HAL
open science

Effect of Palmitic Acid on the Electrical Conductivity of Carbon Nanotubes–Epoxy Resin Composites

Sophie Barrau, Philippe Demont, Emile Perez, Alain Peigney, Christophe Laurent, Colette Lacabanne

To cite this version:

Sophie Barrau, Philippe Demont, Emile Perez, Alain Peigney, Christophe Laurent, et al.. Effect of Palmitic Acid on the Electrical Conductivity of Carbon Nanotubes–Epoxy Resin Composites. Macromolecules, 2003, vol. 36, pp. 9678-9680. 10.1021/ma030399m . hal-00920397

HAL Id: hal-00920397

https://hal.science/hal-00920397v1

Submitted on 18 Dec 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Open Archive TOULOUSE Archive Ouverte (OATAO)
OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : http://oatao.univ-toulouse.fr/
Eprints ID : 10549

To link to this article : DOI:10.1021/ma030399m
URL : http://dx.doi.org/10.1021/ma030399m

To cite this version :
Barrau, Sophie and Demont, Philippe and Perez, Emile and Peigney, Alain and Laurent, Christophe and Lacabanne, Colette *Effect of Palmitic Acid on the Electrical Conductivity of Carbon Nanotubes−Epoxy Resin Composites.* (2003) Macromolecules, vol. 36 (n° 26). pp. 9678-9680. ISSN 0024-9297

Any correspondance concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Effect of Palmitic Acid on the Electrical Conductivity of Carbon Nanotubes−Epoxy Resin Composites

Sophie Barrau,*,† Philippe Demont,† Emile Perez,‡ Alain Peigney,§ Christophe Laurent,§ and Colette Lacabanne†

L2P, CIRIMAT, UMR CNRS 5085, Université Paul Sabatier, 31062 Toulouse Cedex 4, France; IMRCP, UMR CNRS 5623, Université Paul Sabatier, 31062 Toulouse Cedex 4, France; and LCMIE, CIRIMAT, UMR CNRS 5085, Université Paul Sabatier, 31062 Toulouse Cedex 4, France

Introduction. Carbon nanotubes (CNTs) have recently received much attention due to their striking mechanical and electrical properties. Because of their structure and low dimensionality, they have a wide range of potential applications, especially as fiber reinforced composites. For this application, some electrical conductivity is required to provide electrostatic discharge. To allow a conductive path inside the polymer matrix (percolation), a homogeneous network of conductive filler particles is needed. It has been demonstrated that the percolation threshold is directly related to the dispersion of the fillers in the polymer matrix,[1] and to overcome their agglomeration still remains a challenge. Recent experimental studies have shown that use of CNTs as conductive fillers in a polymer matrix implies a very low percolation threshold.[2−6]

The use of surfactants as processing aids in carbon nanotubes−polymer composites was already described.[7] We report here for the first time the key role of amphiphilic molecules like palmitic acid ($C_{16}H_{32}O_2$) on the dispersion of CNTs. Furthermore, we define an optimum concentration of palmitic acid in composites to obtain the lower percolation threshold.

In the literature, there are few examples of the use of surfactant to disperse CNTs in a polymer solution. Vigolo et al.[8] have found in poly(vinyl alcohol) (PVA) solutions an optimal concentration at which the electrostatic repulsion, provided by adsorbed sodium dodecyl sulfate (SDS), stabilizes the CNTs against the van der Waals attraction. Furthermore, only polyoxyethylene 8 lauryl ($C_{12}EO_8$) was used to study the nonionic surfactant effect on the thermomechanical properties of carbon nanotube−polymer composites.[7]

Here, the choice of the amphiphilic molecule is very important because of its ability to disperse the CNTs in the polymer matrix. The hydrophobic part is absorbed onto the nanotube surface. The hydrophilic headgroup induces electrostatic repulsions between nanotubes, preventing their aggregation. So, it is important to optimize the amphiphilic molecules concentration in the composite to obtain the best dispersion of carbon nanotubes in the epoxy matrix. Among the amphiphilic molecules suited for this purpose, the choice was limited because of the necessity to use soluble amphiphilic molecules in an organic phase. For all these reasons, we have selected a fatty acid with a medium chain length: the palmitic acid ($C_{16}H_{32}O_2$). Then, the composite samples with palmitic acid are compared with samples without palmitic acid throughout SEM images and electrical conductivity measurements.

