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SHORT COMMUNICATION

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Synthesis of nano-ZnO/poly(methyl methacrylate) composite microsphere through emulsion polymerization and its UV-shielding property

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Abstract Nano-ZnO/poly(methyl methacrylate)(PMMA) composite latex microspheres were synthesized by in-site emulsion polymerization. The interfacial compatibility between nano-ZnO particles and PMMA were improved by treating the surface of nano-ZnO particles hydrophobically using methacryloxypropyltrimethoxysilane (MPTMS). TEM indicated that nano-ZnO particles present in nanosphere and have been encapsulated in the PMMA phase. FT-IR confirmed that MPTMS reacted with the nano-ZnO particle and copolymerized with MMA. It was clearly found from SEM that ZnO nanoparticles can be homogeneously dispersed in the PVC matrix. The absorbance spectrum of the nanocomposite polymer suggested that increasing the amount of nano-ZnO in composite particles could enhance the UV-shielding properties of the polymers. The nano-ZnO/PMMA composite particle could eliminate aggregation of ZnO nanoparticle and improve its compatibility with organic polymer. This means that the composite particles can be widely applied in lots of fields.

Keywords Nano-ZnO · Nanocomposite · Poly(methyl methacrylate) · In-site emulsion polymerization · Methacryloxypropyltrimethoxysilane (MPTMS)

Introduction

During the past 10 years, many works have been done on the elaboration of nanocomposite system by embedding of inorganic particles into polymeric matrix [1–6], affording a new class of polymeric materials which combine the properties of inorganic particles with the processability and flexibility of organic polymer matrix. Moreover, the inorganic core/organic shell hybrid composite particles have unique electrical, thermal and optical properties that are associated with broad application perspectives in industry. Encapsulation of nano-inorganic particles in polymer shell provides better mechanical properties and chemical resistance [7–12]. Above all, the improvement of dispersion stability is one of the most significant characteristics of nano-inorganic/polymer composite microspheres. Composite materials could be obtained by simply mixing the organic and inorganic components as well, but this method easily gives rise to the aggregation of nanomineral, which would influence the properties of composite materials. In order to enhance the dispersion stability of nanoparticles, to increase interfacial adhesion between the polymers and the mineral, and to make the composite microsphere possess multifunction, the technique of polymer encapsulation to inorganic nanoparticle by in-site emulsion polymerization is becoming more and more popular.

Nano-ZnO, as one of the multifunctional inorganic nanoparticles, has drawn increasing attention in recent years due to its many significant physical and chemical properties, such as chemical stability, low dielectric constant, high luminous transmittance, high catalysis activity, effective antibacterial and bactericide, intensive ultraviolet and infrared absorption. Therefore, nano-ZnO can be potentially applied to catalysts, gas sensors, semiconductors, varistors, piezoelectric devices, antibacterial and bactericide, field-emission displays and UV-shielding materials [13–14]. The introduction of nano-ZnO into polymer could improve the mechanical and optical properties of the polymer owing to their small size, large specific area, quantum effect, and a strong interfacial interaction between the organic polymer and inorganic nanoparticles, respectively. Consequently, these nanocomposites could be widely applied in coatings, rubbers, plastics, sealant, fibers and other applications.

In most recent literatures, nano-inorganic particles, such as TiO_2, SiO_2, Fe_2O_3, were used as seeds to synthesize composite microspheres [15–18]. There is few to apply nano-ZnO as inorganic core to synthesize inorganic–organic composite microspheres. Nano-ZnO acting as UV-shielding material, antibacterial and bactericide, the composite microspheres can enhance the stable dispersion of nano-ZnO, which is being applied in coating, plastics, sealant and fibers. The aim of this study was to synthesize nano-ZnO/poly(methyl methacrylate)(PMMA) composite latex microspheres by in situ emulsion polymerization, which enhances the dispersion stability of nano-ZnO and increase interfacial adhesion between the polymers and nano-ZnO. In order to avoid the aggregation of the nano-ZnO in the polymerization and ensure effective encapsulation, Nano-ZnO was treated with the methacryloxypropyltrimethoxysilane (MPTMS) before polymerization.

