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Novel nanocomposites using carbon nanotubes and melamine–formaldehyde

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The present work deals with a novel, ternary nanocomposite containing single-wall nanotubes (SWNTs), cellulose, and melamine-formaldehyde (MF). Thin sheets are assembled from α-cellulose papers, on which SWNT/MF has been deposited in liquid form, and next hot pressed without venting. The material is transparent/tinted. Dispersion/morphology was characterised by means of transmission electron microscopy (TEM) on ultramicrotome slices cut across a moulded sheet. Isolated thin bundles/nanotubes are found. They are oriented off the slice plane. TEM images of such cross-sections are presented. In-plane nanotubes are also present. The discussed SWNT/cellulose/MF nanocomposite is being developed towards multifunctional coatings.

Key words: *single-wall nanotube; melamine–formaldehyde; multifunctional coating nanocomposite*

1. Introduction

Discoveries in the field of cluster science, particularly in carbon species, are paving the way to new areas of materials science and new technologies. A carbon single -wall nanotube (SWNT) is formed by a hexagonal network of carbon atoms (graphene) rolled up seamlessly on a cylinder of radius *R* with various helicities. A multiwall nanotube (MWNT) is a collection of concentrically arranged SWNTs.

Advances in the production and purification of carbon nanotubes allow us to expect a simultaneous further price decrease and widening range of applications. Probably, the main application of nanotubes today is in polymeric matrix composites. Various polymeric matrices have been used by many researchers worldwide. Epoxy resins and poly(methyl methacrylate) (PMMA) have been frequently used [1]. Nanotube composites have been overviewed in several papers [2–8]. The relatively early stage of development, great expectations, and a bright future for nanotube composites have

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been stated in the literature [9]. Carbon nanotube/melamine–formaldehyde (MF) composites have not been developed, in spite of the wide use of MF.

MF is a water-based amino resin with excellent mechanical, thermal, and coating properties, as well as appearance, and thus MF is extensively used for coating purposes. Processing characteristics are favourable. This resin offers a relatively short cycle time. Its disadvantage, however, is the release of water during production, thus there is a need of mould venting. Besides, formaldehyde is emitted, though this can be reduced with new low emission grades. In this work, we will adapt a non-vented hot pressing technique, used by us earlier, to prepare carbon fibre and carbon black filled MF [10, 11], and will prepare thin sheets of SWNT/cellulose/MF, with multifunctional coatings/laminates in mind.

2. Experimental

2.1. Materials

Madurit Mw 909 (50 wt. % solid content) from UCB (Denmark) and SWNT crude material from CarboLex (USA) were used. The supplied material contained approximately 50-70% of single-wall, closed-ended carbon nanotubes 1.4 nm in diameter (average value), produced by the arc discharge method, as given by the producer. In order to remove impurities (mainly amorphous carbon and catalyst particles), the crude material was purified by an oxidative process – the pristine material was refluxed in nitric acid under magnetic stirring at 110–120 °C for 24 h, followed by filtration through a 0.2 μm PTFE membrane filter, and washed with distilled water.

Purified carbon nanotubes were added to a 50 wt. % aqueous solution of MF. Two concentrations (0.5 and 1.5 wt. %) were used. Mild sonication was applied. The obtained dispersion was used as follows: 50 g/m^2 α-cellulose papers were impregnated with SWNT/MF, stacked and hot pressed at 150 °C and 4 MPa for 10 min. The use of cellulose was motivated by its two main functions: cellulose acts as an absorbing substrate, thus allowing hot pressing without venting, and cellulose practically removes the propensity of MF to microcracking.

2.2. TEM imaging

After the purification, single-wall nanotubes were characterised by transmission electron microscopy, using a Zeiss 912 Omega instrument. A small amount of SWNTs were dispersed in ethanol, sonicated for a few minutes, and then deposited on a copper grid coated with a holey carbon film.

SWNT/cellulose/MF samples were ultramicrotomed using a Reichert–Jung Ultracut E instrument. Slices 0.15 μm thick were cut with a diamond knife moving across the sheet. Slices were studied to determine the degree of nanotube dispersion and other characteristics using a Zeiss 912 Omega instrument.

3. Results and discussion

The obtained composites were transparent and tinted, and were not microcracked. They are shown in Figure 1 where rather good transparency can be noticed (the print is visible through the nanocomposite layer).

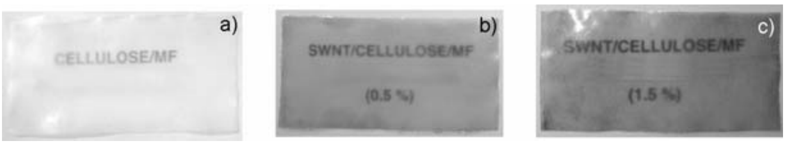

Fig. 1. SWNT/cellulose/MF composites: a) cellulose/MF (without nanotubes), b) SWNT/cellulose/MF with 0.5 wt. % nanotubes, c) SWNT/cellulose/MF with 1.5 wt. % nanotubes

A TEM image of purified single-wall carbon nanotubes is shown in Figure 2.

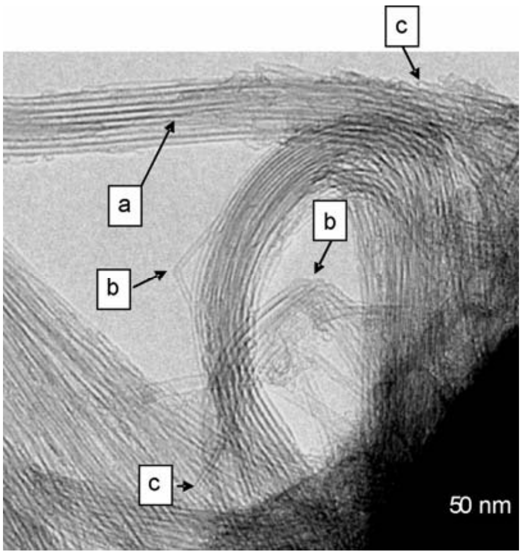

Fig. 2. TEM image of purified SWNTs: a) seemingly endless rope, b) isolated SWNT forming a knee, c) isolated SWNT end

Most of the carbon and catalyst impurities are removed. It can be seen that SWNTs are mainly entangled, forming seemingly endless ropes (arrow a), this type of nanotube architecture being typically mentioned in the literature. Also, isolated nanotubes are found (arrow b). For isolated nanotubes, or even for thin bundles, knees are present (arrow b). Nanotube ends are found both when the nanotube is not aligned with a rope and when it is aligned (arrow c).

TEM images of the nanocomposite are shown in Fig. 3.

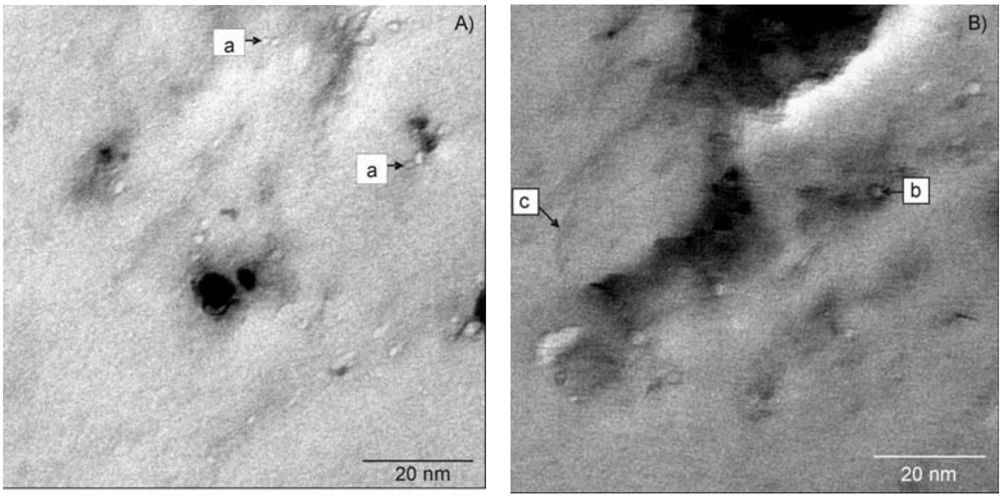

Fig. 3. TEM images of ultramicrotomed SWNT/cellulose/MF composite: A) pairs of off-plane nanotubes (arrow a) are seen. B) off-plane isolated nanotubes (arrow b) and in-plane nanotubes (arrow c) are seen

TEM imaging of this material is rather difficult. Nevertheless, in Figure 3 isolated nanotubes and occasionally pairs of nanotubes can be observed (arrows b and a, respectively). In Figure 3B, microdispersion is seen both for off-plane (refers to the slice) and in-plane nanotubes (arrows b and c, respectively). Interestingly, off-plane nanotubes occasionally assemble in thin bundles of two nanotubes (arrow a). Also, the ultramicrotome slices shown in Figure 3 contain cross-sectional images of nanotubes (arrows a and b). This behaviour can be contrasted with the well known behaviour published in literature, where nanotubes are aligned in the direction of the knife movement. We suggest that high matrix-nanotube interfacial shear strength and high shear strength of the matrix close to the nanotube play a role. Poor adhesion and low polymer strength would more likely cause a nanotube pull-out and the crack to deflect at the nanotube-matrix interface, both favouring nanotube alignment in the direction of the knife movement. The lighter shade inside the cross-sectional images suggests the nanotubes are un-filled. Areas of non-dispersed nanotubes are also present in the composite, as can be seen in Figure 3.

4. Conclusions

Ternary composites containing SWNTs, cellulose, and melamine-formaldehyde were prepared. Thin sheets were produced by hot pressing without venting of stacked α-cellulose papers, on which liquid SWNT/MF was deposited by dipping. The obtained material is transparent and tinted. Ultramirotome slices cut across the sheet were possible to obtain. Dispersion characteristics and morphologies were tested by TEM, and TEM images of nanotubes are shown. TEM imaging of the present nanocomposite is rather difficult, nevertheless in-plane nanotubes (with respect to the slice), and off-plane thin bundles of two nanotubes and isolated nanotubes were possible to find. Their cross-sectional images are rather unusually contained in the TEM image. The latter behaviour, we suggest, is a result of high nanotube-matrix interfacial shear strength and high shear matrix strength in the vicinity of nanotubes. On the whole, nanotube concentration in the matrix was not uniform. Further work towards uniformity is needed in order to develop the material for multifunctional coatings.

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References

[1] RYCHWALSKI R.W., MCQUEEN D.H., VOIGT B., LICEA-JIMÉNEZ L., PIC A., ROUXEL D., *New polymeric micro- and nanocomposites*, Symposium Materials-Energy Supply-Society and Environment, 13 December 2003, Chalmers University of Technology, Göteborg, Sweden.
[2] THOSTENSON E.T., REN Z., CHOU T.W., Comp. Sci. