# Polymer/Carbon Nanotube Composite Emulsion Prepared Through Ultrasonically Assisted In Situ Emulsion Polymerization

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**ABSTRACT:** In this study, ultrasonic irradiation and in situ emulsion polymerization were combined to prepare stable poly(methyl methacrylate-*co-n*-butyl acrylate) (P(MMA-BA))/carbon nanotubes (CNTs) composite emulsion, which solves the dispersion problem of CNTs in the latex. Two stages were adopted. In Stage I, ultrasonically initiated in situ emulsion polymerization was conducted to disperse CNTs and prepare the seed emulsion containing polymer coated CNTs. In Stage II, conventional in situ emulsion polymerization was conducted to further enhance the monomer conversion and solid content. The dispersion behavior of MWCNTs in aqueous solution under ultrasonic irradiation was investigated by spectrophotometry. The effects of CNTs content on the emulsion stability and mechanical properties of composite film were studied. The results suggest that in the composite emulsion the long CNTs with a diameter of 20–40 nm are separated and dispersed by the formed polymer latex nanoparticles with a size of 20–40 nm. The spherical polymer latex nanoparticles adhere to the wall of CNTs to form a structure like "grapes on the twig." The smooth, uniform, and flexible polymer/CNTs composite films were prepared from the composite emulsion. The CNTs can be individually dispersed in P(MMA-BA)/CNTs composite film. Tensile tests suggest that with the increase in the CNTs content, the Young's modulus and the yield strength of the film increase. Only at 1 wt % CNTs, the Young's modulus increases from 124 to 289 MPa, and the yield strength is improved about ~14%. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3123–3130, 2006

**Key words:** ultrasound; carbon nanotubes; dispersion; emulsion polymerization; irradiation

## INTRODUCTION

Polymer/carbon nanotubes (CNTs) composites have attracted much attention recently, since CNTs can be prepared at a large scale.[1–5] CNTs can act as a special filler in plastics, rubber, fiber, adhesive, and coating because it has high aspect ratio, high mechanical strength, and excellent electrical and thermal conductivity as well as low density. Most studies have focused on polymer-wrapped nanotubes,[6,7] polymer-grafted CNTs,[8] CNT-filled thermoplastic polymer,[9–11] and thermosetting polymer.[12,13] The approaches to prepare polymer/CNT composites include in situ bulk and condensed polymerization, solution mixing and casting, and melt blending. The key issues are as follows: (1) to break the entanglement of CNTs and overcome the van der Waals force between CNTs; (2) to improve the dispersion and orientation of CNTs in polymer matrix; and (3) to raise the interfacial interaction between polymer and CNTs.

Until now, to our knowledge, few reports[14,15] involve the preparation of polymer/CNTs composite emulsion. Polymer/CNTs composite emulsion can combine the merits of polymer emulsion and CNTs. When CNTs are introduced into the emulsion, many properties of the materials including mechanical properties, adhesion force, aging resistance, UV resistance, weather resistance, and surface appearance can be improved. At the same time, CNTs can impart the emulsion some special functions such as electrical conductivity, antistatic, microwave absorbance, etc. However, conventional mixing or blending hardly reaches a desirable improvement in the physical properties, and even adversely affect the properties. One reason is that it is very difficult for CNTs with high surface energy and strong van der Waals interaction to redisperse in the polymer emulsion at the nanoscale through simple mixing. Another reason is the low interface affinity between polymer and CNTs.

To overcome the aforementioned drawbacks, a new approach i.e. ultrasonically assisted in situ emulsion polymerization was used to prepare polymer/CNTs composite emulsion in this study. Ultrasound was

employed because it has the functions of dispersion, crushing, activation, and initiation. Ultrasonic cavitation can generate local high temperature ~5000 K, local high pressure ~500 atm, and heating and cooling rate greater than $10^9$ K/s, a very rigorous physicochemical environment for chemical reactions.[16,17] Previously we prepared polymer/inorganic nanoparticles composite emulsion through ultrasonic irradiation.[18–20] This study is going to take advantages of the mutieffect of dispersion, crushing, activation, and initiation of ultrasonic irradiation to redisperse CNTs at the nanoscale, and at the same time to realize the polymerization of monomers on CNTs, and thus to get composite seed emulsion containing CNTs. Furthermore, the conventional in situ emulsion polymerization was conducted to enhance the monomer conversion and the solid content because it is difficult for ultrasonically initiated emulsion polymerization to achieve 90% conversion at high monomer concentration.[21] This method has the following advantages: (1) aqueous media; (2) easy of operation; and (3) polymer can be well designed to meet different requirements. In this study, the dispersion of CNTs in the polymer emulsion and the formed composite film were studied and the mechanical properties of the composite film made from emulsion were examined.

