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Preparation and Absorption Properties in Near Infrared Wavelength of Carbon Nanotubes/Acrylate Coatings[†]

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Carbon nanotubes can be used as absorbent materials at the near infared range. In this study, carbon nanotube was treated with surfactant to prevent aggregation, and the acrylate coating of the carbon nanotube was prepared with the carbon nanotube solution and the near infrared reflection properties of the coating were studied. A series of factors influencing the reflectivity of carbon nanotubes/acrylate coatings at 930 nm, such as PVC concentration, the kinds and concentration of the surfactant and size range of the carbon nanotube, were studied. Based on these, the coating procedure was optimized and the carbon nanotubes/acrylate coating was prepared with good absorption properties. The reflectivity is under 0.1% of the coatings and its transmission is below 1.0% at near infrared wavelength of 840-980 nm.

Key words: Carbon nanotubes, Acrylate, Surface modification, Coating, Absorption property

I. INTRODUCTION

Since Iijima discovered carbon nanotubes in 1991 [1], the preparation and application of the carbon nanotube has become one of the hot fields worldwide. Many have studied the material application of the carbon nanotube materials with their various properties, including electric conductibility, electromagnetism property, structure strengthened material, hot dispersion, light function, compound electrodeposits, corrosion proof, wear resistant material and so on [2-6].

Carbon nanotube is a kind of single-walled or multi-walled tubes material which is mainly made up of hexagonal carbon structure, with the flection parts are usually carbon pentagon and carbon heptagon. Carbon nanotube has very high strength, which is more than 100 times of that of the steel and is about 20 times of that of the carbon fibrous. Furthermore it also has high toughness, hardness and electric property [7-11]. Various electronic devices can be developed using the carbon nanotube. For example, carbon nanotube has been used in high-power mini-battery as the power source for computer systems and also as electronic firestarter of the automobile, because of its small volume, high energy and long lifetime [12]. When carbon nanotube is pressed into slices, they can be made into high-octane capacitance and the energy is two orders of magnitude higher than that of the generic capacitance [14,15]. Electrical conductivity of the carbon nanotube can increase a great deal when the carbon nanotube is made into conductive coatings and is plated on the surfaces of some

parts of apparatus [16,17]. By controlling the carbon pentagons and carbon heptagons in the middle part of carbon nanotube, carbon nanotube can be made into nano electronic switch and nano diode [13], even nano triode transistor. If these studies are successful, the size of the integrate circuit can be reduced by two more orders of magnitude than that before. Carbon nanotube can be made into field emission devices for video systems [18]. Because modified carbon nanotube can have excellent physics and chemical properties, there are also possibilities for applications in the military technology [19].

At present, some major problems which restrict the application of the apparatus and the compound material made of carbon nanotube are the dispersion of the carbon nanotube and matching with basis material. The solubility of the carbon nanotube is very low in all kinds of solvent because its surface has few defect and little active group. In addition, because of the strong van der Waals force between carbon nanotube, the huge specific surface area and big ratio of longth to diameter, carbon nanotubes can easily aggregate or enlace. These strongly limit the applications of carbon nanotubes [20]. To solve this problem people have adopted all kinds of measures to improve its dispersion such as using ultrasonic treatment and mechanical rubbing [21]. At present, the study trends are that the carbon nanotube is treated with the molecular chain of polymer [22,23], and compound of covalent bond and noncovalent bond [24,25]. The research shows that mechanical property of carbon nanotubes will be reduced about 15% by chemical modification with functional group. So, favorable surfactant is one of the best methods to improve dispersive property of carbon nanotubes in the polymer matrix [26].

In this study, carbon nanotubes/acrylate coatings were prepared after the carbon nanotube was surface-

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treated. Then absorption properties of the coating were studied at near infrared range by characterization of the reflectivity curve of the coating. Furthermore, some factors affacting the absorption properties were analyzed and a paint technology was optimally designed. At last, carbon nanotubes/acrylate coatings with excellent absorption properties were prepared.

