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Grafting of maleic anhydride onto carbon black surface via ultrasonic irradiation

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The grafting of maleic anhydride onto carbon black surface based on the Diels–Alder addition via ultrasonic irradiation was investigated. Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA) were used to determine the chemical structure of the resulting products. The anhydride ring in the modified products can be opened into two carboxylic groups. Accordingly, the carboxylated carbon black was analyzed quantitatively through acid-based titration to determine the concentration of anhydride ring on the modified carbon black's surface. The grafted molecules amount calculated from the concentration of the anhydride ring was consistent with the results of TGA data. Comparison of zeta potential measurement demonstrated that there were more negative charges attached to the surface of carbon black after ultrasonic modification. TEM observations showed that the conglomeration degree of modified carbon black decreased more than that of initial carbon black. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: carbon black; ultrasonic irradiation; maleic anhydride; modification

Introduction

Much importance has always been attached to the modification of carbon black (CB).[1–3] A variety of modification methods, such as oxidation processes, plasma treatment, physical adsorption and chemical grafting, have been developed. Among them, introducing reactive dienophiles to react with CB is an effective strategy put forward very recently.[4–6] This strategy is based on the reaction of an activated carbon–carbon double bond with the existing diene structures of the CB surface, i.e. the Diels–Alder reaction. Bergemann *et al*.[5] reported the modification of CB properties by chemical reaction with maleic acid derivatives. The diversity of maleic acid derivatives provides an opportunity to attach different organic groups to the CB surface and, therefore, wide in variations in the properties of the reaction products are possible. In Bergemann *et al*.'s study, CB together with the reagent was treated in solid state or solution under reflux. By utilizing these two routes, a variety of maleic acid derivatives could be grafted onto the CB surface. The same process was also adapted to modify the carbon fiber.[7] However, these processes are time-consuming and need high temperatures.

The application of ultrasonic irradiation in modification of fineparticles has been intensively investigated in recent years.[8,9] Small voids caused by ultrasonic cavitations in the liquid medium periodically collapse, which can lead to transient regions of ultrahigh temperature and ultrahigh pressure.[10] This can also provide an extreme physical chemistry environment for the reaction. Therefore, ultrasound has been widely applied in dispersion, crushing and activation of particles. In our previous CB modification work, the CB encapsulated by poly (*n*-butyl acrylates) was obtained via ultrasonic irradiation.[11] The result showed that this technique could generate efficient polymerization rapidly at relatively low temperatures.

The objective of the present investigation was to apply the ultrasonic irradiation technology to the modification of CB with maleic anhydride (MA). Since the reaction takes place in a unique environment, this process could be performed at ambient temperature and completed in a relatively short time. What is more, with the multiple effects of ultrasonic irradiatio,[12,13] the agglomerates or big aggregates of CB are partly broken down and some fresh surface is formed,[14] which provides new reactive sites for the chemical bonding between MA and CB. This can undoubtedly increase the amount of grafted molecules of modified CB. The hydrolysis of anhydride ring in the modified CB was also studied for further analysis of the modified products. Therefore, the concentration of the carboxylic group on the CB surface after hydrolysis treatment was analyzed through titration.

Experimental

Materials and equipment

Carbon black (Vulcan XC-72) with a 254 $m^2 g^{-1}$ surface area and an average primary particle size of 30 nm was obtained from Cabot Company. The as-received CB was extracted by boiling toluene for 48 h in a Soxhlet extractor and dried in vacuum before use. MA was commercially available and was used without further purification. The solvent, toluene, used was an analytical reagent.

The ultrasonic irradiation instrument was a VCX 750 (Sonic & Material Co.) equipped with a titanium horn with a diameter of 13 mm and adjustable power output. Fourier transform infrared spectra (FT-IR) of the samples were recorded on a Nicolet Avatar 360 FT-IR spectrometer. Thermogravimetric analysis (TGA) was used to quantitatively determine the grafted amount in the modified CB. The particle size distribution and zeta potential measurement were carried out using NICOMP™ 380 ZLS with Zeta

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potential supplement. The morphology and structure of initial CB and modified products were determined by transmission electron microscopy (TEM) on a JEM 1200 EX instrument.

Preparation of modified CB

The ultrasonic modification of CB with MA was prepared as follows: the CB particles mixed with MA (1 g) and toluene (100 ml) were treated with an ultrasonic processor at a power of 300 W for 1 h. A cooling bath was utilized to maintain the temperature at 25 °C. The modified CB was separated by centrifugation. Prior to use following analysis, the resulting samples were extracted by boiling toluene for 48 h in a Soxhlet extractor and then dried at 60 °C under vacuum for 24 h. In addition, reflux modification of CB was synthesized as described in the literature[5] for a comparison of the modification effects.