## EXPERIMENTAL

### Materials

Multiwalled CNTs (MWCNTs) were provided by Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. MWCNTs were synthesized by dissociation of methane at high temperature, with a $NiO/La_2O_3$ catalyst. The outer diameter of MWCNTs was 20–40 nm, and the inner diameter was 5–10 nm. The purification process of CNTs is as follows. The products were submerged into concentrated hydrochloride acid at 60°C for 24 h, and centrifuged and filtered to remove the catalyst and the carrier of catalyst. Next, the CNTs treated in the aforesaid way were regurgitated with concentrated $HNO_3$ at 150°C for 8 h, and centrifuged and filtered again to remove the amorphous carbon particles. *n*-Butyl acrylate (BA; CP) was obtained Tianjin Chemical Reagent Factory and methyl methacrylate (MMA; AR) from Beijing Chemical Reagent. The monomer BA and MMA were purified by the following procedure: first washed three times with 10% aqueous solution of sodium hydroxide and distilled water to remove the inhibitor hydroquinone, dried with anhydrous sodium sulfate, then vacuum distilled. Acrylic acid (AA) was obtained from Tianjin Chemical Factory, China; sodium lauryl sulfonate (SLS) from Shanghai Xiangde Chemical Factory, China; polyethylene glycol mono-4-octylphenyl ether (OP) from Beijing Chemical Reagent Company, China;

cetyl trimethylammonium bromide (CTAB; AR) from Beijing Chemical Reagent Company, China; sodium dodecyl benzene sulfonate (SDBS; CP) from Shanghai Xiangde Chemical Factory, China; polyvinylpyridine (PVP; K30; $M_W = 40,000$; CP) from Aldrich; and potassium peroxydisulfate ($K_2S_2O_8$; AR) from Chengdu Kelong Chemical Reagent Company, China.

### Apparatus

The reaction apparatus was described in the previous paper.[18] The ultrasonic irradiation instrument is VC-1500 (Sonic and Material, USA). It has the following features: standard titanium horn with the diameter of 22 mm, adjustable power output, replaceable flat stainless steel tip, digital thermometer to determine temperature, and gas flow meter to measure gas flow rate. The glass reactor was self-designed and made in house.

### Preparation of polymer/CNTs composite emulsion through ultrasonically assisted in situ emulsion polymerization in the presence of CNTs

Preparation of polymer/CNTs composite emulsion was attained in two stages:

1. *Stage I: preparation of seed emulsion by ultrasonically initiated in situ emulsion polymerization.* MWCNTs (0.1–0.6 g), 1 mL BA, 2 g SLS, 1 mL OP, 0.12 g $NaHCO_3$, and 90 mL distilled water were introduced into the sonochemical reaction vessel. The mixture was deoxygenated by bubbling with oxygen-free nitrogen for 2 min in the reaction vessel, and water bath was circulated to maintain at 30°C. Ultrasonic irradiation was carried out with the probe of ultrasonic horn immersed directly into the mixed system. The power output was set at 600 W and the $N_2$ flow rate was 12 mL/min. After 20 min irradiation, the reaction was stopped. The obtained emulsion was called seed emulsion in this study.
2. *Stage II: preparation of concentrated emulsion by conventional in situ emulsion polymerization.* The seed emulsion was rapidly transferred into a four-neck flask fitted with a stirrer and a condenser. $K_2S_2O_8$ (0.1 g) and 0.4 mL AA were first added, then a feed solution consisting of 9 mL monomer BA and 10 mL monomer MMA was added drop by drop. Polymerization was conducted with a stirring rate of 400 rpm under nitrogen atmosphere, and the temperature was maintained at 70°C. After 3 h, the reaction was stopped. One part of the prepared black composite emulsion was kept to examine the stability of emulsion. Another part was used to prepare the composite film.
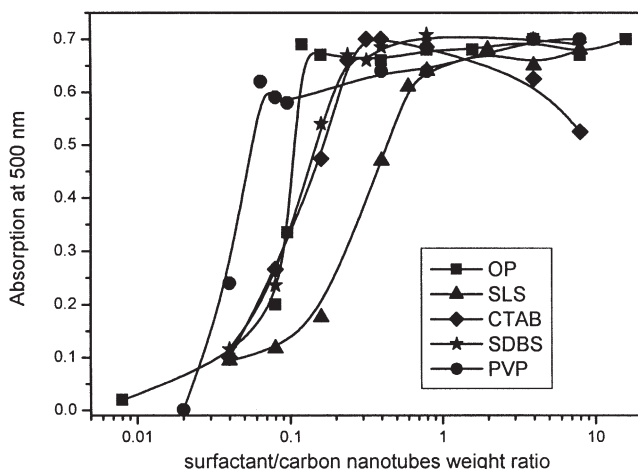
**Figure 1** Effect of surfactant/CNTs weight ratio on the absorption of diluted surfactant aqueous dispersions containing 0.1 wt % CNTs.