Experimental Section. a. Materials and Sample Preparation. Carbon nanotubes were synthesized by a catalytic chemical vapor deposition (CCVD).[9] A $Mg_{0.95}Co_{0.05}O$ solid solution prepared by combustion was reduced under a H_2-CH_4 atmosphere. At high temperature (1000 °C), the reduction provided very small transition metal (Co) nanoparticles. The decomposition of CH_4 provided the carbon necessary for the growth of CNTs from catalyst nanoparticles of cobalt. A CNTs−Co−MgO composite powder was then obtained. An acid attack (HCl, 1 mol L^{-1}) dissolved MgO and partly Co, without damage tubes.[10] The CNTs−Co−MgO composite powder in HCl was sonicated for 15 min and afterward allowed to rest for 24 h; CNTs were obtain in suspension. More than 80% of CNTs have one or two walls with an average diameter of 2.4 nm.

A commercially available bisphenol A type epoxy resin (LY5641, Hexcel Composites) was used as a prepolymer. As a curing agent, an amine hardener (HY2954, Hexcel Composites) was used according to the manufacturer's recommended resin/curing agent weight ratio 100/35. The density of epoxy resin is close to 1.2 g cm^{-3}, and the carbon nanotubes average density is about 1.8 g cm^{-3}. Then, CNTs volume fraction corresponds to the two-thirds of the weight fraction.

The palmitic acid ($C_{16}H_{32}O_2$) has an hydrophobic part (long alkyl chain: $CH_3-(CH_2)_{14}-$) and an acid hydrophilic headgroup (−CO−OH).

A suitable experimental processing assisted by amphiphilic molecules was set up. After an acid attack, CNTs were obtained in suspension in HCl and next in suspension in H_2O after successive washings. CNTs were not dried to prevent their agglomeration in bundles. After a first sonication, epoxy resin was added and the mixture was sonicated again for 1 h. The mixture was then dried in a vacuum oven at 100 °C for 1 h in order to completely evaporate the water. Palmitic acid was added, and the obtained mixture was sonicated for 1 h at ambient temperature. The ratio of nanotube to palmitic acid varied from 1:2 to 2:1 by weight. Hardener was then added and mechanically mixed. The final mixture was poured into a Teflon mold and cured in an oven at 120 °C for 20 min and 145 °C for 4 h. Pellets of composites of 10 mm diameter and 1 mm thick were obtained. CNTs−$C_{16}H_{32}O_2$−epoxy composite samples were prepared by varying the content of CNTs between 0.05 and 0.8 wt % and the CNTs to palmitic acid weight ratio from 1:2 to 2:1.

The CNTs dispersion within the epoxy matrix was observed by field emission scanning electron microscopy (SEM). CNTs−$C_{16}H_{32}O_2$−epoxy composites samples were fractured at the liquid nitrogen temperature and examined without metallization at a low acceleration voltage (2.5 kV).

b. Conductivity Measurements. Electrical conductivity measurements were carried out by recording the complex conductivity $\sigma^*(\omega)$ using a Solartron-Schlumberger frequency response analyzer together with a

† L2P, CIRIMAT, UMR CNRS 5085.
‡ IMRCP, UMR CNRS 5623.
§ LCMIE, CIRIMAT, UMR CNRS 5085.
* Corresponding author: Fax 33-5-61 55 62 21; e-mail sophie.barrau@cict.fr.

Table 1. Electrical dc Conductivity σ_{dc} of CNTs−$C_{16}H_{32}O_2$−epoxy Composites at Different CNTs to $C_{16}H_{32}O_2$ Weight Ratio

	σ_{dc} (S cm^{-1}) for CNTs to $C_{16}H_{32}O_2$ weight ratio		
CNTs (wt %)	2:1	1:1	1:2
0.1	3.6×10^{-16}	1.7×10^{-8}	3.0×10^{-16}
0.2	2.8×10^{-9}	7.1×10^{-7}	9.7×10^{-8}
0.4	1.4×10^{-6}	1.1×10^{-5}	8.2×10^{-6}

Novocontrol interface (broad-band dielectric converter). The measurements were carried in the frequency range between 10^{-2} and 10^6 Hz at room temperature. The real part, $\sigma'(\omega)$, of the complex conductivity $\sigma^*(\omega)$ was investigated. The dc conductivity σ_{dc} was taken as the value of $\sigma'(\omega)$ at 10^{-2} Hz.

Results and Discussion. The dc conductivity of the different composite samples is reported in Table 1 as a function of the weight ratio of CNTs to palmitic acid. The conductivity of the composites depends strongly on the palmitic acid concentration. Among the three used CNTs's weight fraction, the composite with 1:1 as CNTs to palmitic acid ratio displays the highest dc conductivity. At 0.1 wt % CNTs, a variation of 8 orders of magnitude is obvious according to the palmitic acid content. We assume that the measured conductivity value is taken as a criterion of the dispersion state. The 1:1 ratio provides the highest conductivity value at which we associate the best CNTs dispersion. Therefore, the optimum CNTs to $C_{16}H_{32}O_2$ weight ratio has taken as 1:1.