Quantitative assessment of the functional groups

The anhydride ring of the grafted CB can be hydrolyzed to two carboxylic groups. Acid-based titration of the hydrolyzed product can quantitatively provide their concentration on the CB's surface. The analysis procedure was as follows. Grafted CB was put into deionized water and bath-sonicated for 1 h at 80 °C. Then a solution of 0.10 M NaOH was added and the mixture was stirred for 1 h. The dispersion was then centrifuged at 15 000 g until the supernatant was colorless and transparent. The supernatant was decanted, and then titrated with 0.02 M HCl solution to determine the NaOH in the supernatant, and from that to assess the amount of the NaOH molecules that attached to the carboxylated CB. The same procedure was done on the initial CB.

Results and Discussion

FT-IR analysis

Figure 1 shows FT-IR spectra of initial CB and two modified CBs. It can be seen that there are no apparent absorption peaks in the spectrum of initial CB because of the highly absorbing nature of CB and the lack of functional groups on the surface of this material.[15] Some new absorptions appeared for modified CB which were easily confirmed using the ultrasonic modificated CB curve: (1) 2918 and 2848 cm^{-1} ascribed to ν_{asymm} CH and ν_{symm} CH vibration in CH_2 groups; (2) 1828 and 1778 cm^{-1} ascribed to ν_{asymm} and ν_{symm} vibration in $C{=}O$; and (3) 900 cm^{-1} ascribed to stretching vibration in C–O–C. The absorption bands associated with the cyclic anhydride of maleic anhydride (1850 and 1800 cm^{-1}) were distinctly displaced by 22 cm^{-1} shorter wave numbers after grafting on the carbon black, indicating a strong interaction between the organic molecule and CB. For the curves of two modified CBs, distinct discrepancies were found. In comparison with the curve of reflux modificated CB, the relevant absorption peaks of ultrasonic modified CB curve were stronger or more apparent. Ultrasonic irradiation promoted the reaction and increased the amount of maleic anhydride grafted onto the CB surface.

TGA analysis

Figure 2 displays the TGA curves of initial CB and two modified CBs. The insert in Fig. 2 shows the TGA curve of pure MA. For the raw MA, the weight loss was entirely at 170 °C. Correspondingly, the weight loss of the modified CBs and initial CB curves were almost the same below 170 °C. It can be concluded that the unbonded maleic anhydride was removed thoroughly. In the TGA curves of modified CBs, the weight loss between 170 and 460 °C was attributed to decomposition of grafted components. It can be seen that the amount of grafted components of ultrasonic modified CB was larger than that of reflux modified CB, which is in agreement with the observation in Fig. 1. The corresponding grafted amounts determined by TGA were 7.34 and 1.93 wt%, respectively.

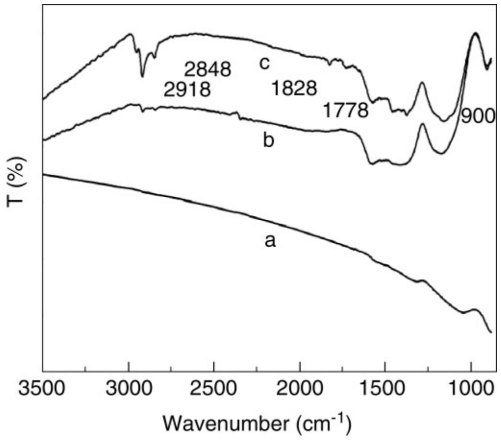

Figure 1. FT-IR spectra of (a) initial CB, (b) reflux-modified CB and (c) ultrasonic modified CB.

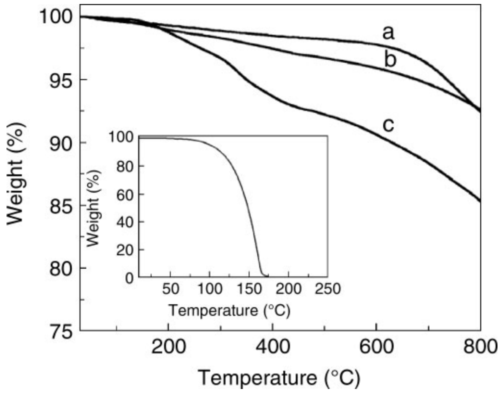

Figure 2. TGA curves of (a) initial CB, (b) reflux-modified CB and (c) ultrasonic modified CB. Inset: TGA curve of pure maleic anhydride.