Experimental

Materials

Methyl methacrylate (MMA, CP) was purified by distillation under nitrogen at reduced pressure. Initiator used was potassium persulfate ($K_2S_2O_8$) (analytical grade). Nano-ZnO particle was purchased from Zhejiang Zhoushan Mingri Nanometer Materials Co. Ltd. (China). TEM images showed spherical particles of about 20–70 nm. MPTMS and Polyoxyethylene nonylphenyl ether (OP-10) were supplied by Tianjin Research Institute of Synthetic Material (China) without further purification. Ethyl alcohol, *n*-propanol, toluene were used as received. Bi-distilled water was used throughout the experimental work.

Preparation of nano-ZnO/PMMA composite microsphere

Modification of nano-ZnO with MPTMS

ZnO nanoparticles (2 g) were mixed with methanol (50 ml) or a mixture of water and methanol, and then MPTMS (0.5 g) was added to the system. The mixture was first dispersed for 20 min through an ultrasonic instrument (HQ-50,100 W, China) at room temperature and then the mixture was heated to reflux for at least 4 h. At the end of the reaction, the mixture was cooled down and diluted four or five times with *n*-propanol to improve the solubility of the homocondensates. This sample was centrifuged at 15,000 rpm for 2 h at room temperature. The clear supernatant, that contains the homocondensates and unreacted MPTMS, was decanted from the deposit composed of the particles with the grafted MPTMS. The deposit was dried at 40 °C in vacuum for at least 8 h.

In-site emulsion polymerization procedure

Emulsion polymerization was carried out in a four-neck flask equipped with a stirrer, thermometer, nitrogen inlet and condenser. First, the water solution of nonionic surfactant (OP-10, 0.3 g/l) was introduced in an amount lower than the one corresponding to saturation of the surface so as to avoid the formation of emulsifier micelles. Then modified nano-ZnO was added to the system, and the dispersion was treated by ultrasonic instrument for 30 min at room temperature. Second, the stirring speed was controlled at 250 rpm and the flask was heated to 65 °C under a nitrogen atmosphere. Monomer and initiator solution were respectively introduced into the flask to react. During the polymerization, the reaction mixture was maintained at 75 °C for 8 h. The monomer conversion was determined by conventional gravimetric method. The resulting composite microsphere was separated from the mixture by centrifugation at 12,000 rpm and washed with toluene repeatedly.

Analysis of conversion, percentage of grafting and grafting efficiency

The monomer conversion was determined by conventional gravimetric method. Its result was calculated by the following equation:

$$\text{Conversion } (\%) = (A - B)/C \times 100$$

where A is the weight of total resulting particle, B is the weight of charged nano-ZnO particle, and C is the weight of charged monomer.

To determine the percentage of grafting and grafting efficiency, it is necessary to separate the polymer-grafted nano-ZnO particles from the reaction mixture containing ungrafted polymer. The product was dispersed in toluene and centrifuged at 1.2×10^4 rpm until composite particle was completely precipitated. The supernatant solution was removed and the precipitate was dispersed again in toluene. These procedures were repeated until no more polymers were detected in the supernatant solution. The percentage of grafting and its efficiency of polymer onto the surface were calculated by the following equations:

$$\text{Grafting } (\%) = D/E \times 100$$

$$\text{Grafting efficiency } (\%) = D/F \times 100$$

where D(g) is the grafted polymer, E(g) is the charged nano-ZnO particles, and F(g) is the total polymer (grafted and ungraftedpolymer) formed. The amount of polymer grafted onto the nano-ZnO surface was determined by thermogravimetric analysis (TGA, Netzsch Co., TG 209, Germany). Samples were heated to 700 °C from room temperature at the speed of 10 °C per minute.

Other characterization and measurements

A Fourier transform infrared spectrophotometer (FT-IR) analysis was performed on spectrophotometer (Nicolet Co., NEXUS, USA). FT-IR was used to characterize the functional groups of the nano-ZnO, modified nano-ZnO and nano-ZnO/PMMA composite microspheres. The composite microspheres were separated from the free latex particles through toluene extraction under reflux. The operation was repeated three times to ensure the complete extraction of the free polymer particles from the composite microspheres.

