Surface Modification of Nano-SiO_2 by Grafting PMMA/PBA

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The surface of nano-SiO_2 was modified by being encapsulated with hydroxy-propyl-methyl cellulose (HPMC), and then co-grafted with acrylates. The grafting conditions, such as pH of the medium, and initiator concentration have been studied. The modified nano-SiO_2 particles were characterized by TEM, DSC and FT-IR spectra. TEM images show that the surface of the nano-particles has been successfully modified by a thick layer of film-like polymer in this way. The DSC results show that the decomposition temperature of modified nano-particles of SiO_2 is 90 ℃ higher than that of grafted-on polymer. According to the FT-IR spectra, it is convinced that poly-methyl methacrylate (PMMA) and poly-acrylic butyl-ester (PBA) were co-grafted onto the surface of nano-SiO_2.

Keywords hydroxy-propyl-methyl cellulose, nano-SiO_2 particle, surface modification, co-graft polymerization

Introduction

Thanks to their sizes at nano-level, the nano-particles have some new and preternatural properties different from normal materials, and they can be applied in many fields such as catalysts, light filtration, light absorbing, medicine, magnetic medium and new materials as well.[1,2] It is also recognized as one of the most prosperous materials in the 21 century. Nowadays, scientists and researchers pay more attention to polymer-nano-inorganic compounds, because polymer is easy to process, and it can avoid the oxidation and coagulation of the nano-particles, so the stability can be enhanced to a large extent, and the preternatural properties can be fully developed. Nevertheless, the surface activity makes the nano-particles easily come together, so it is indispensable to modify the surface. After surface modification, the properties of the surface will be changed, and its compatibility with and dispersion in the matrix will be improved. In a word, the surface modification may be key to obtain real nano-materials. In recent years, there have been a lot of work from many research groups on the elaboration of nano-composite systems. In order to achieve a good dispersion of the inorganic compound and to increase interfacial adhesion between the polymer and the mineral, techniques for synthesizing nano-composites made of inorganic particles surrounded by polymers have been developed.[3,4] Although a lot of procedures exist, emulsion polymerization is by far the technique most frequently used for the encapsulation reaction of minerals with polymer. One difficulty, however, resides in the fact that inorganic surfaces are hydrophilic, while polymers are hydrophobic. In order to promote polymerization on the inorganic surface, surfactants have been widely used, which will result in the weak interaction between polymers and inorganic particles. To avoid this problem, coupling agents can be used,[5] however a large quantity of organic solvent will be consumed, which is not benign to enviroment.

In this work, we use a kind of water soluble cellulose, hydroxy-propyl-methyl cellulose (HPMC), to encapsulate the nano-particles, then methyl methacrylate (MMA) and acrylic butyl-ester (BA) were co-grafted onto HPMC. To the best of our knowledge, no study using HPMC and nano-inorganic SiO_2 particles has been reported in literature.

Experimental

Chemicals

Hydroxyl-propyl-methyl cellulose (friendly donated by Wuhu Shanjiang Chemicals Co. Ltd), nano-SiO_2 (average diameter is 30 nm), methyl methacrylate and acrylic butyl-ester (polymerization grade, distilled under reduce pressure before using), $K_2S_2O_8$, $NaHSO_3$ and H_2SO_4 (chemical reagent) were used as received.

Procedure

2 g HPMC and some purified water were introduced into a three-necked flask. After HPMC dissolved, 8 g nano-SiO_2 was added to the system, then the whole system was agitated by JL-120 ultrasonic cleaner for about 10

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min. Then an exact quantity of H_2SO_4 was added to adjust the pH value. The temperature was set at about 60 ℃ for a needed period of time. Nitrogen was bubbled into the reaction system prior to and through the reaction, then an exact quantity of MMA, BA, $K_2S_2O_8$ and $NaHSO_3$ were poured into the system to start the reaction. Finally, the reaction solution was centrifuged to obtain the compound particles, namely SiO_2/HPMC-g-PMMA/PBA and PMMA or PBA mixture. The mixed product was then extracted by acetone in Solex extractor for about 72 h to remove PMMA and PBA. Then the graft-on acrylates were weighted in the same way as indicated in one article:[6] the mixture was saponified with KOH, then the over quantity of KOH was titrated with HCl whose exact concentration was known. The percentage of graft add-on and graft efficiency were determined respectively as:

