

## Preparation of Poly (*n*-butyl acrylates) Encapsulated Carbon Black *via* Ultrasonic Irradiation Initiating Emulsion Polymerization

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**ABSTRACT:** The encapsulation of poly (*n*-butyl acrylates) (PBA) onto carbon black (CB) surface *via* ultrasonic irradiation initiating emulsion polymerization was investigated. The results showed that the route performed at ambient temperature can efficiently prepare PBA encapsulated CB as proved by the aggregation of PBA encapsulated CB in the precipitator of PBA. The surface properties of CB coated with PBA were analyzed by FT-IR and XPS. The content of PBA encapsulated on the CB surface reaches 11.87% determined by TGA. Compared with the conventional chemical modification of CB, it was found that the particle size of CB obtained by the present approach can be controlled, and dynamic light scattering results quantified that CB particles with narrower size distribution and smaller size were obtained. The PBA encapsulated CB can be dispersed uniformly in the polymer matrix.

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**KEY WORDS** Carbon Black / Ultrasonic Irradiation / Emulsion Polymerization / Poly (*n*-butyl acrylates) /

Carbon black (CB) is widely used in rubber, plastics, paints and inks that act as a reinforcing agent, black pigment, and electrically conductive filler. Although the primary particles of CB are known as nano-material, they are quite easy to fuse together to form aggregates and further to big agglomerates, which often result in the poorer mechanical properties of the filled polymer materials. So, the dispersion, compatibilization, and stabilization of CB in the polymer matrices are the key to develop the potential application of CB for functional composites. To solve these problems, many researchers have concentrated on the surface modification of CB. Approaches of the surface modification in the early include physical adsorption, heat treatment, oxidation, and plasma treatment. Grafting of polymers onto the surface of CB<sup>1–7</sup> or encapsulating CB by heterophase polymerization, emulsion polymerization<sup>8,9</sup> has been proved to be an effective method. However, all of these methods have somewhat disadvantages, respectively. For example, grafting of polymer onto CB surface required many complicate steps, involving the pretreatment of the CB surface to introduce functional groups. The rigorous pretreatment involved HNO<sub>3</sub> oxidation is dangerous and unfriendly to environment. Recently, Wang<sup>10,11</sup> reported a method of coacervation for encapsulating CB. Another significant advantageous of this route was the polymer encapsulated CB nanoparticles were free from aggregation except for without involving of complex polymerization. Although the

method avoided the complicated polymerization, the process of ball milling to pulverize CB particles was involved and many organic solvents were added. So, it is of great interesting to develop a relatively simple polymerization technique for preparation of polymer encapsulated CB with controlled particles.

The application of ultrasonic irradiation in emulsion polymerization has been intensively investigated in recent years.<sup>12–17</sup> Without involving any chemical initiators, the polymerization process can be performed at ambient temperature (30–40 °C) due to the radicals formation arisen from the ultrasonic cavitation. Cavitation cause small voids in the liquid medium which periodically collapse leading to transient regions of high temperature of around 5000 K<sup>18</sup> and pressure of about 500 atm. Most of radicals are generated from the surfactant decomposition caused by the localized extreme conditions.<sup>16</sup> The ultrasonic irradiation initiate some monomer such as methyl methacrylate, *n*-butyl acrylates and aniline *in situ* emulsion polymerization in the presence of nano materials included in multi-walled carbon nanotube, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> have been studied in details by Wang and coworkers,<sup>19–22</sup> in which nano materials were encapsulated by polymer and nano materials can be redispersed at the nano scale. So it is possible to use this ultrasonic irradiation initiating encapsulating emulsion polymerization to prepare polymer encapsulated CB and to our knowledge, there is no report on applying this technique to modify CB.

