at 2930 and 2851 cm^{-1}, which are characteristic peaks of H–C–H asymmetric and symmetric stretching vibrations, appeared besides the characteristic peak of $Mg(OH)_2$ at 3700 cm^{-1}. The absorption peaks at 1640 and 1563 cm^{-1} illustrate the existence of magnesiumcarboxylic. Both of these facts indicate that OA is chemically bonded onto the surface of $Mg(OH)_2$. The content of oleic acid immobilized on the surface of $Mg(OH)_2$ particles is about 0.35 mmol/g calculated from the carbon element analysis (Tabl. 1) [18]. The spectrum of PS–$Mg(OH)_2$ composite is shown in Fig. 1c. Typical absorption bands for

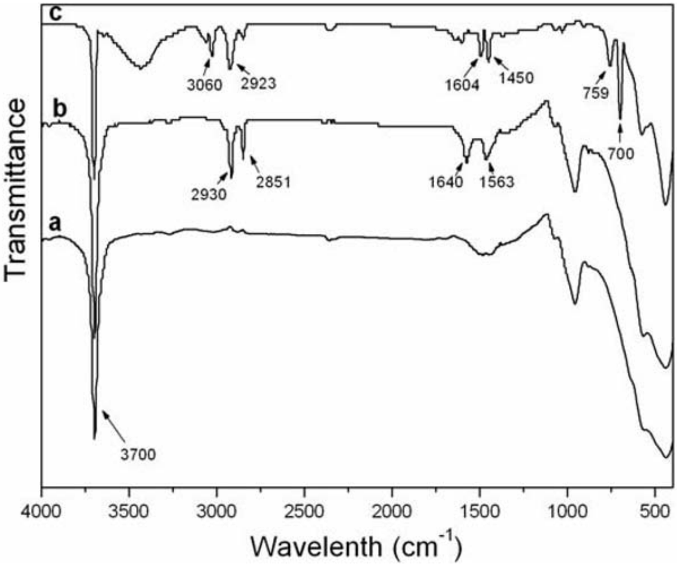


Figure 1. IR spectra of (a) pure $Mg(OH)_2$, (b) OA–$Mg(OH)_2$, and (c) PS–$Mg(OH)_2$.

polystyrene, including the C–H aromatic stretching vibration at 3060 cm^{-1}, the C–H stretching vibration at 2923 cm^{-1}, and the phenyl ring stretching vibration at 1604, 1450, 759 and 700 cm^{-1}, are clearly observed. This indicates the existence of polystyrene on the particle surface. At the same time, the disappearance of C=C stretching vibration at 1641 cm^{-1} shows that PS has been covalently grafted onto the surface of OA-$Mg(OH)_2$ through the copolymerization of styrene and oleic acid [17,19].

The grafted PS improves the interaction between the polymer and inorganic $Mg(OH)_2$ and, as the TEM (Fig. 2) shows, improves the dispersibility of $Mg(OH)_2$ nanoparticles in polystyrene.

The preparing procedure of the $Mg(OH)_2$/PS composite could be shown schematically as Scheme 1. Comparing with normal $Mg(OH)_2$, the surface of nanoparticles became more favorable to the grafting reaction when they were modified by oleic acid. The double bonds on the particles surfaces might take part in the initiation reaction to form particulate nucleation. This process was believed to be easier than the formation of polymer particles through micellar nucleation. More important, the amount of introduced monomers remained low at the beginning of the reaction and may be fully adsorbed onto the surfaces of $Mg(OH)_2$ nanoparticles due to their hydrophobic surface feature. With the reaction proceeding, monomer droplets might inevitably emerge due