The morphology analysis was performed on transmission electron micrograph (TEM) analyzer (Jeol 100CX—II, Japan).

The mean size and size distribution of microspheres were determined by particle size analyzer (Brookhaven Instruments Co., BI-90Plus, USA).

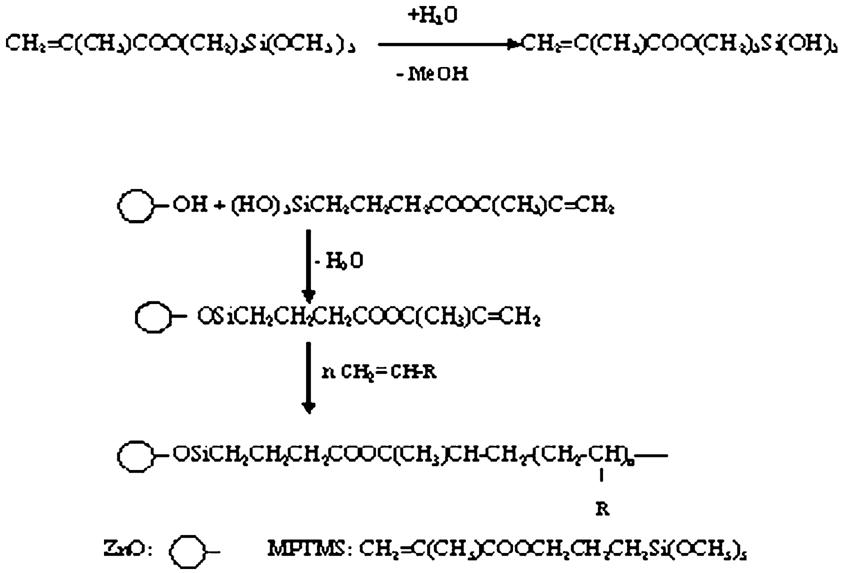
The dispersion morphology of the composite particles on PVC matrices was observed using scanning electron microscope (SEM, Phlilps Co., XL30ESEM, Netherlands).

The absorbance spectra of the polymer films to which were added the composite particles with various amounts of nano-ZnO were tested by UV-VIS spectrophotometer (Hitachi Co., U-1800, Japan).

Results and discussion

The functionalization of nano-ZnO particle surface

In order to get complete encapsulation of ZnO nanoparticles without formation of pure latex, a set of experimental conditions must be fulfilled. The concentration of surfactant should be lower than its critical micelle concentration in the presence of ZnO nanoparticles. The monomer must be fully adsorbed onto the surface of the nano-ZnO. The surface of the nano-ZnO must be enough hydrophobic to adsorb the monomer. This is governed by the composition of the functional groups of the nano-ZnO surface. So we firstly treated the surface of nano-ZnO with a reactive silane coupling agent (MPTMS) to obtain the functionalization of nano-ZnO surface. The reaction scheme for the grafting of MPTMS on the nanoparticles, given in Schemes 1 and 2, shows the hydrolysis of MPTMS. This reaction can take place for each Si–OCH$_3$ group regardless of which reaction the MPTMS unit has



Scheme The grafting of MPTMS onto zinc oxide particles and copolymerizing with PMMA already undergone. Scheme 2 shows that MPTMS is grafted on the surface of nano-ZnO by reacting with the oxide and later copolymerize with MMA.

The terminal of MPTMS is organic polymer chain, which can fulfill steric hindrance between inorganic nanoparticles and prevent their aggregation. The organic polymer chains on nano-ZnO particle surface have affinity to the monomer of methylacrylate. Therefore, the oligomers are anchored on the surface of the inorganic particles where they form a layer in which further polymerization takes place [19]. In addition, MPTMS contains a polymerizable group (unsaturated double bond), which can copolymerize with the unsaturated groups of MMA to obtain covalent grafted at least a part of the polymer during the emulsion polymerization. Consequently, MPTMS, as a bridge, links up the polymer and ZnO nanoparticles through chemical bonds. Therefore, in these composite particles, the interfacial adhesion and compatibility between inorganic nano-ZnO and organic polymer can be enhanced.