## Preparation of polymer/CNTs composite film

The prepared composite latices were filtered by filter cloth to remove the coagulum, and then were poured into a metallic mold. The water was slowly evaporated at 30°C. After 2 weeks, the films were matured. The thickness of the films was 0.2–0.5 mm.

## Characterization

The dispersion of CNTs in aqueous solution was evaluated by spectrophotometry. The sample was prepared as follows. CNTs (0.1 g) were added to 80 mL surfactant aqueous solution, and then the suspension was subjected to ultrasonic irradiation at power output of 600 W for 5 min. Then, 15 mL dispersion was centrifuged for 20 min at 4000 rpm, and the 0.5 mL upper dispersion was withdrawn and was diluted to 25 mL. The absorption of the diluted suspension at 500 nm was determined by spectrophotometry with a 721 model spectrophotometer. The higher the absorption, the better is the dispersion of CNT.

The particle morphology of all the samples was observed by TEM on a JEM 100-CX instrument, with a accelerating voltage of 20 kV. The emulsion after dilution was dropped on a copper grid. Scanning electron microscope (SEM) observation was conducted with a HITACHI X-650 instrument. The specimens were cryogenically fractured in liquid nitrogen. The fractured surface was sputter-coated with gold before observation. Tensile properties were tested according to ASTM D-638. An instron machine (Instron 4302) was used for testing dumbbell-like specimens with a standard size. The drawing rate was 100 mm/min.

## RESULTS AND DISCUSSION

### Ultrasonic dispersion of CNTs

High intensity ultrasound has an excellent dispersion effect on CNTs in aqueous solution. The aqueous suspensions containing 0.1 wt % CNTs and 0.1 wt % surfactant SLS become homogenous dispersion after 2 min ultrasonic irradiation. As a contrast, the aqueous suspensions containing 0.1 wt % CNTs and 0.1 wt % surfactant SLS remain undisperse even after 1 h conventional stirring, with a stirring rate of 400 rpm, and the suspensed agglomerates of CNTs can be clearly seen by eyes. Also, we examined the effects of surfactant type and concentration on the dispersion of CNTs sin aqueous dispersion. Figure 1 shows the effect of surfactant/CNTs weight ratio on the dispersion of CNTs in diluted aqueous dispersions with different surfactants. It can be seen that with the increase in surfactant concentration, the absorption at 500 nm increases. When surfactant/CNTs weight ratio (S/C) increases, the absorption at 500 nm remains nearly unchangeable, suggesting that the good dispersion is attained. The minimum S/C values for the good dispersion of CNTs are 0.064, 0.12, 0.24, 0.24, and 0.8 for PVP, OP, CTAB, SDBS, and SLS, respectively. All surfactants have good dispersing effects. As the PVP and OP have low S/C value, it can be reasonably concluded that they are the best dispersant agents for CNTs in aqueous solution in this study. Figure 2 shows the variation of the absorption of OP aqueous dispersions containing 0.1 wt % CNTs, with the irradiation time. Under ultrasonic irradiation with a 600 W power output, it takes only 2 min to reach the good dispersion of CNTs in 0.1 wt % OP aqueous solution. Figure 3 shows the effect of CNTs content on the absorption of surfactant OP aqueous dispersions containing CNTs. When the CNTs content in aqueous
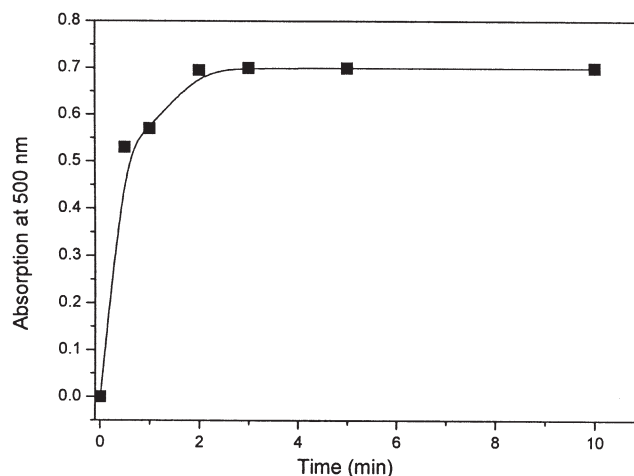