II. EXPERIMENTS

A. Material and instrument

Multi-walled carbon nanotubes (MWCNTs) were obtained from the Chengdu organic chemistry academy of Chinese Academy of Sciences. The tube diameter is in the range of 8-15 nm and the tube length is about 50 μm. Acrylate with condensate solid dosages of 38%-45% was from the Woods Sciences Forestry Chemical Industry in China. Anhydrous alcohol with analytical grade was obtained from Shanghai Nanxiang reagent limited company. Additive SXD-1, SXD-2, and SXD-3 were prepared in our laboratory with standard procedures.

The following instrument were used: JY98-3D type ultrasonic cell disruptor (Shanghai Laboratory Apparatus Plant), TGL-16 type table model refrigerated centrifuge (Changsha XIANGYI Centrifuge Instrument Limited Company), 79-1 type magnetic force heat beater (Tanjing City HENGFENG Instrument Plant), XB-30 type stuck leveler (Shanghai Modern Environment Engineering Institute), HG101-2 type electrothermal blowing dry box (NanJing Laboratory Apparatus Plant); and UV-3101PC type spectrophotometer (Japan SHIMADZU Corporation).

B. Process

Figure 1 shows the experimental process flow. MWCNTs powder was put into anhydrous alcohol to dissolve the surface additives. The homodispersive carbon nanotube slurry was prepared with ultrasonic. Then the slurry was centrifugalized, dried, and rubbed to powder. The powder was again dissolved into alcohol solution. After ultrasonic dispersion, acrylic ester emulsion was dropped into the slurry and then the carbon nanotube with acrylate coating was prepared.

III. RESULTS AND DISCUSSION

A. Factors influencing the reflectivity of the carbon nanotubes/acrylate coatings at near infrared range

Crbon nanotube usually disperses badly in solvents because of its surface properties. Carbon nanotube can easily aggregate and is very difficult to be stabilized for a long time in solution. The ability of carbon

nanotube to combine with other matrix is very weak. The slide between the carbon nanotubes and the matrix with shear force can be easily formed. So the performance of the material made with carbon nanotube will be greatly influenced [27]. Surfactants with hydrophilic and oleophilic group are used to treat the carbon nanotube surface. These functional groups serve as the bridge between the carbon nanotube and other materials. Better functional material with carbon nanotube can be prepared by using such properties of the good surfactants.

1. The influence of different surfactants

Owing to small particle size and big specific surface area, carbon nanotube has large surface energy to induce attraction force larger than mutual exclusion force among particles. In order to reduce their total surface energy, the particles aggregated easily. Carbon nanotube surface is generally hydrophobic. In order to disperse carbon nanotube, surfactant was dropped into alcohol solvent. Surfactant can reduce the surface tension of the carbon nanotube and change its interface state. So equality dispersive carbon nanotube slurry and carbon nanotubes/acrylate coatings were prepared. Then the reflectivity of coatings in the near infrared range was measured with the Ultra-Visible light spectrophotometer.

Figure 2 shows the reflectivity of the carbon nanotube/acrylate coating treated with SXD-1, SXD-2 and SXD-3. We can see that the reflectivity of the carbon nanotube/acrylate coating is the lowest when treated with SXD-3. SXD-1and SXD-2 are the surfactants with long chain and high molecular weight. Polyalkane can disperse nano particles with the static space steric hindrance stability mechanism [28]. However, their dispersion ability on the carbon nanotube in alcohol solution was less than SXD-3. While molecular weight of the polyelectrolyte is very high, bridging or vacancy flocculation is easy to occur which makes the powder slurry aggregate stongly. SXD-3 is a sort of coupling agent. One end has alkoxy group which can couple and hydrolyze with mineral. Single-monolayer group was formed on the surface of carbon nanotube [29]. Because the carbon nanotube is dispersed in alcohol solution, its surface could bind with numerous hydroxide groups. The alkoxy of SXD-3 hydrolyzed with hydroxide groups to couple. The other end maintains the base group which could have chemical reaction or connect with acrylic ester and dissolve with each other. Carbon nanotube and acrylic ester can bind closely to the whole through the middle bridging action of the coupling agent, which brings the best adsorption property of the coatings in the near infrared.