Nano-ZnO/PMMA composite synthesis by in-site emulsion polymerization

From the above result we can infer that the polymerization reaction may take place in surface layer of nano-ZnO particles. In order to get a stable dispersion of functionalized ZnO nanoparticles in aqueous system, the nonionic surfactant (OP-10) was introduced in an amount lower than the one corresponding to saturation of the surface so as to avoid the formation of emulsifier micelles. The functionalized ZnO nanoparticles are surrounded by the surfactant. The hydrophilic terminal of surfactant points to the water phase to ensure the stable suspension of the nanoparticles in the aqueous system of emulsion polymerization. The other terminal (hydrophobic end) points to the MPTMS phase (grafted on oxide surface) where they form a layer in which further polymerization takes place. The reaction locus is favored because of the much larger surface area of the nano-ZnO particles and easier adsorption of monomer at the particle surface, which results in a very high monomer concentration in the vicinity of the particles compared with the relative limited one in bulk. The main chain propagating was carried out on the surface of the nano-ZnO particle on which the encapsulation composite was formed. In other words, the nano-ZnO particles served as seeds to fulfill emulsion polymerization.

We explored the conversion of monomers, percentage of grafting and grafting efficiency. Figure 1 shows the time-conversion and the time-percentage of grafting curve on the course of copolymerization. It was shown that the conversion of MMA increased with the progress of polymerization. The percentage of grafting polymer onto the surface increased at the initial stage of copolymerization and exceeded 400%, however, it became almost constant at the last stage of copolymerization. Figure 2 shows the relationship between conversion and grafting efficiency. It was found that the grafting efficiency decreased with the progress of polymerization.

Based on the above results, it was inferred that the copolymerization of unsaturated groups (double bond) of MPTMS with MMA on the particle surface had taken place which implies that the polymer chains were grafted on the ZnO particle surface. Otherwise, the polymer would be removed completely from the particles on the course of separation. Besides, it also indicated that the grafting reaction could appear no longer at the last stage of copolymerization. It is possible that the unsaturated groups (double bond) of MPTMS were used up at the initial stage of the polymerization, which blocks further grafting reaction on the surface of ZnO particle.

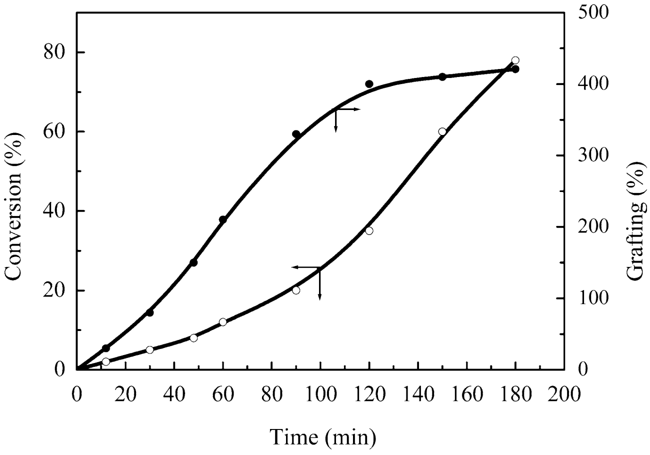


Fig. 1 Time versus conversion and percentage of grafting curve obtained in the course of copolymerization

