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Dispersion of carbon nanotubes in polymer matrix by *in-situ* emulsion polymerization

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Since the carbon nanotubes (CNTs) were discovered by Iijima [1], they have been attracting tremendous interest because of their unique combination of electronic, mechanical, chemical, and thermal properties, which promises a wide range of potential applications [2–6]. For example, in electronic application, CNTs are used to dissipate unwanted static charge build-up [2]. In the automotive industry, CNTs are used as conducting agents to aid in electrostatic painting [3]. However, CNTs can hardly disperse in polymer matrix because of their nonreactive surface. So, the CNTs usually require treatment before they can be applied, in order to obtain a better dispersion. With the aid of ultrasound, which helps the particles to overcome the van der Waals forces of attraction among CNTs, stable homogeneous aqueous dispersions have been prepared with sodium dodecyl sulfate (SDS) as dispersing agent [7]. The use of ultrasound, however, has been shown to damage CNTs [8]. In fact, appropriate chemical oxidation of CNTs' surfaces can dramatically raise the stability of aqueous suspensions and also introduce the carboxylate groups onto the surface of CNTs [9]. Furthermore, environmental concerns also drive researchers to disperse CNTs in aqueous matrix. Therefore, it is of great practical interest to disperse CNTs in polymer latex.

In this paper, a process to efficiently disperse CNTs in polyacrylic latex was reported. This process involves *in-situ* emulsion polymerization of acrylic monomers, including methyl methacrylate (MMA), butylacrylate (BA), methacrylic acid (MAA), and hydroxyethyl methacrylate (HEMA), with the presence of CNTs with oxidation treatment. The obtained latex has good storage stability because good interfacial bonding between CNTs and polymeric matrix has been formed by efficiently using reactive groups on the surface of CNTs.

The CNTs used in this study were catalytically grown, and the chemical oxidation treatment was given using a mixture of concentrated nitric and sulphuric acids in a ratio of 1:3, respectively [10]. These treated CNTs were suspended in a solution of SDS surfactant (2 wt%) distilled water with stirring for 1 h. After heating the solution to 75–80 °C, the initiator, ammonium persulfate (APS) solution, was added to the obtained CNT suspensions. Five minutes later, MMA (42 wt%), BA (50 wt%), MAA (5 wt%), and HEMA (3 wt%) were continuously introduced dropwise into the suspensions. After 2 hr of reaction, the latex containing CNTs was obtained.

The storage stability of resulting latex containing CNTs is evaluated by particle size distribution. Generally, the particle size of latex is in the range of 100–400 nm, whereas the size of CNTs is about tens of nanometers. So the latex particle size distribution changes little if a certain amount of CNTs is incorporated in latex.

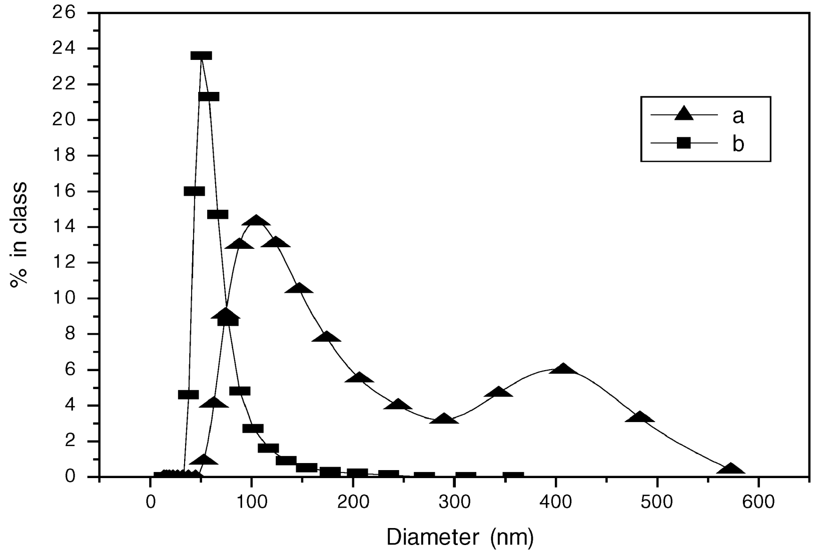

Figure 1 Particle size distribution of latex containing CNTs prepared by direct mixing (a) and *in-situ* polymerization (b), respectively, after one month's storage.