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The aim of the present research is to prepare polymer encapsulated CB by ultrasonic irradiation initiating emulsion polymerization. Scheme 1 shows the routine of this new study. By adopting the dispersion, crushing, activation and initiate effect of ultrasonic irradiation, the big agglomerates or aggregates of CB are partly broken down and vinyl monomer proceeds to polymerize, which finally formed a polymer coated CB with smaller particle size and uniform particle size distribution. The dispersibility of polymer encapsulated CB in polymer matrix is also presented.

## EXPERIMENTAL

### *Materials and Reagents*

CB used is Printex-XE2-B provided by Degussa Corp. The as-received CB was extracted by boiling toluene for 24 h in a Soxhlet extractor and dried in vacuum before use. *n*-Butyl acrylate (BA) was purified using 10% NaOH and distilled water for three times in order to remove the inhibitor before being distilled under vacuum. The purified BA was stored in refrigerator at 5 °C for use. Sodium dodecane sulphonate (SDS) and cetyltrimethylammonium bromide (CTAB) were used as supplied. BR-106 is a kind of acrylic resin obtained from Mitubishi Rayon. Other reagents were used without any further purification.

### *Preparation of PBA Encapsulated CB*

1.0 g CB, 4 mL BA and 96 mL 0.2% SDS aqueous solution was introduced firstly into the reaction vessel. Then the mixture in the reaction vessel was thoroughly deoxygenated by bubbling with nitrogen thermo stated at 40 °C. A JY92-IID (Shanghai xin zhi) sonifier with a titanium horn was used to deliver 22 kHz ultrasonic wave to the reaction mixture. After 30 min of irradiation at 300 W power output under nitrogen, the samples were frosted in refrigerator for two days and then precipitated by methanol. Finally, the precipitated mixtures were filtered, washed, vacuum dried at 60 °C. Ultrasonic irradiation initiating emulsion polymerization in the absence of CB was also carried out. The experimental procedures were as the same as the above.

### *Characterizations*

UV-vis absorption spectrophotometer (VARIAN Cary 500) was used to evaluate the dispersion of CB in surfactant aqueous solution by the determination of absorption at 267 nm. Fourier transform infrared spectra (FT-IR) of the samples in KBr pellets or ATR were recorded on a Nicolet AVATAR 360 FT-IR spectrometer. X-Ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with

Mg K $\alpha$  radiation ( $h\nu = 1253.6$  eV, 250 W, 14.0 kV). The base pressure of the analyzer chamber was about  $5 \times 10^{-8}$  Pa. The sample was directly pressed to a self-supported disk (10  $\times$  10 mm) and mounted on a sample holder then transferred into the analyzer chamber. Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV). Thermo gravimetric analysis (TGA) was used to measure the polymer content in the polymer encapsulated CB. It was analyzed under a heating rate of 10 K/min from room temperature to 800 °C and a dynamic nitrogen flow of 50 cm<sup>3</sup>/min. The aggregate particle size of PBA encapsulated CB or CB was determined by dynamic light scattering (DLS). The measurements were carried out by NICOMP<sup>TM</sup> 380 ZLS attached with Zeta potential supplement. A He Ne argon ion laser was light source and the wavelength of the laser light was 639 nm. The detection angle was 90° and the temperature was set at 25 °C.

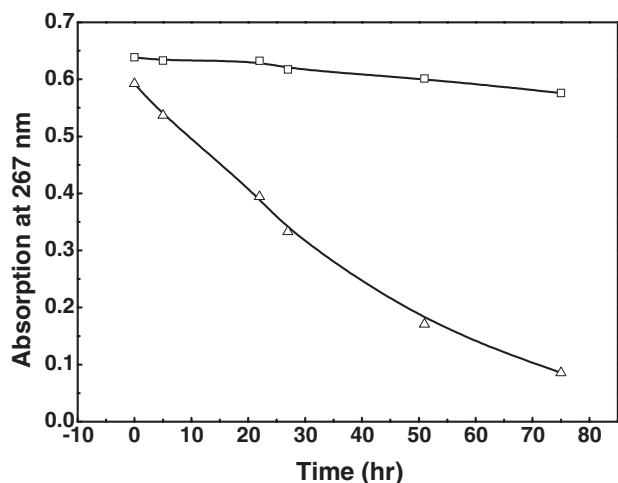
To investigate whether or not the PBA encapsulated on the surface of CB, 50 mL of ethanol added 0.005 g PBA encapsulated CB or CB was dispersed by ultrasonic cleaning wash for 10 min. Then 2 mL dispersion diluted by 13 mL ethanol was centrifuged for 1 min and 2 min at 2000 rpm, respectively.