We can also see that the reflectivity of the carbon nanotube/acrylate coating is almost flat. Carbon nanotube as absorbent are made of a series of hollow tubes.
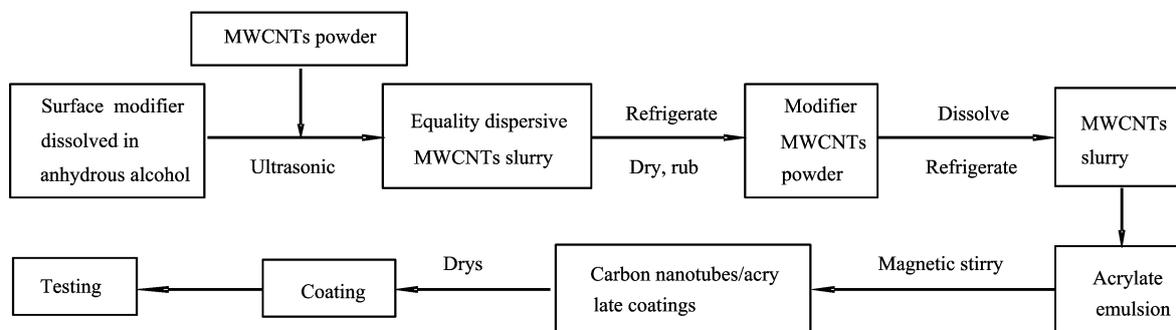

FIG. 1 Process flow of carbon nanotubes/acrylate coatings.

TABLE I Reflectivity of the coatings treated with the different concentrations of SXD-3 at $\lambda=930$ nm

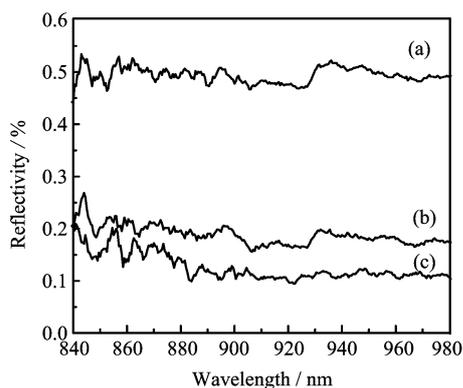| Modification's concentration/vol%	0.25	0.5	0.75	0.25	0.5	0.75
PVC concentration	0.20	0.20	0.20	0.15	0.15	0.15
Reflectivity/%	0.2625	0.2075	0.2899	0.4395	0.3906	0.4715

FIG. 2 Reflectivity of the coatings treated with different surfactants at near infrared wave. (a) SXD-1, (b) SXD-2, (c) SXD-3.

When travels in the nanotube, the wave was subjected to multiple reflection and refraction of tube walls. So the wave was absorbed strongly and the absorption was non-selective.

2. The influence of concentration of the surfactant

Six share equivalent carbon nanotube were selected and dissolved in alcohol solution to form carbon nanotube slurry. In the slurry, we dropped SXD-3 with different volume percentage composition (relative to solvent volume). After ultrasonic dispersion, we prepared the coatings with PVC concentration of 0.20% and 0.15%. Then, we compared their reflectivity at $\lambda=930$ nm.

The reflectivity of the coatings treated with SXD-3 of the different concentrations at $\lambda=930$ nm is shown in Table 1. The reflectivity of the carbon nanotube

treated with 0.5% SXD-3 had the lowest reflectivity at $\lambda=930$ nm. So the optimal content of SXD-3 to treat with carbon nanotubes was 0.5%. Because the concentration of the surfactant was very low, the alkoxy which could hydrolyze with hydroxy on the surface of carbon nanotubes was very small in the dispersive system. With the increase of concentration, the surfactant became saturation adsorption on the surface of the carbon nanotube. Carbon nanotube closely joined up with the acrylate by the coupling agent as the middle bridge. In this case, the reflectivity of coating was the lowest at $\lambda=930$ nm. Following with the increase of the concentration of the surfactant, the surface of the carbon nanotube was thicker that they extruded the functional group. This squeezing action made the $C-O-H$ changing into $C-O$ on the surface of the carbon nanotube. As a result, its external electronic shell structure was changed. The change of the electronic level transition affected the absorption directly, the reflectivity of the material was also influenced at $\lambda=930$ nm.