Figure 1a shows the SEM image of the CNTs−$C_{16}H_{32}O_2$−epoxy composite for 0.8 wt % CNTs and 1:1 CNTs to palmitic acid weight ratio. Well-separated individual CNTs, of a diameter about 2−3 nm, are clearly observed as indicated by the white arrows A. CNTs are homogeneous dispersed in the epoxy matrix, confirming that amphiphilic molecules used are efficient as dispersing agent. The SEM image also reveals some nanotubes covered by the amphiphilic molecules, indicated by the white arrows B. During the fracture of the composite at the liquid nitrogen temperature, the breaking occurs at either the amphiphilic molecules−polymer interface or the amphiphilic molecules−CNTs interface. Without palmitic acid, SEM images (Figure 1b) shows bundles of CNTs with diameter about 30−40 nm.

The dc conductivity value of the pristine epoxy resin is only 7.9×10^{-16} S cm^{-1}. σ_{dc} strongly increases with addition of a low weight content of CNTs. As shown in Figure 2, a sharp increase of conductivity is observed between 0.05 and 0.1 wt % or 0.03 and 0.06 vol % of CNTs. The dc conductivity increases by 8 orders of magnitude and reaches 7×10^{-5} S cm^{-1} for 0.8 wt %. This behavior is indicative of a percolation phenomena in CNTs−$C_{16}H_{32}O_2$−epoxy composites. At the percolation threshold p_c, CNTs form the first active pathway of conducting fillers. A such low value of percolation threshold is explained by the very high aspect ratio of CNTs.

Balberg et al.[11] defined a relationship between the aspect ratio L/r and percolation threshold in the isotropic case of randomly sticks: $(L/r)p_c \approx 3$ where L and r are respectively the length and the radius of an individual nanotube. According to a percolation threshold lying between 0.03 and 0.06 vol %, the expected aspect ratio is then between 5000 and 10 000, close to the value of individual CNTs (5000−50 000). Thus, the conduction

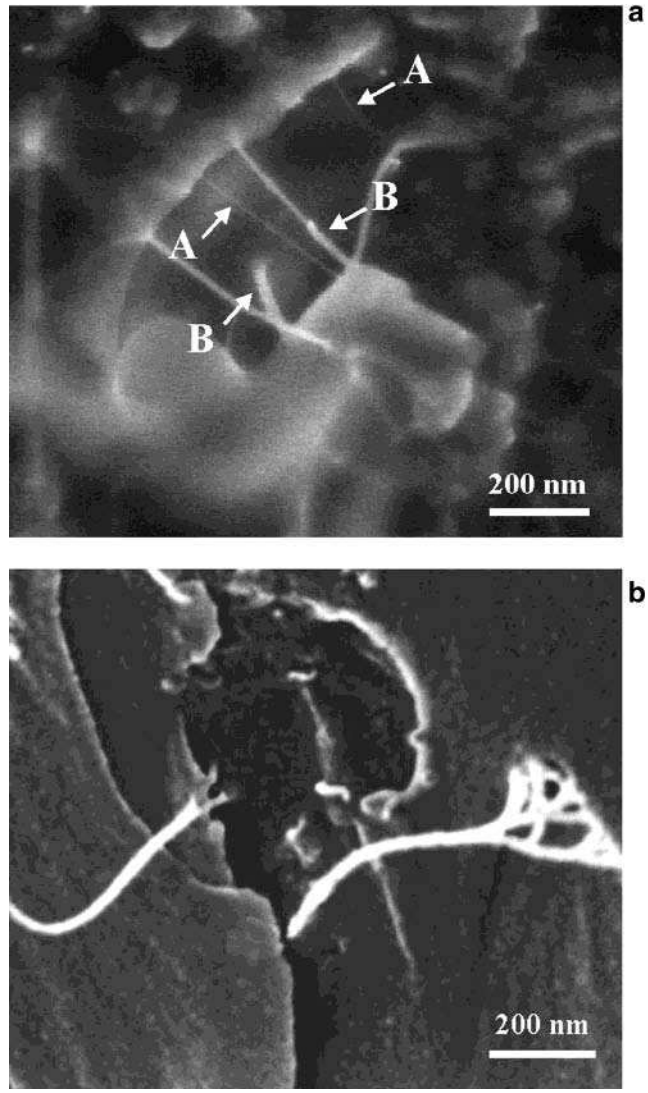

Figure 1. (a) Field emission SEM images of CNTs−$C_{16}H_{32}O_2$−epoxy composite for 0.8 wt % CNTs and 1:1 CNTs to $C_{16}H_{32}O_2$ weight ratio. The arrows indicate (A) individual CNTs and (B) CNTs covered with palmitic acid. (b) Field emission SEM images of CNTs−epoxy composite for 0.8 wt % CNTs without palmitic acid. The scale bar corresponds to 200 nm.

in CNTs−$C_{16}H_{32}O_2$−epoxy composites is essentially carried out through individual CNTs. This result is in agreement with SEM image; the composite contains a great number of individual CNTs.