Table 1. Elemental analysis results

Element (%)	OA–$Mg(OH)_2$	PS–$Mg(OH)_2$
C	7.158	20.81
H	2.625	6.192

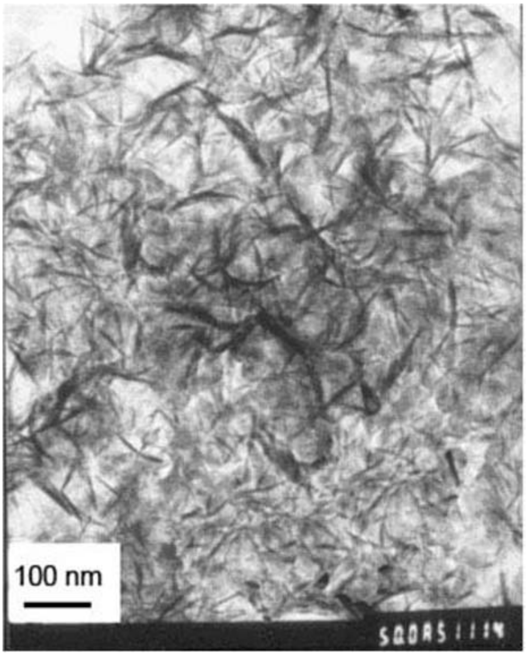
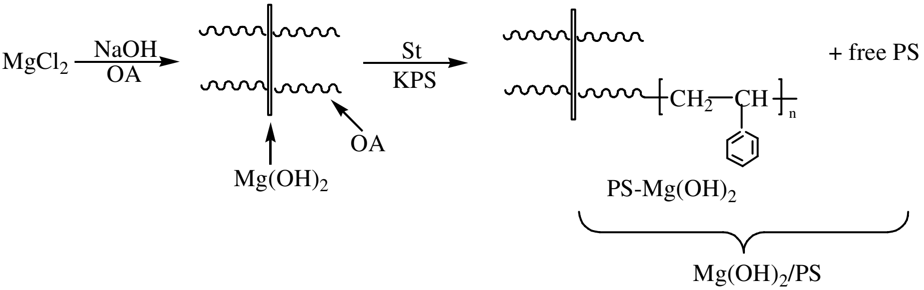


Figure 2. TEM image of $Mg(OH)_2$/PS.



Scheme 1. The preparation procedure of $Mg(OH)_2$/PS nanocomposite.

to the fact that monomer was fed into the system within a relatively short period of time compared with the entire period of the polymerization. However, reaction sites could be less probable to be inside monomer droplets due to the rather low amount of these droplets compared with that of $Mg(OH)_2$ nanoparticles. On the other hand, because the saturated concentration of St in water is 0.066%, homogeneous nucleation process might slightly exist. So the dominating polymerization was believed to be at the surface of the nanoparticles, and polymerization of St in aqueous phase should only be a little part of the whole reaction [20]. The yield of magnesium hydroxide/polystyrene nanocomposite [$Mg(OH)_2$/PS] was 4.1g, corresponding to a monomer conversion of 52% [21]. Magnesium hydroxide grafted by polystyrene [PS–$Mg(OH)_2$] was 3.4g, corresponding to a grafting percentage of 29.1% calculated from the carbon element analysis (Tabl. 1) [18].

The glass transition temperatures (Tg) of the pure PS and the $Mg(OH)_2$/PS nanocomposite were found to be 99 and 107°C (Fig. 3), respectively. It suggests that $Mg(OH)_2$ nanoneedles can improve the thermal stability of the nanocomposites. This result is correlated to the good nanoparticle dispersion in the polymeric matrix (Fig. 2)