3. The influence of PVC concentration

The reflectivity chart of the carbon nanotubes/acrylate coatings treated with the different PVC concentration at $\lambda=930$ nm was shown in Fig.3. PVC concentrations were 0.15%, 0.20%, 0.25%, 0.30%, and 0.34%, respectively. With the increase of PVC concentration, the reflectivity of carbon nanotube decreased at $\lambda=930$ nm. After PVC concentration was above 0.25%, the change went flat and the reflectivity was all below 0.2%

While the content of the carbon nanotubes is constant, the more PVC concentration, the less resinous content. When PVC is 0.15%, the resinous content is the highest. In this case, the reflectivity of the coat-
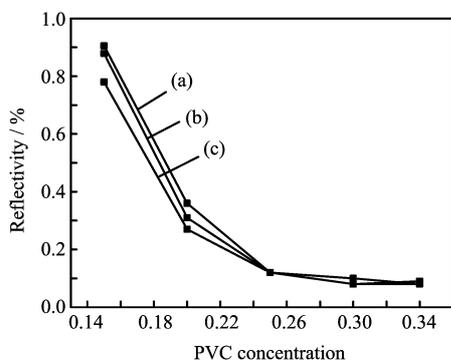
FIG. 3 Reflectivity curve of the coatings treated with the different PVC concentration at λ=930 nm. (a) SXD-1, (b) SXD-2, (c) SXD-3.

FIG. 4 Reflectivity of the coatings prepared with different preparation process at λ=930 nm. (a) The first process, (b) The second process.

ing was mostly determined by the acrylic ester. With acrylic ester content being reduced, the influence of the carbon tube became predominant towards coating reflectivity when PVC concentration was more than 0.25%. Because carbon nanotubes formed by curled plumbago plane and hooded seal curve surface of carbon atom at its double end. Multiwalled carbon nanotubes are made up of several monowalled concentricity tubes. Near infrared light was subjected to multiple reflection and refraction of tube wall to be absorbed strongly when light was traveling in the middle-blank pipe. Wherefore the reflectivity of the coating was low and the change went flat at the near infrared wavelength (for example λ=930 nm). The conclusion was as the same as the Fig.3(b).

4. The influence of tube length of carbon nanotubes

We chose two different processes following as the Fig.4. One was that homodispersive carbon nanotubes slurry was centrifugalized, dried, and rubbed to powder. The powder was dissolved into alcohol solution. After ultrasonic dispersion, acrylic ester emulsion was dropped into the slurry and then carbon nanotubes/acrylate coating was prepared. The other was that acrylic ester emulsion was dropped directly into homodispersive carbon nanotubes slurry and carbon nanotubes/acrylate coatings formulated by magnetic stirring. Then the coatings were painting on the aluminium plate and dried.

From Fig.4, the reflectivity of the carbon nanotubes/acrylate coatings which were prepared according to the second process were all the lowest at different PVC concentration. In the first process carbon nanotube was multiple curtailed after rubbing and the second ultrasonic dispersion action. Furthermore the traveling of the wave undergoing was limit in the carbon nanotube. The refraction and diffraction effect were weakened, which influenced the absorption of tube wall. While PVC concentration was over 0.25%, it did not
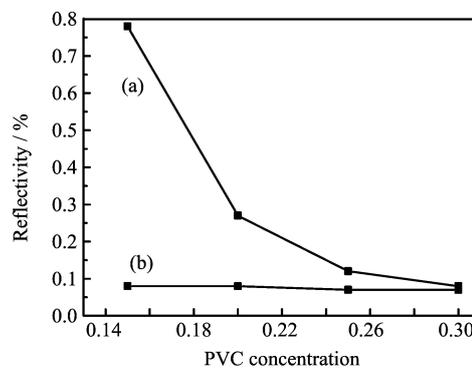
quite influenced the reflectivity of the coatings which were prepared by two kinds of process. While PVC was equal to 0.15%, the reflectivity of the coatings prepared by the second process reduced at λ=930 nm. It was explained that tube range was longer so that the absorption went over distinctness. Whereas by this time the content of the carbon nanotube was at the lowest, so the economic cost of the coatings were also reduced greatly.