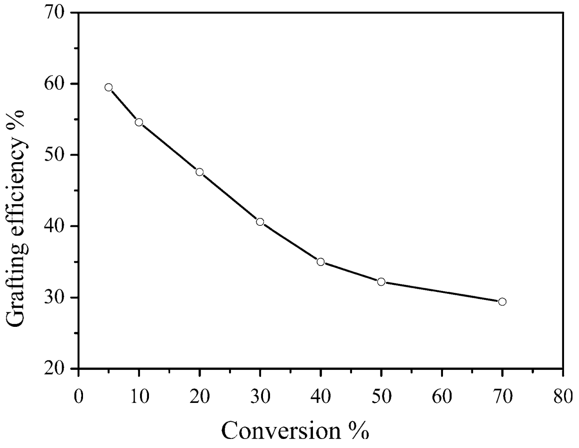


Fig. 2 Relationship between grafting efficiency and conversion

TEM images of ZnO nanoparticles and composite latexes

Figure 3a shows the morphology of ZnO nanoparticles. It can be shown that ZnO nanoparticles display an approximately spherical morphology and a homogeneous dispersion of nanoparticles with a mean size from 20 to 70 nm. In order to check the formation of polymer on the surface of nano-ZnO, the composite microspheres were characterized by TEM as shown in Fig. 3b. The central black spot and translucent parts in the microspheres show nano-ZnO particles and PMMA polymer, respectively. It can be clearly found that the ZnO nanoparticles were encapsulated into the polymer phase. The nano-ZnO particle is too small and irregular, so it is very difficult to ensure that there is only individual nano-ZnO particle in a composite microsphere. Figure 4a and b shows size distribution of nanoparticles and composite microspheres. Comparing Fig. 4a and b, the composite microsphere is obviously larger than the nano-ZnO particle, which further explains the encapsulation to nano-ZnO particle.

FT-IR analysis

Figure 5a–c shows the spectrum of original nano-ZnO particle, modified nano-ZnO particle and the composite microsphere, respectively. In the spectrum of nano-ZnO particle, the appearance of peak at 3,410 cm^{-1} (Fig. 5a) indicates the presence of –OH. In the FT-IR spectrum of the modified nano-ZnO particle (Fig. 5b), the strong absorption bands of 1,725 cm^{-1} should correspond to C=O of MPTMS. The appearance of peak at 1,640 cm^{-1} indicates the presence of C=C in the molecule of MPTMS. The peak at 1,100 cm^{-1} was assigned the Si–O groups. The absorption peaks in the region 2,800–3,000 cm^{-1} correspond to the CH_2 and CH_3 group of MPTMS. In the FT-IR spectrum of the composite extracted by toluene (Fig. 5c), the absorption bands at 1,730 cm^{-1} are characteristic of C=O stretching vibration from PMMA. The absorption bands at 1,150, 1,192, 1,240 and 1,270 cm^{-1} represent C–O–C in PMMA. The absorption peaks in the region 2,900–3,000 cm^{-1} correspond to the CH_2 and CH_3 group stretching vibration from PMMA. The peak at 1,640 cm^{-1} (characteristic of unsaturated double bond)

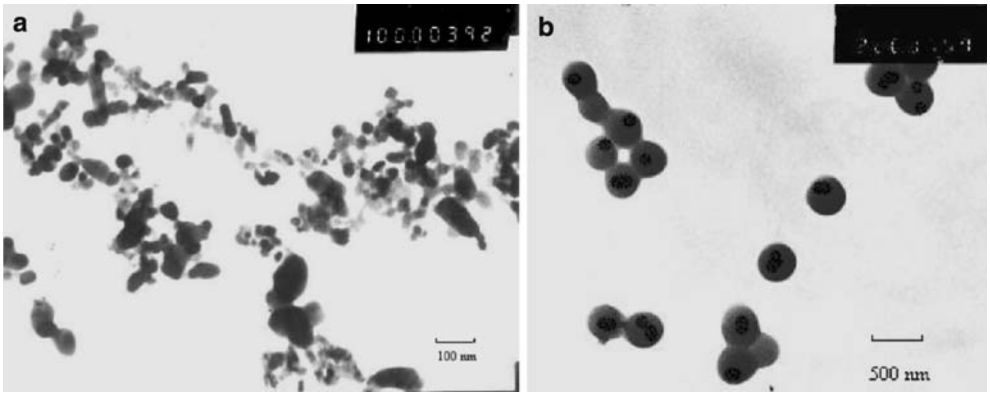


Fig. 3 TEM images of pure nano-ZnO particles modified with PMTMS (**a**) and nano-ZnO/PMMA composite particles (**b**)

