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LETTER

Effects of dispersants on dispersion of carbon nanotubes and properties of fluorocarbon resin nanocomposites

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Because of their unique structural characteristics and outstanding properties, carbon nanotubes (CNTs) have lots of potential applications in many scientific and technological fields, such as hydrogen storage [1], supercapacitors [2, 3], lithium ion batteries [4, 5], catalyst supports [6], electronic devices [7], etc. CNTs also have been taken as a superior candidate for use as fillers in composite materials because of their extremely high Young's modulus, stiffness, flexibility, conductivity, and other special properties. Much research has been carried out using CNTs as fillers in thermoplastics, epoxy resins, phenolic resins, and rubbers which demonstrated greatly enhanced mechanical, electrical, and thermal properties [8–11]. Although the applications of CNTs in polymers have been widely studied, little attention has been paid to coatings, especially for fluorocarbon coatings. As one of the fluorocarbon resins, a unique solvent called soluble fluoro-olefin/vinyl ether copolymer (abbreviated as FEVE copolymer trade name “LUMIFLON”) was developed in 1982 by Asahi Glass. This copolymer comprises alternating sequences of fluoro-olefin and several specific vinyl ether units. In recent years, FEVE resin has been widely investigated [12–15] since this polymer has excellent weather resistance and as paint material is convenient to handle and process just like conventional paint resins such as acrylic urethane. In this paper, CNT/FEVE composite coatings are prepared for the first time. As we all know, the dispersion of CNTs in matrix is the most important factor that influences the properties of composites. The composites would demonstrate inferior performances if CNTs were poorly dispersed. So, the paper focused on the effects of dispersants on dispersion of CNTs in FEVE matrix and the tensile and thermal properties of the nanocomposite coatings.

Multi-walled CNTs (MWNTs) were produced by a catalytical pyrolysis method using a vertical furnace [16]. In brief, benzene was used as carbon source and ferrocene (0.5 g/mL) as catalyst precursor with thiophene (0.12 mL/mL), and the reaction temperature was between 1150 °C and 1,170 °C with 730 mL/min and 5,400 mL/min of the flow rate of nitrogen and hydrogen, respectively. The morphology of MWNTs was characterized by TEM (JEOL JEM-1200 EX 100 KV). Figure 1 shows that the MWNTs have straight morphologies and smooth walls. The diameters of most MWNTs are in the range of 40–90 nm.

For preparing MWNT/FEVE nanocomposite coatings, appropriate quantities of the wetting and dispersing additives (Anti-Terra®-U, Disperbyk®-140, Disperbyk®-163, Disperbyk®-2001, Disperbyk®-2050, bought from BYK Chemical Inc.) were resolved well in butyl acetate firstly. Then MWNTs were added into these solutions and sonicated for about 1 h. The mass ratio of MWNTs, dispersants, and butyl acetate was kept as 5:5:90. After ultrasonication, the MWNT-dispersed butyl acetate solutions and the curing agents were added into FEVE resin (Daikin Industries Company, GK-570, solvent grade, 65%) and agitated for about 30 min (the mass ratio of MWNTs, FEVE, and curing agents was 5:100:50). After being kept agitation, the mixtures were brushed manually on the polyester films. After being kept at room temperature for 24 h, the MWNT/FEVE coatings were transferred into an