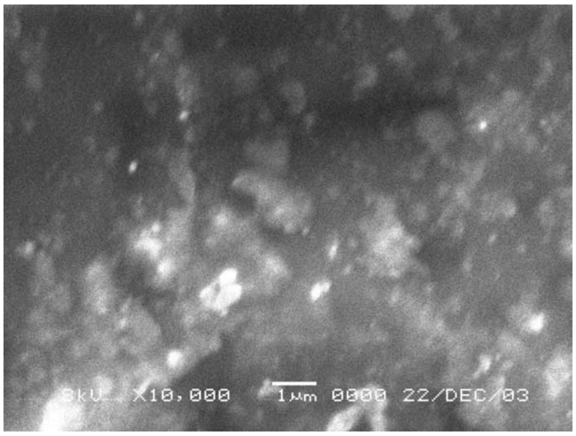

Figure 2 SEM picture of CNTs/polyacrylate film prepared by *in-situ* emulsion polymerization.

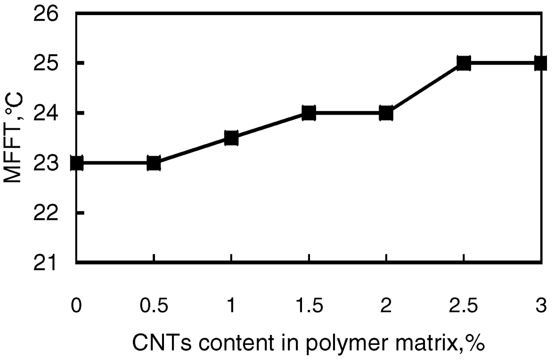

Figure 3 Effect of CNT content on MFFT of resulting latex.

However, CNTs often tend to aggregate up to a few tens of micrometers because of intrinsic van der Waals forces of attraction among tubes and their high surface area and high aspect ratio, when they disperse in polymer or other matrix. The particle size distribution of latex containing CNT prepared by *in-situ* polymerization after one month's storage is given in Fig. 1. Also given is the particle size distribution for the CNT suspension via direct mixing. It is evident that the former has a relatively narrow particle distribution and one peak at about 50 nm, which is similar to the distribution of latex particles without CNTs. However, two peaks at 104.5 and 407.4 nm respectively are formed for the latter. Apparently, the latex containing CNTs prepared by *in-situ* polymerization has better storage stability than that by direct mixing. These results may be explained by the fact that chemical bonds have formed between carboxylate groups in CNTs and hydroxyl group in polymer chain during *in-situ* emulsion polymerization, which prevents the aggregation of CNTs.

To observe the morphology of the CNTs/polyacrylate film prepared by *in-situ* emulsion polymerization, scanning electron microscopy (SEM) was used. Fig. 2 shows SEM picture of the film. It can be seen that CNTs could disperse homogeneously in the polymer matrix except for a little CNT aggregates, though the CNT content is not high (2%). These aggregates may have resulted from the film formation process. As the water evaporates, CNT are more easily approachable, thus aggregates would appear. The dispersion of CNTs in latex can be improved by changing the ingredients of monomers, for which further research is needed.

In coating industry, improving mechanical strength often results in the increase of the minimum film-forming temperature (MFFT). As CNTs are rigid particles, their incorporation in polymer matrix has been demonstrated to improve the tensile strength of composite film [11]. However, MFFT of latex containing CNTs has a slight increase with the increase of CNT content, which can be seen in Fig. 3. This means the mechanical strength can be improved, but not at the cost of film formation too much, which is very important for coating and other industries.

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