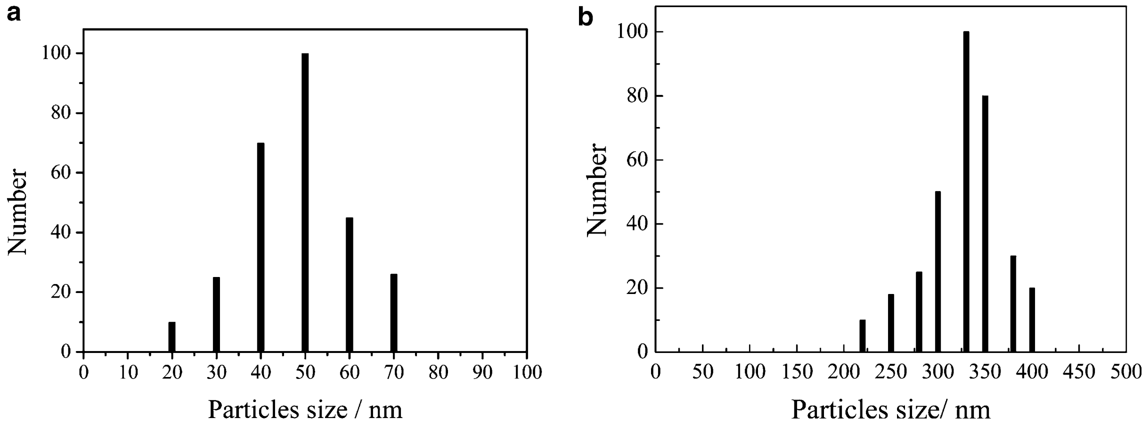


Fig. 4 Particle size distribution of nano-ZnO (**a**) and composite particles (**b**)

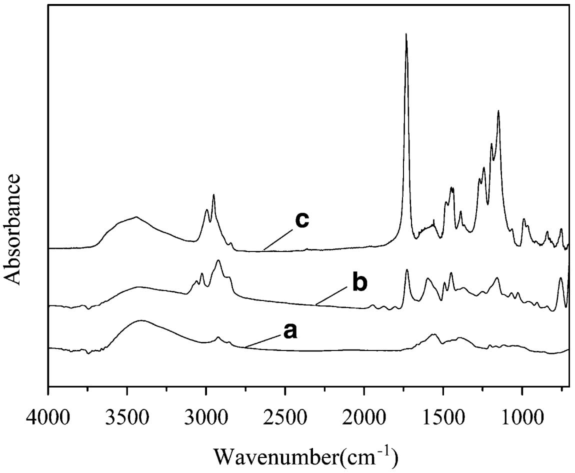


Fig. 5 FT-IR spectrum of nano-ZnO (*a*), modified nano-ZnO (*b*)and composite microspheres (*c*)

presented in the modified particles disappeared in the spectrum of the composite particles, implying that MPTMS had been covalently copolymerized with MMA by the unsaturated double bond in the polymerization. It can be inferred from above results that MPTMS links up the polymer and ZnO nanoparticles through chemical bonds. Thus, it leads to the enhancing adhesion and compatibility between nano-ZnO and the molecule chain of PMMA.

The dispersion and UV-shielding properties of nano-ZnO/PMMA composite particle

The nano-ZnO/polymer composites synthesized with in-site emulsion polymerization not only eliminate aggregation of inorganic nanoparticles but also resolve the compatibility between inorganic nano-ZnO and organic polymer. It is because of the polymer on the shell of composite acting as a transition layer between nano-ZnO and organic matrix.