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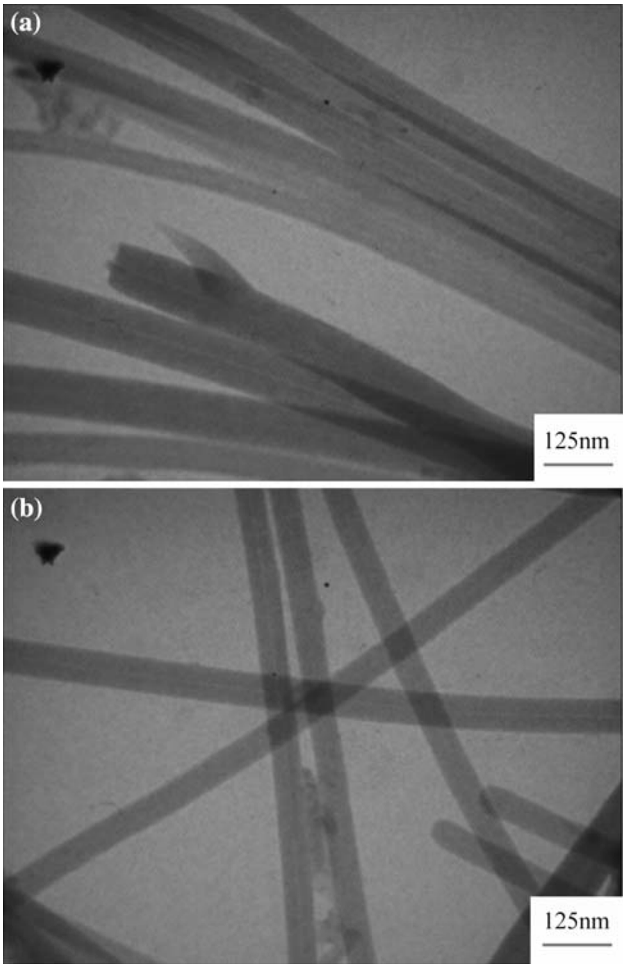

Fig. 1 TEM images of MWNTs prepared by the catalytical pyrolysis method

oven at 50 °C for 48 h to cure. By macrographic observation, it was found that the viscosities of the mixtures of MWNTs, dispersants, butyl acetate, and FEVE are as follows: no dispersant > Anti-Terra®-U > Disperbyk®-140 > Disperbyk®-163 > Disperbyk®-2001 > Disperbyk®-2050. This means that Disperbyk®-2050 improved the MWNTs' wetting effectively and reduced the viscosity significantly, which could make MWNTs uniformly dispersed in FEVE resin and also enable the formation of highly filled concentrates of solid agents. Adding dispersants also avoided thixotropy.

The dispersion of MWNTs in FEVE resin was evaluated by TEM imaging as shown in Fig. 2. Thin sections of MWNT/FEVE nanocomposites for TEM observations were cut from the as-prepared composites under cryogenic conditions using an ultramicrotome with a diamond knife. As can be seen from the TEM images, MWNT aggregations were observed and they did not separate during ultrasonic treatment in FEVE matrix for samples without the addition of dispersants. That is to say, MWNTs were very difficult to disperse in the FEVE resin for the blank sample. The dispersity of MWNTs in FEVE resin was improved by adding dispersants. MWNT aggregations were still found in samples that had addition of Anti-Terra®-U, Disperbyk®-140, but the status has improved. After adding other dispersants, MWNTs could be dispersed well in FEVE matrix. Figure 2f shows that a fine and homogeneous dispersion at almost individual nanotube level of MWNTs was achieved throughout FEVE matrix for samples that had Disperbyk®-2050. The results confirmed that the lower viscosity redounds to dispersion of MWNTs in FEVE resin. Anti-Terra®-U and Disperbyk®-140 are acidic polymer solutions. Disperbyk®-163 and Disperbyk®-2001 are copolymer solutions with pigment affinic groups, while Disperbyk®-2050 is an acrylate copolymer solution with basic pigment affinic groups. Those kinds of high molecular weight wetting and dispersing additives adsorb on surface of MWNTs and prevented reflocculation and aggregation of MWNTs via steric hindrance and made MWNTs disperse in the resin. The polymer in Anti-Terra®-U and Disperbyk®-140 could not be absorbed firmly on the surface of MWNTs due to the repulsion force between their and MWNTs' acidic groups. The basic affinic groups in Disperbyk®-2050 could react with oxygen-containing groups (–COOH and –OH) on the wall of MWNTs. Those high molecular polymers could be encapsulated on the surface of MWNTs firmly, which stabilizes further MWNTs in FEVE resin and obstructs the aggregation of MWNTs effectively. That is the reason why the mixture adding Disperbyk®-2050 had the lowest viscosity and MWNTs could disperse well in FEVE matrix.