$G\%$ = weight of graft add-on polymer/total weight of composite particles

$E\%$ = weight of graft add-on polymer/total weight of monomer

Characterization

IR spectra was recorded on NICOLET 5DX FT-IR spectrometer (U.S.A.) and KBr was used as matrix material, DSC analysis was performed on NETZSCH DSC 204 in N_2 atmosphere at a heating rate of 20 ℃/min. TEM was measured on a H-600 microscope to observer the morphology of the compound particles of SiO_2/HPMC-g-PMMA/PBA. For TEM experiments, a drop of diluted dispersion was put on a carbon film supported by a copper grid using the accelerated voltage of 80 kV.

Results and discussion

FT-IR (KBr) spectra of HPMC and SiO_2/HPMC-g-PMMA/PBA show a broad band (3445 cm^{-1}), indicative of hydroxyl in HPMC. The peak at 1736 cm^{-1} attributes to stretch vibration of $\nu_{C=O}$, the bands attribute to asymmetry and symmetry stretch vibration of ν_{Si-O} appear at 1105 and 802 cm^{-1} respectively. The peak at 437 cm^{-1} corresponds to the bent vibration of ν_{Si-O}. The absorption peak at 2957 cm^{-1} attributes to the asymmetry vibration of ν_{CH_2}, and the absorption peak at 962 cm^{-1} corresponds to planar swing vibration in butyl ester. The peak at 1386 cm^{-1} is the feature absorption peak of ν_{CH_3}. Thus we concluded that PMMA and PBA have been co-grafted onto the surface of the nano-inorganic particles of SiO_2.

TEM *Image*

The TEM image of surface modified composite nano-particles of SiO_2/HPMC-g-PMMA/PBA is shown in Fig. 1.

Fig. 1 TEM image of SiO_2/HPMC-g-PMMA/PBA (20000:1).

It can be very clearly seen that the nano-particle has been encapsulated by a thick layer of film-like polymer. Our experiment was carried out at low pH value and in ultrasonic cleaner, so the nano-particles can be in a good condition of dispersion, because the inorganic nano-particles will be charged with electric charge,[1] and the electrostatic action may prevent nano-particles from coming together.

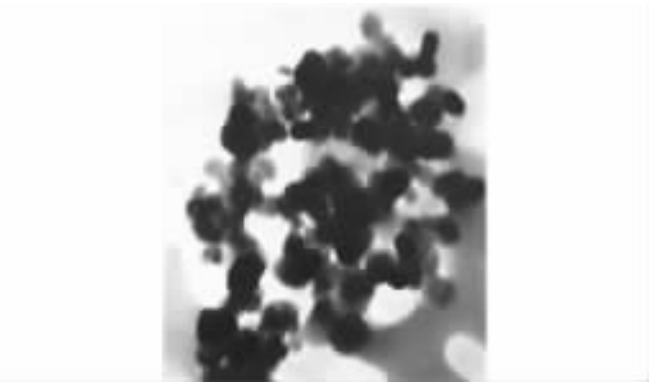

Fig. 2 TEM image of SiO_2/HPMC-g-PMMA/PBA (150000:1).

The image in Fig. 2 shows nano-composite latexes with a rough surface due to the presence of small PMMA/PBA beads surrounding the inorganic seed particles. Because HPMC functions as a bridge between polymer and SiO_2, it can be expected that part of the polymer formed strongly adheres to the mineral surface and can not be extracted with acetone. TEM analysis still reveals the formation of nano-composite particles with a strawberry-like morphology characterized by small latex beads deposited on the silica surfaces. Some researchers have drawn the similar conclusions.[4] It is well known that the surface of the non-modified nano-particles of SiO_2 is hydrophilic while the the surface of the modified nano-particles of SiO_2 is hydrophobic. That is, the surface behavior of nano-particles of SiO_2 has been successfully altered. Thus we have found an efficient way to change the surface behavior of nano-inorganic particles by grafting of different polymers onto the surface. As a result, the nano-inorganic particles can be tremendously used in many fields.