**Figure 2** Variation of the absorption of diluted 0.1 wt % OP aqueous dispersions containing 0.1 wt % CNTs, with the irradiation time.
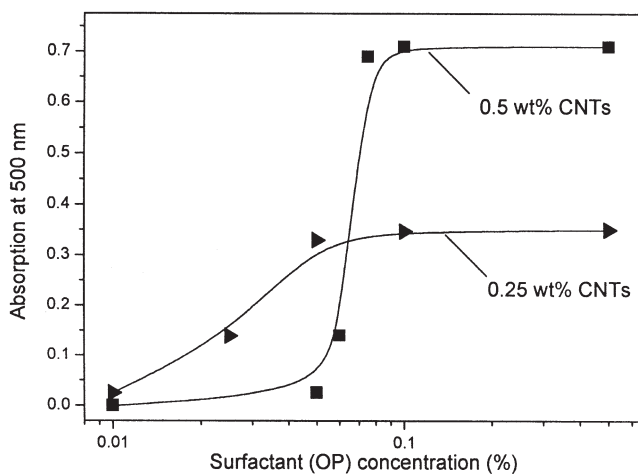
**Figure 3** Effect of the CNTs content on the absorption of diluted OP aqueous dispersions containing CNTs.

solution is 0.25 wt %, the minimum surfactant content needed is ~0.05 wt %, and when the CNTs content in aqueous solution is 0.5 wt %, the minimum surfactant content needed is ~0.075 wt %. With the increase in the CNTs content, the surface area of CNTs increased, and the required surfactant content increased to reach the good dispersion.

**Polymer/CNTs composite emulsion prepared through ultrasonically assisted in situ emulsion polymerization**

Ultrasound can initiate polymerization of monomers without any chemical initiator. The conversion of monomer BA amounts to 91% in 11 min[21]. As mentioned earlier, ultrasonic cavitation can generate local high temperature and high pressure, a very rigorous environment for chemical reaction.[17] Under these rigorous conditions, radicals can be generated due to the decomposition of water, monomer, surfactant, or rupture of polymer chains to initiate the polymerization of monomer.[16] Polymer/CNTs composite emulsion was prepared through ultrasonic assisted in situ emulsion polymerization in the presence of CNTs. Both anionic surfactant SLS and nonionic surfactant OP were chosen because they have good synergetic dispersion and stabilization effect on CNTs in emulsion, and in ultrasonically initiated emulsion polymerization without any added chemical initiator, SLS can be decomposed to radicals by ultrasonic cavitation to initiate polymerization of monomer.[21] The two stages for preparing the composite emulsion were adopted in this study. Figure 4 is the schematic illustration of the preparation process. Stage I involves the ultrasonic dispersion of CNTs in aqueous solution and the ultra-
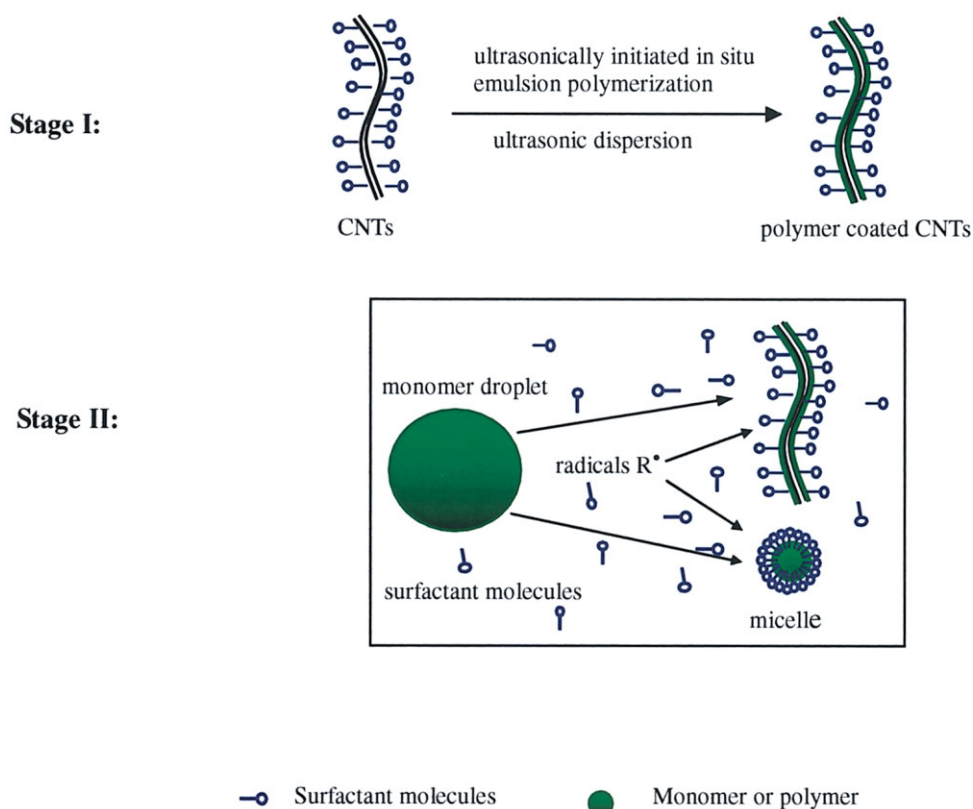