B. Optimal design of the procedure

After analyzing the factors influencing the behavior of the carbon nanotubes/acrylate coating, we optimized the experiment process. The optimization process is that the acrylic ester emulsion was dropped directly into the homodispersive carbon nanotubes slurry and carbon nanotubes/acrylate coatings formulated by magnetic stirring. Then the coatings were painting on the aluminium plate and dried.

Figure 5 shows that the reflectivity of the carbon nanotubes/acrylate coating was below 0.1% at near infrared wavelength range of 840-980 nm. The transmission of carbon nanotubes/acrylate coating is below 1.0% at near infrared wave of 840-980 nm (Fig.6). It was non-
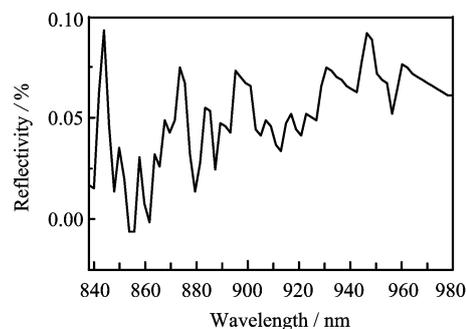

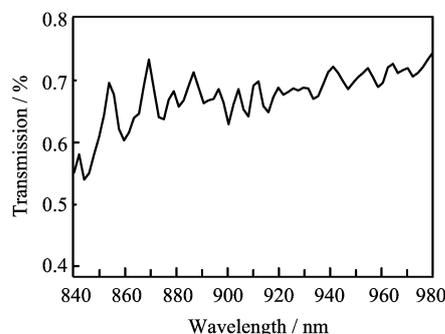FIG. 5 Reflectivity of the coatings at near infrared wave.

FIG. 6 Transmission of the coatings at near infrared wave.

selective that the coatings absorbed at near infrared wave. While carbon nanotube was treated with SXD-3 for 0.5%, its dispersion was in the groove in alcohol solution. By this time, the base group in coupling agent molecule closely coupled with carbon nanotubes and acrylate. Carbon nanotubes formed continuous passage in acrylate. The wave was absorbed strongly by tube walls when it traveled in carbon nanotubes. So the reflectivity of the coatings was very low.

IV. CONCLUSION

We studied the influence of the absorption properties of the carbon nanotubes/acrylate coatings in near infrared. The research was based on changing PVC concentration, the kind of surfactants and their concentration as well as the tube range of the carbon nanotubes. The reflectivity of the preparative coatings was tested by the application of ultraviolet visible complementary filter. The following conclusion can be reached. (i) Carbon nanotube was dispersed with SXD-3. When its PVC concentration was below 0.25%, its performance was better than the carbon nanotube modified with SXD-1 and SXD-2. The optimal dosage of SXD-3 was 0.5%. (ii) The tube diameter of the carbon nanotube is 8-15nm. The longer the tube range, the stronger the absorption. (iii) We prepared carbon nanotubes/acrylate coatings after optimal designing the process. The reflectivity of the coatings prepared is below 0.1% and its transmission is below 1.0% in the near infrared range. It is explained that carbon nanotubes/acrylate coating caused intensive absorption in the near infrared range and the absorption was non-selective.

Known from the application background of the stealth material, the less the reflectivity of the material the better the stealth effect. So optimal treating carbon nanotube may have the possibility to be used as good absorbent materials with military applications in the near infrared range.

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