DSC *analysis*

DSC curves of HPMC-g-PMMA/PBA and SiO_2/

HPMC-g-PMMA/PBA are shown in Fig. 3.

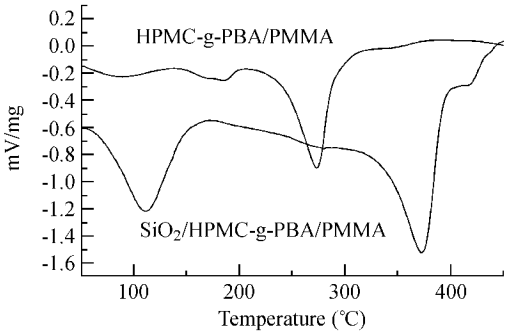

Fig. 3 DSC curves of HPMC-g-PMMA/PBA and SiO_2/HPMC-g-PMMA/PBA.

The figure shows that the decomposition temperature of HPMC-g-PMMA/PBA and SiO_2/HPMC-g-PMMA/PBA are 280 and 370 ℃ respectively. The decomposition temperature of the latter is 90 ℃ higher than that of the former. In another word, the decomposition temperature has been increased greatly, because of the introduction of nano-inorganic particles SiO_2 into polymer as reported in the literature.[7,8]

Effect of pH *value on the G% and E% of grafting*

Effect of pH value on the *G%* and *E%* is shown in Table 1.

Table 1 Effect of pH value on the *G%* and *E%*

pH	1	2	3	7	9	11
G%	28	57.8	45.9	40.5	38.0	37.8
E%	42	71.0	63.4	51.2	45.5	45.5

It can be seen that: *G%* and *E%* were 57.8% and 71.0% respectively when pH = 2, then *G%* and *E%* decreased with the increase of pH. *G%* and *E%* were 40.5% and 51.2% respectively when pH value was 7. The reason for this phenomenon may be that: at lower pH value, the initiator decomposed at higher rate and the stability of radicals was improved. One can also see that the decreasing tendency of both *G%* and *E%* with the increase of pH value slows down when pH value is higher than 7. When pH value is lower than 2, the lower the pH value is, the faster the free radicals are generated, which will result in the increase of teminating rate, and the silica surface becomes more and more protonated.

Effect of initiator concentration on the G% and E% of grafting

Effect of initiator concentration on the *G%* and *E%* of grafting is shown in Table 2.

Table 2 Effect of initiator concentration on the G% and E%

Initiator concentration (mmol/L)	2.5	5.0	7.5	10.0	15.0
G%	53.2	55.9	57.8	54.7	47.8
E%	61.0	63.4	71.0	61.2	55.6

One can see from Table 2 that both *G%* and *E%* increased with the increase in initiator concentration up to 7.5 mmol/L, then-after, *G%* and *E%* decreased with the increase in initiator concentration. Because the increase in initiator concentration increased the number of radicals and polymerization sites on the backbone of HPMC, when the initiator concentration was higher than 7.5 mmol/L, no more polymerization sites were created, on the other hand, much more monomers were polymerized in the aqueous solution rather than grafted onto HPMC on the surface of nano-SiO_2, resulting in the decrease in *G%* and *E%*.

Conclusions

A kind of water soluble cellulose, hydroxy-propylmethyl cellulose, containing many hydroxyl group, was used as a bridge between nano-inorganic particles and the out-layer of polymer, the binding force between the two parts was very strong, as a result of a large number of hydrogen bond formed. By this way, different polymers, which are compatible with different matrixes, can be grafted onto nano-inorganic particles, thus the organic-inorganic nano-particles can be used in many fields.

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