**Figure 4** Schematic illustration of ultrasonically assisted in situ emulsion polymerization. Stage I: ultrasonically initiated in situ emulsion polymerization; Stage II: conventional emulsion polymerization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sonic preparation of seed emulsion. It includes ultrasonic dispersion, surface activation of CNTs, surfactant absorption on CNTs, monomer adsorption, and adsolubilization in the admicelle (adsorbed micelle) on the surface of CNTs, as well as in situ polymerization of monomer on CNTs. In this step, the polymerization of monomer was initiated by ultrasonic cavitation and the polymerization proceeded while ultrasonic dispersion, and polymer-encapsulated CNTs were formed. Ultrasound contributes to improve the encapsulation rate of PBA on the surface of CNTs. The reasons are as follows: (1) ultrasonic cavitation can break the aggregates of CNTs and effectively disperse the nanotubes in aqueous solution. The increase in the accessible surface area of CNTs leads to an increase in the adsorption capability of CNTs to the monomer and radicals. (2) The polymerization temperature is low, about 0–50°C. Such a low temperature contributes to an increase in the adsorption capability to monomer compared to a high temperature in conventional emulsion polymerization. (3) Ultrasonic cavitation reduces the monomer droplet size from several micrometers to several hundred nanometers,[22] leading to a marked increase in the chance of collision between monomer droplet and CNTs. (4) The radicals are preferably formed on the surface of CNTs. CNTs are the main sites of absorbing the bulk of the energy and are the primary cavitation sites, and so the surfactant molecules absorbed on the surface of CNTs will preferably be decomposed to the radicals. The radicals induced by ultrasound cavitation can initiate the polymerization of monomer. The formed polymer layer on the surface of CNTs introduces a steric repulsive force between the CNTs to prevent the self-aggregation of CNTs. The formed polymer encapsulated CNTs in this step were characterized. FTIR and XPS confirm that the interaction between polymer and MWCNTs is strong after a soxhlet extraction experiment.[23] However, a drawback of ultrasonically initiated emulsion polymerization is that it requires a low monomer content. Because of the damping effect of ultrasonic cavitation in high concentrated emulsion system, the monomer conversion is low and polymerization rate is slow under such conditions; therefore, it is difficult to prepare high solid content latex by ultrasonically initiated emulsion polymerization. To obtain high concentrated polymer/CNTs composite emulsion with high monomer conversion, conventional emulsion polymerization (Stage II) in the presence of polymer-coated CNTs was further conducted. Stage II involves the conventional in situ emulsion polymerization on the surface of CNTs and micelle polymerization. In this step, the left monomer and initiator were added. The polymerization in the micelles and in the surface of CNTs occurred simultaneously, as shown in Figure 4. The thickness of polymer layer was increased and the synthetic latex particles from micelle polymerization adhered to the surface of polymer coated CNTs, which was confirmed by TEM (Fig. 7). A detailed explanation is given in the following section. The effect of the charged content of CNTs on the emulsion stability was examined. When 0.2 g (1 wt %) CNTs were added into 90 mL emulsion, the prepared composite emulsion was uniform black, and no sediment was observed when filtering with filter cloth. The composite emulsion can remain stable for at least a month. When the content of charged CNTs was too much, the flocculation occurred during polymerization, and CNTs were precipitated. The prepared composite film from filtered emulsion at a charged content of 0.4 g (2 wt %) CNTs were gray and semitransparent, indicating the decrease in the content of CNTs in the latex. When the charged CNTs amounts to 0.6 g (3 wt %), the prepared composite film from filtered emulsion was white blue and transparent like that from pure polymer emulsion, suggesting that all CNTs have been precipitated. This can be explained as follows: the long polymer-coated CNTs behave like a flocculent with a long molecular chain; when the content of charged CNTs increased to a value, they can connect latex particles together like bridging-mechanism to precipitate. So, it is very difficult to reach a stable composite emulsion with a high charged CNT content because of the intrinsic geometry of one-dimensional (1D) long CNTs. The control experiment was conducted. The conventional emulsion polymerization in the presence of CNTs without ultrasonic polymerization stage was carried out. The stable polymer/CNTs composite emulsion can not be obtained even at a low CNTs content such as 0.1 wt %. After filtering, all the CNTs were not passed through the filter cloth and the emulsion was white blue. This is because CNTs can not be redispersed in the aqueous dispersion under conventional mechanical stirring. Therefore, Stage I, i.e. ultrasonically initiated in situ emulsion polymerization, is necessary for obtaining a stable polymer/CNTs composite emulsion.