Dispersibility of PBA encapsulated CB in BR-106 polymer was also studied. 0.05 g PBA encapsulated CB or CB and 5 g BR-106 were introduced in 50 mL ethyl acetate. After dispersing by ultrasonic cleaning wash for 20 min, a thin-film was prepared on glass substrates by casting methods. Then the optical microscope was used to observe the disperse state of PBA encapsulated CB or CB in BR-106 thin-film.

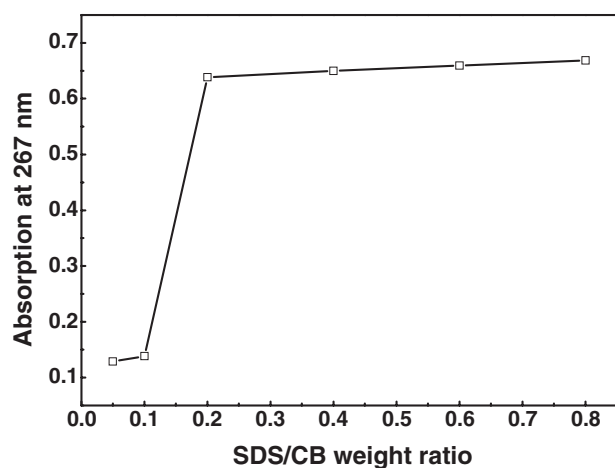
## RESULTS AND DISCUSSIONS

### *Determination of Surfactant for Polymerization*

Surfactant is a radical source necessary for the ultrasonic irradiation initiating emulsion polymerization. For systems dispersed the nanoparticles, surfactant bilayers called admicelles can be formed on the surface of the nanoparticles and is the main polymerization location when the concentration of the surfactant solution is below the critical micelle concentration (cmc).<sup>23,24</sup> The monomer will diffuse into the admicelles and occurs to polymerize, which lead to the formation of polymer-coated nanoparticles. Therefore it is necessary to discuss the dispersion stability of CB in surfactant aqueous solution before ultrasonic irradiation initiating polymerization. Figure 1 showed the absorption dependence of time curves of CB in SDS and CTAB aqueous solution in which the weight ratio of surfactant to CB is 0.4. The higher the absorption is, the better the dispersion of CB is. It is seen that the absorption of CB in SDS is clearly higher than that