Figure 2 shows also a comparison of the CNTs content dependence of the conductivity in composites with and without palmitic acid, elaborated according to the same experimental process. Palmitic acid addition allows to disperse a larger proportion of CNTs because the resulting electrostatic repulsion prevent the bundles formation. CNTs are then mainly individual nanotubes that leads to a reduction of the percolation threshold by two. Above the percolation threshold, the dc conductivity increases by 1 order of magnitude. For 0.8 wt % CNTs, the dc conductivity is 7.3×10^{-6} S cm^{-1} for the composite without palmitic acid whereas with palmitic acid σ_{dc} is then 6.9×10^{-5} S cm^{-1}. Using palmitic acid as an amphiphilic molecule allows to improve the electrical conductivity of CNTs−polymer composites.

Conclusions. In summary, we found that the palmitic acid allows an efficient dispersion of carbon nanotubes in the epoxy matrix. We have set up an experi-

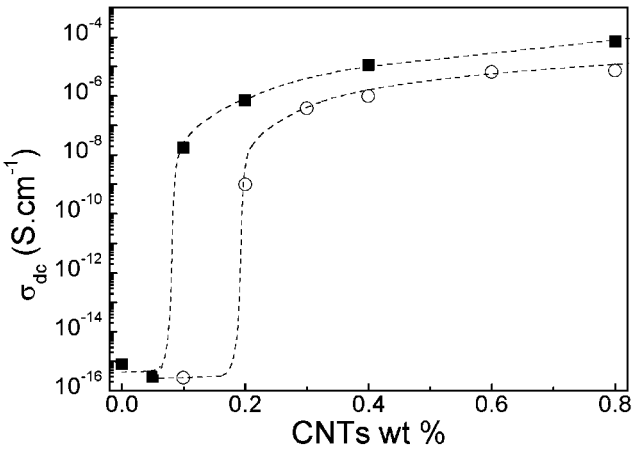

Figure 2. Comparative plot of the dc conductivity dependence on the CNTs content at room temperature (■) with palmitic acid at 1:1 CNTs to $C_{16}H_{32}O_2$ weight ratio and (○) without palmitic acid. Dashed lines connecting symbols are guides for the eyes.

mental protocol in order to enhance the CNTs dispersion in epoxy resin. Electrical conductivity is optimal using a 1:1 CNTs to palmitic acid weight ratio. The associated percolation threshold is found between 0.05 and 0.1 wt % CNTs, i.e., between 0.03 and 0.06 vol %. The SEM image shows essentially individual CNTs which is in agreement with conductivity measurements. In comparison with composites without palmitic acid, the use of palmitic acid improves the electrical properties of CNTs−epoxy resin composites.

References and Notes

(1) Roldughin, V. I.; Vysotskii, V. V. *Prog. Org. Coat.* **2000**, *39*, 81.
(2) Benoit, J.-M.; Corraze, B.; Lefrant, S.; Blau, W. J.; Bernier, P.; Chauvet, O. *Synth. Met.* **2001**, *121*, 1215.
(3) Stephan, C.; Nguyen, T. P.; Lahr, B.; Blau, W.; Lefrant, S.; Chauvet, O. *J. Mater. Res.* **2002**, *17*, 396.
(4) Kilbride, B. E.; Coleman, J. N.; Fraysse, J.; Fournet, P.; Cadek, M.; Drury, A.; Hutzler, S.; Roth, S.; Blau, W. J. *J. Appl. Phys.* **2002**, *92*, 4024.
(5) Barrau, S.; Demont, P.; Peigney, A.; Laurent, Ch.; Lacabanne, C. *Macromolecules* **2003**, *36*, 5187.
(6) Sandler, J. K. W.; Kirk, J. E.; Kinloch, I. A.; Shaffer, M. S. P.; Windle, A. H. *Polymer* **2003**, *44*, 5893.
(7) Gong, X.; Liu, J.; Baskaran, S.; Voise, R. D.; Young, J. S. *Chem. Mater.* **2000**, *12*, 1049.
(8) Vigolo, B.; Penicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P.; Poulin, P. *Science* **2000**, *290*, 1331.
(9) Flahaut, E.; Peigney, A.; Laurent, Ch.; Rousset, A. *J. Mater. Chem.* **2000**, *10*, 249.
(10) Bacsa, R. R.; Laurent, Ch.; Peigney, A.; Bacsa, W. S.; Vaugien, Th.; Rousset, A. *Chem. Phys. Lett.* **2000**, *323*, 566.
(11) Balberg, I.; Anderson, C. H.; Alexander, S.; Wagner, N. *Phys. Rev. B* **1984**, *30*, 3933.