Table 1. Diameter of initial CB and modified CB particles

Sample	Mean diameter (nm)	Standard deviation (%)
Initial CB	305.3	31.80
Reflux modified CB	278.4	42.10
Ultrasonic modified CB	231.9	23.30

Particle size analysis

Besides the facile preparation of modified CB via ultrasonic irradiation, another advantage of adopting this technology is that a smaller size and narrower size distribution of carbon particles were

Table 2. Results of the titrations of carboxylated and initial CB

Sample (weight)	Mol of NaOH added to dispersion	Mol of HCl used for the titration of supernatant	COOH concentration on the CB (mol COOH/g CB)	Anhydride concentration on the CB(mol anhydride/g CB)
Initial CB (100 mg)	4.00×10^{-4}	3.88×10^{-4}	1.20×10^{-4}	0.600×10^{-4}
Reflux modified CB (100 mg)	4.00×10^{-4}	3.65×10^{-4}	3.50×10^{-4}	1.75×10^{-4}
Ultrasonic modified CB (100 mg)	4.00×10^{-4}	2.65×10^{-4}	13.5×10^{-4}	6.75×10^{-4}

obtained, as shown in Table 1. This was proved in our previous report.[11] This finding is very important when considering the optimization of the performance of carbon black particles. In this investigation, the reduction of particle size could be used to explain the increase in the grafted amount of CB modified with ultrasonic. Along with the pulverization of big agglomerates or some aggregates of CB, some fresh surface is formed, and this provides more reactive sites for the chemical bonding between MA and CB.

Quantitative analysis of the anhydride ring on the carbon black

The results of the titrations are presented in Table 2. The titrations also provided further evidence regarding the molecules anchored onto CB. The concentration of the anhydride ring of CB was much higher after modification, and CB modified with ultrasonic had more groups than when modified with reflux. Again, the grafted molecule amount on modified CB can be calculated from the corresponding concentration of the anhydride ring. The calculated molecule amounts, CB modified with ultrasonic and reflux, were 6.82 and 1.72 wt%, respectively. The calculated results were close to those obtained by TGA.

Surface charge of carbon black particles aqueous dispersions

Table 3 shows the variation of zeta potential after the modification of CB. The modified CB became much more negative than the raw material. Undoubtedly, more negative zeta potential corresponds to a more stable dispersion system. This result further demonstrates the attachment of the functional groups onto the CB.

Table 3. Results of zeta potential of initial CB and ultrasonic modified CB

	Initial CB	Ultrasonic modified CB
Zeta potential (mV)	−3.47	−19.21

TEM observation

Owing to the high elemental carbon content and the lack of functional groups of the initial CB, it was strongly hydrophobic and prone to heavily aggregate when dispersed in water. As can be seen from Fig. 3(a), initial CB existed with large agglomerates whose size was up to the micrometer scale. Correspondingly, after grafting MA, CB could be well dispersed in water. No obvious agglomeration of carbon aggregates in the image of ultrasonic modified product [see Fig. 3(b)] was discovered. This is possibly due to the hydrolysis of grafted MA in water.

Conclusions

In summary, ultrasonic irradiation was utilized to promote the reaction between maleic anhydride and CB. With the aid of the multifunction of ultrasonic irradiation, maleic anhydride could be grafted onto CB at ambient temperature in a relatively short time. Ultrasonic irradiation could increase the amount of grafted molecules compared with reflux modification, and another advantage under ultrasound was that CB particles could

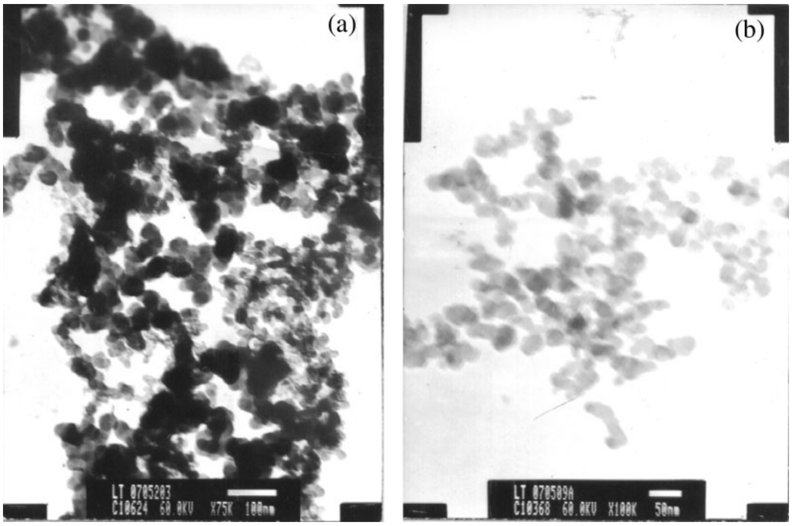

Figure 3. TEM photographs of (a) initial CB and (b) ultrasonic modified CB.

be pulverized into smaller sizes with narrower distribution. The anhydride ring in the modified CB could be hydrolyzed to two carboxylic groups. The presence of carboxylic groups on the CB's surface was significant because a variety of chemical reactions can be accomplished by means of this group. It is anticipated that this group can be further utilized to tailor the surface properties of CB. Furthermore, the procedure presented can be easily adapted to the modification of other carbon nanostructures such as carbon nanotubes and carbon fiber due to the similarity of their structures.

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