**Figure 1.** Absorption-time curves of CB in (□) SDS and (△) CTAB in 0.4% aqueous solution.

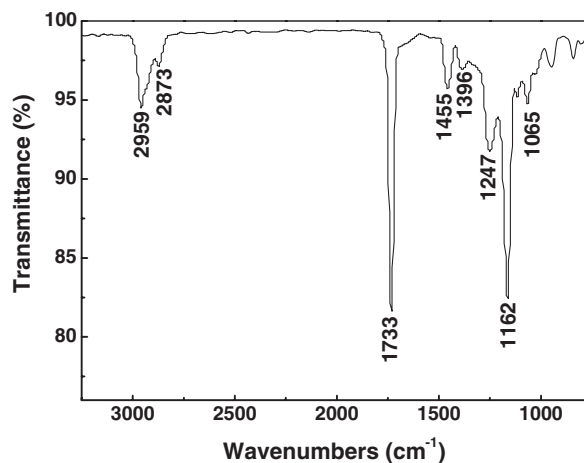


**Figure 2.** Effect of SDS/CB weight ratio on the dispersion of CB.

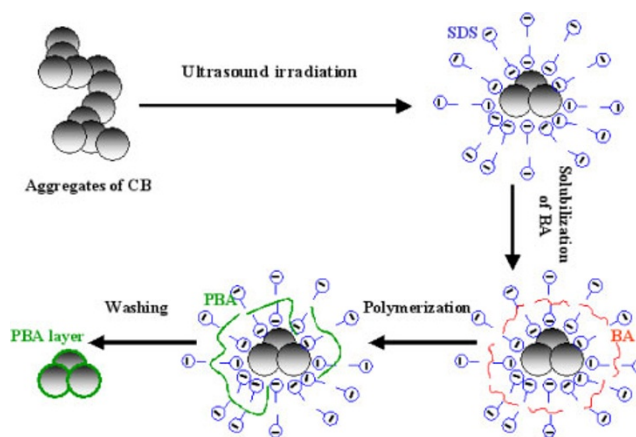
of in CTAB and does not vary apparently with the time increasing, indicating that CB has better dispersion stability in SDS than in CTAB. The reason is that Zeta potential of the CB surface is positive and the CB surface is favorable to absorb anion surfactant SDS. Effect of SDS concentration on the dispersion of CB was further investigated, as shown in Figure 2. It can be seen that with the increasing of SDS concentration, the absorption at 267 nm increases. When SDS/CB weight ratio reaches 0.2/1, the absorption varies little, suggesting that the good dispersion is obtained. So in the following preparation of PBA encapsulated CB under ultrasonic irradiation, SDS surfactant in 0.2% of aqueous solution was chosen.

#### Polymerization of PBA

Although the ultrasonic irradiation initiating emulsion polymerization of BA has been reported detailedly,<sup>9</sup> different ultrasonic horn and reaction conditions may result in different effects. As a systematic re-



**Figure 3.** FT-IR spectra of PBA obtained from ultrasonic irradiation initiating emulsion polymerization of BA.

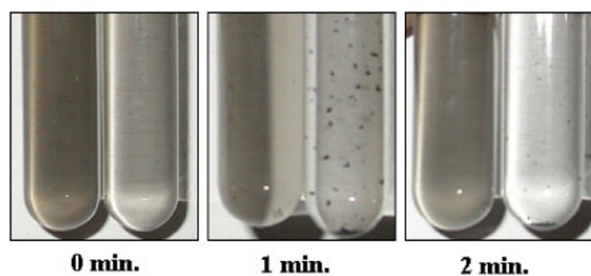


**Scheme 1.**

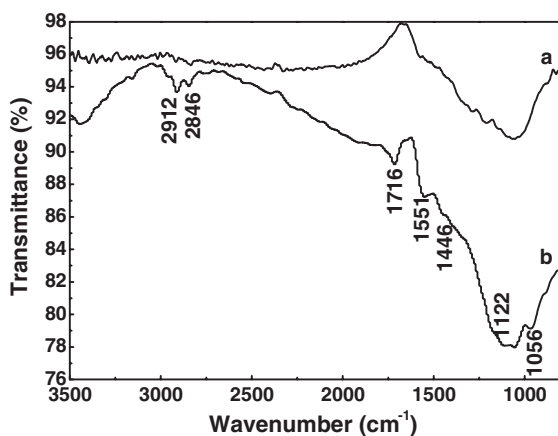
search, the ultrasonic irradiation initiating emulsion polymerization of BA in the absence of CB and chemical initiator requires to study. The FT-IR spectra of synthesized PBA shown in Figure 3 manifested that the characteristic peaks of the sample are consistent with that of standard PBA. The significant peaks at  $1733\text{ cm}^{-1}$  corresponds to the C=O, and the peaks at  $1000\text{--}1250\text{ cm}^{-1}$  suggest the presence of C–O group.  $2959$  and  $2873\text{ cm}^{-1}$  is assigned to the stretch vibration of C–H bond.  $1455$  and  $1396\text{ cm}^{-1}$  is attributed to the bend vibration of  $-\text{CH}_2$  or  $-\text{CH}_3$  group. These experiment results suggested that PBA could be synthesized by this method.