TEM photograph of original MWCNTs is shown in Figure 5. The diameters of original CNTs are in the range of 20–40 nm. Figure 6 shows the morphology of poly(methyl methacrylate-*co-n*-butyl acrylate) (P(MMA-BA)) latex particles in the absence of CNTs. The size of P(MMA-BA) latex particles are in the range of 30–80 nm. In the P(BA-MMA)/CNTs composite emulsion, there are two nanostructures: one is the spherical latex nanoparticle with a high concentration, and the other is 1D polymer-coated CNTs with relatively low concentration. The length of polymer-coated CNTs is shorter than that of the original CNTs because power ultrasound can cut and shorten CNTs [8,24]. How about the interaction and the combination way between spherical nanoparticles and CNTs in such a mixed system? Can the spherical latex nanoparticles separate
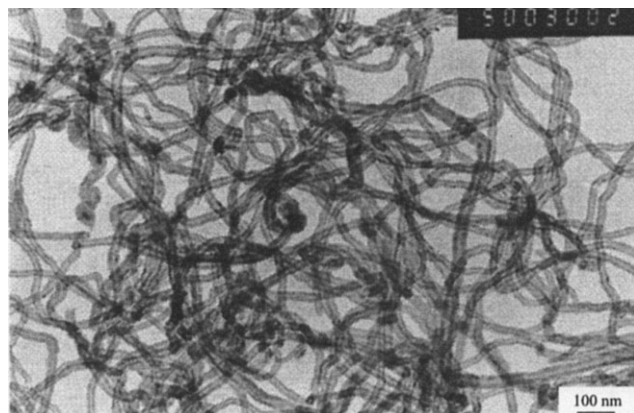
**Figure 5** TEM photograph of original MWCNTs.



a



b

**Figure 7** TEM photographs of (a) P(MMA-BA)/CNTs composite latex particles after staining with phosphorus tungsten acid and (b) CNTs in P(MMA-BA) composite thin film.