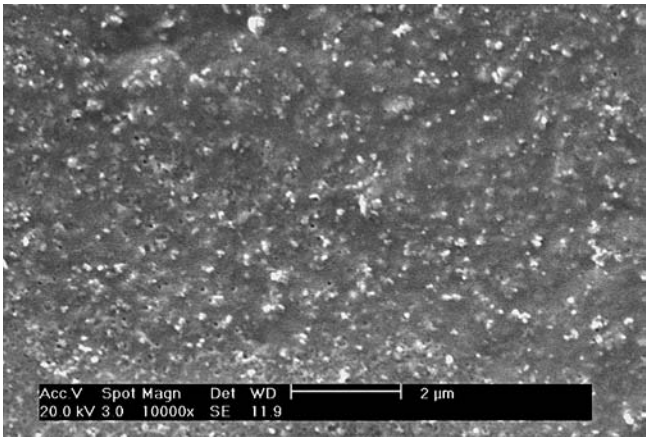


Fig. 6 SEM of the dispersion of composite particles in PVC matrices

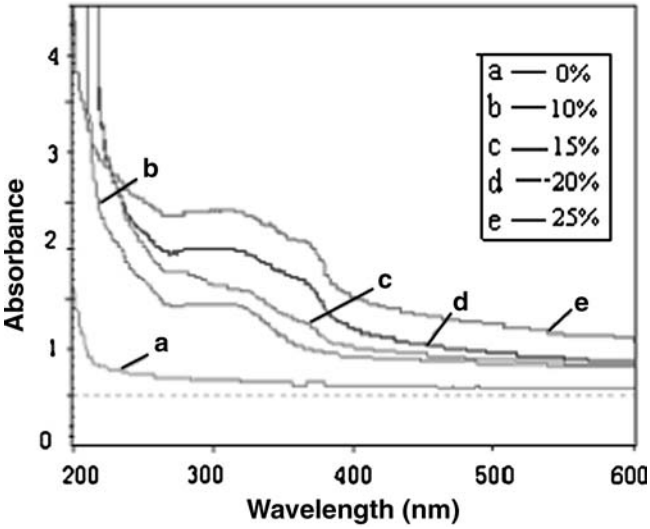


Fig. 7 The UV absorbance of the nano-ZnO/PMMA composites

To examine the dispersion of composite particles in polymer matrix, we added the composite particles into PVC matrix and pressed into film. The morphology of the composite particles in PVC matrices was observed using scanning electron microscope (SEM; see Fig. 6). The white spots are ZnO nanoparticles. The encapsulated polymer was merged with PVC matrices using the thermal procedure, because of their compatibility, so that the morphology of ZnO nanoparticles can be observed. It was clearly found that ZnO nanoparticles were homogeneously dispersed in the matrices. Consequently, the ZnO nanoparticles were integrated with PVC matrices by the grafting copolymer chains.

Figure 7 presents the ultraviolet-visible absorbance of PVC film to which were added the quantitative nanocomposites. The UV absorbance increased as the nano-ZnO content increased in composite microspheres. The absorption peak appeared at 370 nm for the nanocomposite polymers. The intensity of this peak increases with nano-ZnO content. There is almost no UV absorbance in the pure polymer. This optical change is caused by a quantum effect of the nanoparticles when the size of particles is reduced to a nanoscale [20–22]. The nanocomposite thus prepared can protect against UV light. This means that nano-ZnO/PMMA composites can improve the weatherability of the polymer film and the undercoats. As a result, it can be potentially applied to UV-shielding materials such as fibers, coatings, cosmetics, plastics etc.

Conclusion

Nano-ZnO/PMMA nanocomposite latex microspheres were synthesized through in-site emulsion polymerization and nano-ZnO was encapsulated in PMMA phase. Nano-ZnO modified by MPTMS can fulfill steric hindrance between inorganic nanoparticles and have affinity to the monomer of methylacrylate. ZnO nanoparticles display approximately spherical morphology and a homogeneous dispersion of nanoparticles with a mean size from 20 to 70 nm. MPTMS was grafted on the surface of nano-ZnO and copolymerized with MMA in the polymerization. Nano-ZnO/PMMA composites could limit aggregation of nano-ZnO and enhance the compatibility between inorganic nano-ZnO and organic polymer. The materials by being added with composite particles present perfect UV-shielding properties. These results indicate that the composite particles have potentially remarkable features of interest.

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