#### Characterization of PBA Encapsulated CB

As Scheme 1 shown, the preparation procedure of PBA encapsulated CB by ultrasonic irradiation initiating emulsion polymerization consists of four steps. Firstly the big agglomerates of CB were broken down into small aggregates and many new surface of CB particle were formed. Meanwhile, admicelle by the adsorption of the surfactant with different charge from



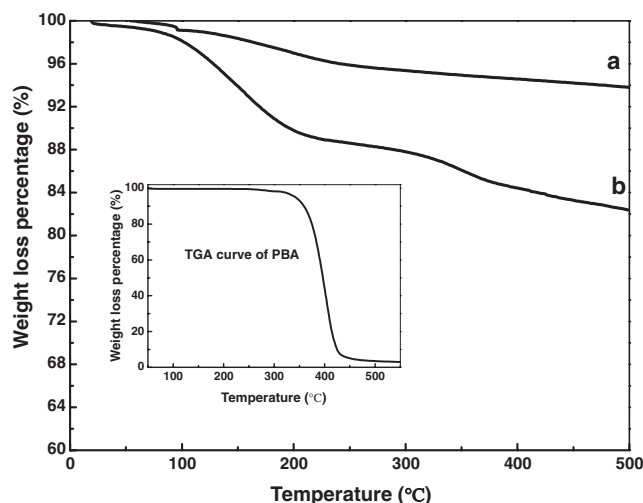
**Figure 4.** Photographs of (left) CB and (right) PBA encapsulated CB suspension in ethanol at different centrifuged time.



**Figure 5.** FT-IR spectra of (a) CB and (b) PBA encapsulated CB.

CB is formed onto the surface of CB. In order to get as many as admicelle on the surface of CB, surfactant concentration should be below the cmc and this also helped to prevent the competing of bulk polymerization.<sup>25</sup> Secondly is the solubilization of BA into the admicelle. Then the polymerizations in the admicelle proceed. Because the surfactant concentration used here is below cmc the main polymerization location is in the admicelle adsorbed on the surface of CB. The last step is the washing to remove the surfactant using plenty of water. In order to check whether the CB has been coated by PBA or not we investigated the dispersion stability of the samples in ethanol. Because ethanol is the precipitator of PBA, if CB was encapsulated with PBA it will not disperse well and precipitate. As shown in Figure 4, PBA encapsulated CB begins to coagulate and precipitate to bottom with centrifugation time increasing, which verified that CB has been encapsulated by PBA.

Figure 5 showed FT-IR spectra of purified CB and PBA encapsulated CB prepared by ultrasonic irradiation initiating emulsion polymerization. It is obvious that there are no any absorption peaks in the spectra of CB because the CB used here has little functional groups. Furthermore, because of strong absorption of CB, it is difficult to detect the few functional groups

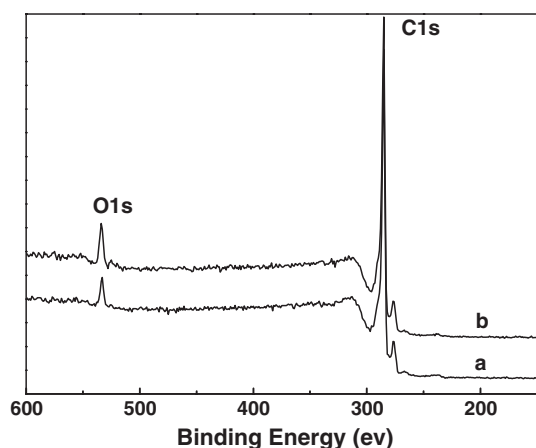


**Figure 6.** TGA curves of (a) CB and (b) PBA encapsulated CB.

onto the CB surface. For the FT-IR spectra of PBA encapsulated CB, there appear new absorptions that are the characteristic peaks of PBA shown in Figure 3. The FT-IR difference between PBA and PBA encapsulated CB is the general shift of wavenumbers and the reason may arise from the interaction of PBA and CB.