the CNTs? To observe the morphology of CNTs and latex particles in the composite emulsion, two methods of sample preparation were utilized. First, the synthesized latex was diluted 20 times, then was dropped on a copper grid and stained using phosphorus tungsten acid (PTA). Then, it was dried at ambient temperature, and the morphology of latex particles and a few CNTs due to low concentration can be clearly observed by TEM, as shown in Figure 7(a). Clearly, the spherical polymer latex nanoparticles with some deformation and aggregation adhere to the wall of 1D CNTs to form a structure like "grapes on the twig" and the CNTs were well separated and dispersed by the latex particles. The spherical latex particles were absorbed on the surface of CNTs, which formed an encapsulation structure to cause better dispersion of CNTs. This is a new way to separate the CNTs. Polymer-encapsulated MWCNTs formed at the first step of ultrasonically initiated emulsion polymerization will contribute to the adsorption of spherical latex nanoparticles on the surface of 1D CNTs. When
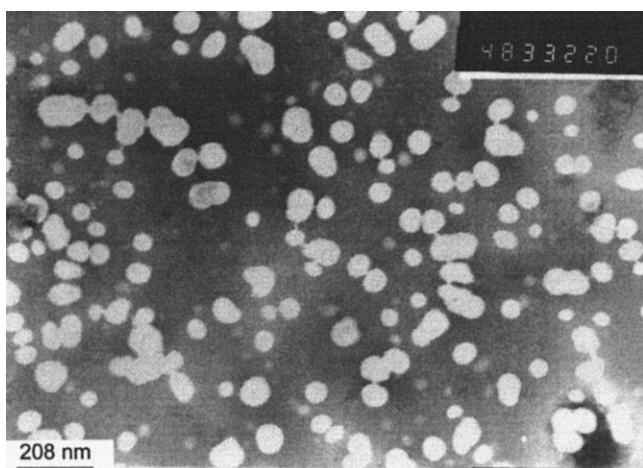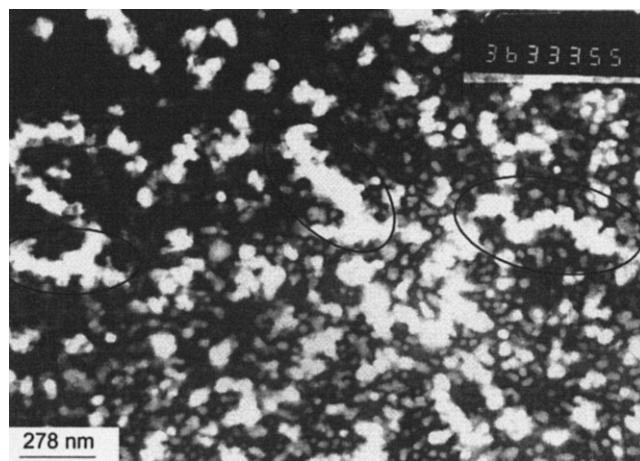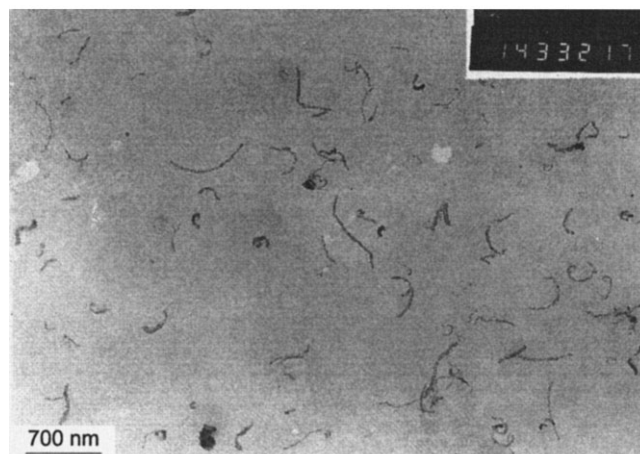


**Figure 6** TEM photograph of P(MMA-BA) latex nanoparticles after staining with phosphorus tungsten acid.

compared with Figure 6, it can be noted that the size of latex particles are in the range of 20–40 nm, and the average particle size decreased in the presence of CNTs. This should be attributed to that some monomer was in situ polymerized on the surface of CNTs. Second, the synthesized latex with five times dilution was dropped on the copper grid and then drying at ambient temperature, the morphology of spherical latex particles could not be observed by TEM, because the latex particles were fused together and connected to form a very thin film due to the high concentration of the latex particles and the good film forming property of P(MMA-BA) emulsion. In this case, the concentration of CNTs is relatively high, and so a lot of CNTs can be observed. As shown in Figure 7(b), clearly, the individual CNTs were completely separated and the good dispersion of CNTs in the thin P(MMA-BA) film was attained. The results suggest that ultrasonically

assisted in situ emulsion polymerization provides us a good method to separate and disperse CNTs. The good dispersion should be attributed to the ultrasonic treatment in Stage I. The ultrasonic dispersion and polymer-wrapped CNTs formed through ultrasonically in situ emulsion polymerization in Stage I are very important. The aforementioned control experiments without ultrasonic treatment support this point.