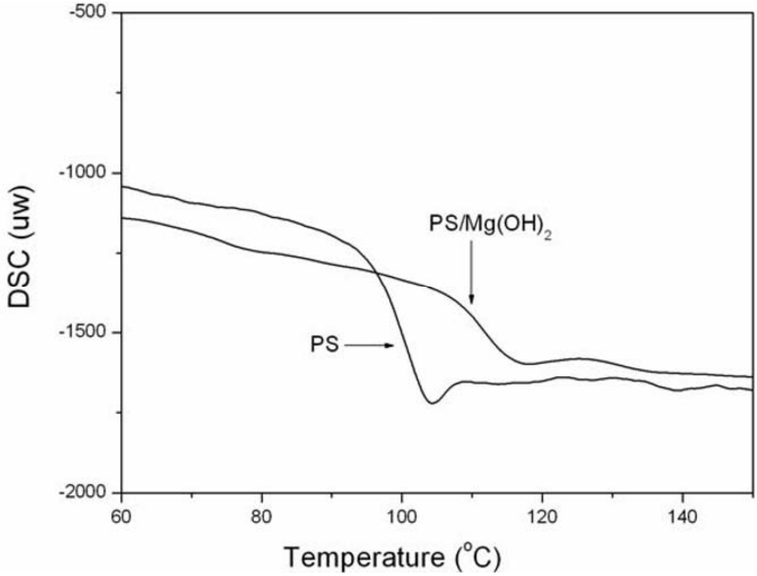


Figure 3. DSC plots of PS, and $Mg(OH)_2$/PS nanocomposite.

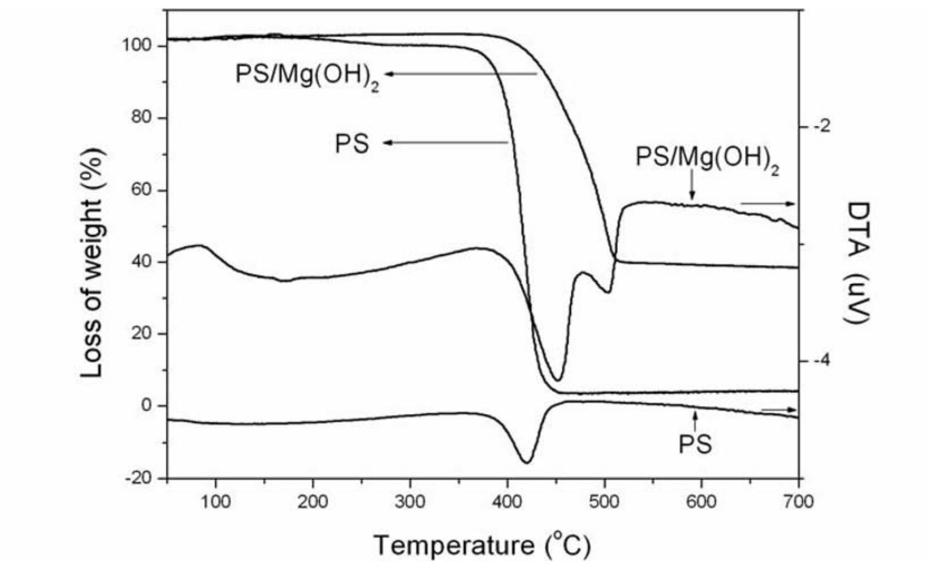


Figure 4. TGA/DTA curves of the PS, and $Mg(OH)_2$/PS nanocomposite.

that guarantees a larger matrix/filler interface. In this case, mobility of PS chains was limited due to strict interconnections between the two phases.

The initial degradation temperatures (T_d) of pure PS and $Mg(OH)_2$/PS nanocomposite were determined using TGA and DTA (shown in Fig. 4). The T_d of pure PS was 387°C, and there was no residue at the end of degradation. The degradation of $Mg(OH)_2$/PS nanocomposite showed two-step weight loss (380–470 and 470–520°C). The first step corresponds to the decomposition of $Mg(OH)_2$, and the second was assigned to PS in $Mg(OH)_2$/PS. The degradation of the $Mg(OH)_2$/PS nanocomposite starts at a higher temperature, and the weight loss is slower, in other words, the degradation of $Mg(OH)_2$/PS nanocomposite can be effectively retarded by $Mg(OH)_2$ nanoparticles.

Conclusions

$Mg(OH)_2$/PS nanocomposite was prepared for the first time via soapless emulsion polymerization of styrene monomers with C=C groups of OA on $Mg(OH)_2$ nanoneedle surface. FT–IR provids the evidence of the presence of polystyrene grafted on $Mg(OH)_2$. TEM photograph shows $Mg(OH)_2$ is dispersed well in the composite with needle-like morphology. Compared with pure PS, the $Mg(OH)_2$/PS nanocomposite exhibits better thermal stability.

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