The exactly PBA content in PBA encapsulated CB can be calculated from TGA analysis, as shown in Figure 6. It appears two weight losses flat in the TGA curve for PBA encapsulated CB of which the higher weight loss flat from 250–500 °C is consistent with the decomposition of PBA (inserted in Figure 6) synthesized in the absence of CB and the corresponding content is 7.36%. While the lower arises from on the one hand the oily matters contained in CB and the content is about 6.2% calculated from the TGA results of CB. However, the weight loss lower than 250 °C for PBA encapsulated CB is 10.71%. So the rest 4.51% should be PBA that has different thermostability from PBA fabricated in the absence of CB.

XPS is another useful characterization method to identify the surface properties of CB. The original CB and the PBA encapsulated CB were monitored by XPS. Figure 7 shows the XPS survey scan spectra of CB and PBA encapsulated CB. The figure shows the peaks corresponding to the C and O elements of which binding energies is 285 and 532, respectively. The high-resolution scan spectra of C1s and O1s region were shown in Figure 8 and the corresponding element atomic percent concentrations at the surface were listed in Table I. As can be seen from Table I, the increasing of O/C atom ratio in the PBA encapsulated CB compared with CB further identifies the presence of PBA on the surface of CB. Although the changes in atomic concentration were in the direction expected for the encapsulation of the PBA, the ratio of



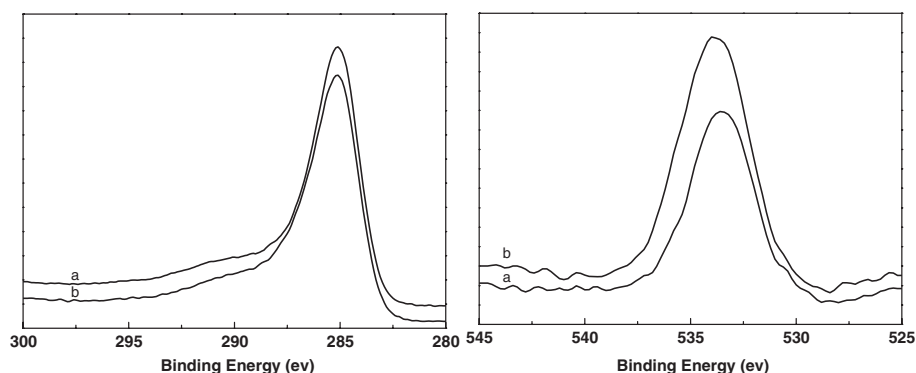
**Figure 7.** XPS survey scan spectrum of (a) CB and (b) PBA encapsulated CB.

**Table I.** The carbon and oxygen content of CB and PBA encapsulated CB

	CB (%)	PBA encapsulated CB (%)
O	3.87	6.54
C	96.05	93.38

**Table II.** Diameter of CB and PBA encapsulated CB particles

	Average particle size (nm)	Standard deviation (%)
CB	247.6	47.10
PBA encapsulated CB	169.0	43.60



**Figure 8.** High-resolution (left) C1s and (right) O1s XPS spectra of (a) CB and (b) PBA encapsulated CB.

the oxygen and carbon determined from XPS is not 2:7, which should correspond to the PBA; instead it is 2:28.6. There is still much more carbon which does not originate from the PBA. This indicates that the surface coverage by the PBA is incomplete.