Tensile properties were acquired by an Instron model DXLL 1000–20000 testing machine at a speed of 10 mm/min. Specimens with dumbbell shape for tensile test were cut from the films that were prepared on the polyester films substrates. The polyester films were peeled off before test. A 30-mm benchmark and the original cross-sectional area were utilized to calculate their tensile properties. The tensile properties of the MWNT/FEVE nanocomposite coatings are listed in Table 1. The tensile strengths and fracture strains were obtained using the average of five obtained values. As we can see, the tensile strength of the MWNT/FEVE coatings without adding dispersant is only 6.03 MPa. After adding the dispersants, the tensile strength of the coatings is improved. The tensile strengths have positive correlation with the viscosities of MWNT/FEVE mixtures before cure. By adding a Disperbyk®-2050, the tensile strength can reach 20.94 MPa, which is about three times larger than that of the sample without adding a dispersant. These results suggest that the dispersion of MWNTs in matrix is one of the most important factors that affect the properties of nanocomposites, and Disperbyk®-2050 is an excellent dispersant for MWNT/FEVE nanocomposites.

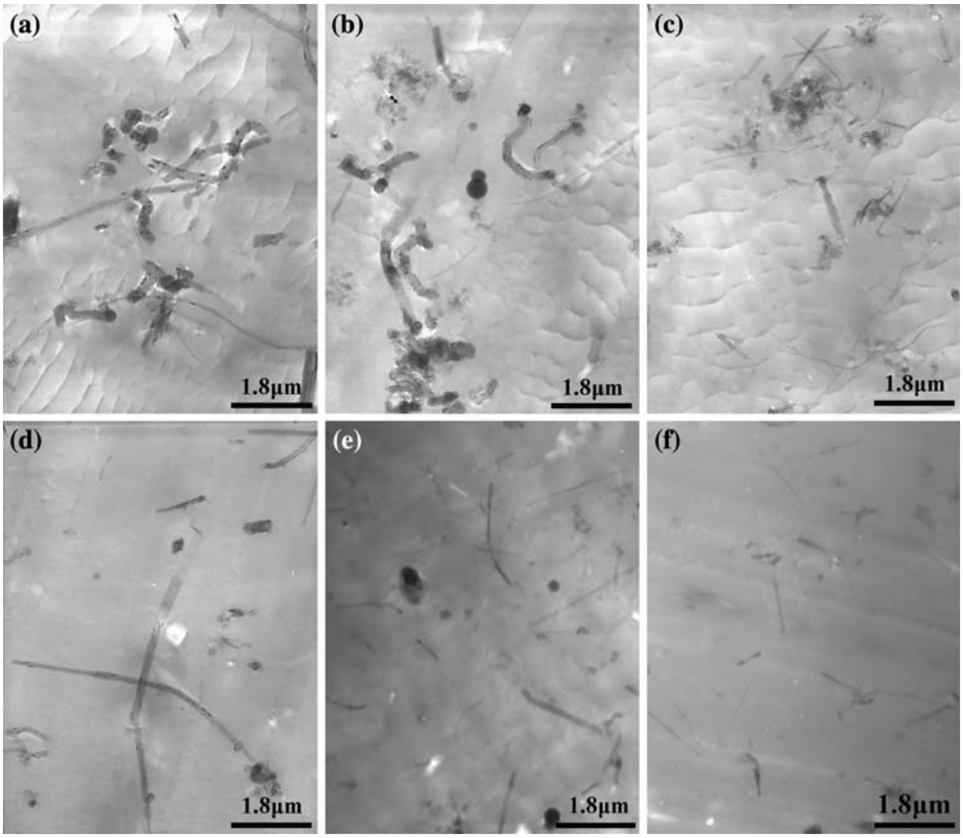

Fig. 2 TEM images of MWNT/FEVE nanocomposites with the addition of different dispersants (**a**) Blank, (**b**) Anti-Terra®-U, (**c**) Disperbyk®-140, (**d**) Disperbyk®-163, (**e**) Disperbyk®-2001, (**f**) Disperbyk®-2050

Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 thermogravimetric analyzer. The TGA samples were placed in aluminum crucibles and heated from the ambient to 600 °C under a nitrogen atmosphere (10 mL/min) at a heating rate of 10 °C/min. Figure 3 shows the TGA curves of MWNT/FEVE nanocomposites with the addition of different dispersants. As shown in this figure, there is only a little difference between each TGA curve, which indicates that the dispersants have only a little effect on decomposition temperature of the nanocomposites. The onset decomposition temperatures of nanocomposites are all about 300 °C, which was the decomposition temperature of FEVE resin. The results show the high thermal stability of FEVE resin. The decomposition temperature of the nanocomposite with Disperbyk®-2050 is a little higher than that of other nanocomposites. We define the half-weight loss as a marker for structural decomposition of the samples. The thermal decomposition temperatures of nano-composites with no dispersant, Anti-Terra®-U, Disperbyk®-140, Disperbyk®-163, Disperbyk®-2001, and Disperbyk®-2050 are 336.1 °C, 336.3 °C, 339.0 °C, 340.0 °C, 340.7 °C, and 344.1 °C, respectively. The difference shows that the dispersity of MWNTs in FEVE resin has some effect on thermal property of the nanocomposites and the addition of

Table 1 Tensile properties of MWNT/FEVE nanocomposite coatings with the addition of different dispersants

Dispersants	Tensile strength (MPa)	Elongation (%)
No dispersant	6.03	26.31
Anti-Terra®-U	8.55	57.51
Disperbyk®-140	10.45	16.11
Disperbyk®-163	11.61	38.22
Disperbyk®-2001	14.72	23.21
Disperbyk®-2050	20.94	4.98

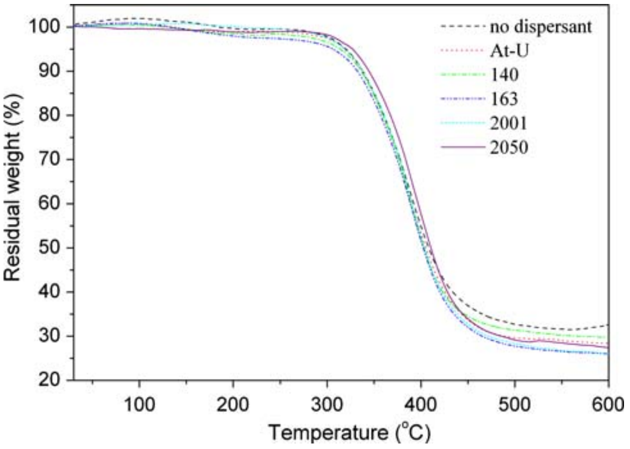

Fig. 3 TGA curves of MWNT/FEVE nanocomposites with the addition of different dispersants

Disperbyk®-2050 could improve the thermal stability of the MWNT/FEVE nanocomposite to some extent although it is not very obvious.

In conclusion, CNTs/FEVE nanocomposites with the addition of different dispersants were prepared. Dispersants decreased the viscosities of FEVE paints. Good-dispersion at individual MWNT level was achieved after adding Disperbyk®-2050. The tensile strength of MWNT/FEVE nanocomposite with the addition of Disperbyk®-2050 is 20.94 MPa, i.e., about 2.5 times larger than the value of the sample without adding the dispersant, and the decomposition temperature also improved from 336.1 °C to 344.1 °C.

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