## Polymer/CNTs composite film

The P(BA-MMA)/CNTs films were obtained from the nanocomposite emulsion. The film with a thickness of 0.2–0.5 mm is flexible, uniform, and black. Figure 8(a) shows the SEM photograph of the surface of P(MMA-BA)/CNTs composite latex film. It can be seen that the CNTs are well distributed on the surface of polymer/CNTs composite film. Figure 8(b) shows SEM photograph of cryogenically fractured surface of P(MMA-BA)/CNTs composite film in liquid nitrogen. Some white dots represent the end of CNTs. It can be observed that the holes were left after CNTs were pulled out. The size of the holes is larger than that of original CNTs, suggesting that the interfacial adhesion between CNTs and P(MMA-BA) is strong. Some white dots with larger size can be observed, Which can be ascribed to the surfactant sediments during the filming process. Also, we examined the reinforcing effect of MWCNTs on polymer film. The mechanical properties are listed in Table I. It is evident that with the increase in the CNTs content, the Young's modulus and the yield strength increased. Only at 1 wt % CNTs, the Young's modulus is enhanced from 124 to 289 MPa, 133% higher, and the yield strength is improved ~14%. The reinforcing effect should be attributed to the good dispersion of CNTs, the improved interfacial adhesion between P(MMA-BA) and CNTs, as well as the good mechanical properties and long aspect ratio of CNTs themselves. As aforementioned, with 2 wt %
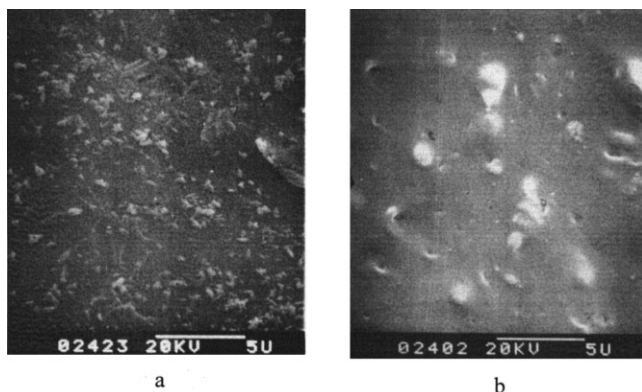
**TABLE I**
**Mechanical Properties of the Polymer/CNTs Composite Films**

| Charged content of CNTs (wt %) | Elongation at break (%) | Young's modulus (MPa) | Yield strength (MPa) |
|---|---|---|---|
| 0 | 360 | 124 | 1.4 |
| 0.5 | 402 | 153 | 1.6 |
| 1 | 361 | 289 | 1.1 |
| 2 | 444 | 142 | 1.4 |

charged CNTs, the real content of CNTs in composite film is lower than the charged content of CNTs because of a large amount of flocculation of CNTs during polymerization, and so the mechanical properties decrease.

## CONCLUSIONS

Ultrasonic irradiation has an excellent dispersion effect on CNTs in surfactant aqueous solution. The stable P(MMA-BA)/CNTs composite emulsion with high monomer conversion and high solid content were prepared through ultrasonic assisted in situ emulsion polymerization in the presence of CNTs. Two stages including ultrasonically initiated in situ emulsion polymerization (Stage I) and conventional emulsion polymerization (Stage II) were adopted. In the prepared composite emulsion, the latex nanoparticles adhere to the wall of CNTs to form a structure like "grapes on the twig" and thus separate and disperse the CNTs. The composite emulsion has a very good film forming property. The smooth, uniform, flexible, and black polymer/CNTs composite film can be prepared from the composite emulsion. CNTs (1 wt %) in composite film can reach a good dispersion. When the charged content of CNTs in emulsion exceeds 2 wt %, the flocculation occurs and emulsion is no longer stable. It is noteworthy that the stable polymer/CNTs composite emulsion can not be obtained through conventional in situ emulsion polymerization even at the low content of CNTs such as 0.1 wt % because of the redispersion problem of CNTs. Tensile tests suggest that with the increase in the CNTs content, the modulus and the yield strength of composite film increased. Only at 1 wt % CNTs the Young's modulus is enhanced from 124 to 289 MPa, and the yield strength is improved ~14%.



**Figure 8** SEM photographs of (a) the surface and (b) the cryogenically fractured surface in liquid nitrogen of P(MMA-BA)/CNTs composite latex film.

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