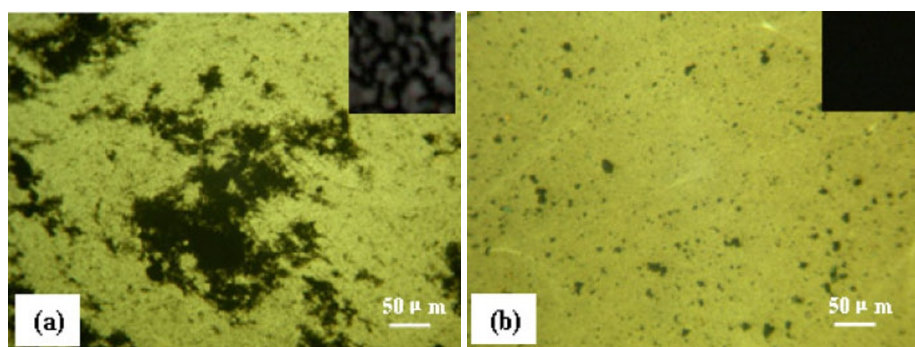
Ultrasonic irradiation can not only initiate polymerization to prepare polymer encapsulated CB, but crush the agglomerates of CB and form small aggregates. This fact has been proved by DLS analysis result, as shown in Table II. DLS provides the information on the aggregate size of CB. The CB particles have a diameter of 247.6 nm while the particle diameter of PBA encapsulated CB is 169.0 nm decreased 31.8% compared to CB particle size. The difference in the particle size between CB and PBA encapsulated CB is the outcome of the ultrasonic crushing effect produced from turbulent flow and shock waves during bubble collapse.<sup>26</sup> The turbulent flow and intensive shock waves induce the high-speed interparticle collisions and the agglomerates and bigger aggregates are crushed into smaller aggregates. Noted that the standard deviation of PBA encapsulated CB is 43.60% also smaller than that of CB. The lower the standard deviation is, the more uniform the particle size distribution is.

It was concluded from the above results that CB with the smaller particle size and uniform particle size distribution could be obtained by the unusual sonochemical effect, which could not be achieved by the other conventional chemical encapsulated CB methods.

#### *Dispersibility of PBA Encapsulated CB in BR-106 Polymer*

The dispersibility of PBA encapsulated CB in BR-106 polymer matrix was also examined. The thin-film prepared by PBA encapsulated CB/BR-106 and CB/BR-106 was shown in the photograph inserted in Figure 9. Clearly, compared to CB/BR-106 thin-film, PBA encapsulated CB/BR-106 thin-film is much more flatness, suggesting that PBA encapsulated CB has better compatibility with BR-106 polymer. Optical microscope images (Figure 9b) show the particle size distribution of PBA encapsulated CB in BR-106 is more uniform and not congregate into agglomerates like CB in BR-106 (Figure 9a). This result evidenced the DLS results. The fact that the dispersion of PBA encapsulated CB in BR-106 has been improved may be attributed to ultrasonic irradiation make the CB





**Figure 9.** Optical microscope images of the thin-film of (a) CB/BR-106 and (b) PBA encapsulated CB/BR-106.

agglomerates crush into smaller aggregates and the PBA layer introduced on the surface of CB overcome the congregation of CB when filled in polymer matrix.

The purpose to encapsulate polymer to CB is to resolve the problems of dispersion, compatibilization and stabilization of CB in the polymer matrices, and further to endow with functionality of the corresponding composites. As the CB used in this present study is a kind of conductive CB, the electric conductivity of the PBA encapsulated CB/BR-106 thin-film was studied. The primary results showed that the surface resistance of film filled with PBA encapsulated CB is a little higher than that of film filled with non-modified CB when the content is 20 wt%. A large number of publications has shown that the conductivity of CB/polymer composite depends on many factors, such as CB content, the dispersing extent of the aggregate of CB, the aggregate size and aggregate size distribution of CB etc. So, it is necessary to further discuss the application of PBA encapsulated CB in the conductive composites in the further work.

## CONCLUSIONS

The preparation of PBA encapsulated CB *via* ultrasonic irradiation initiating encapsulating emulsion polymerization provide an alternative route for the modification of CB. The preliminary results indicated that this route could generate efficient polymerization modifying in a rapid reaction at relatively low temperature. In addition, one of the most advantages of this method is to get uniform particle size distribution. These points made this preparation method for CB modification worth investigating further.

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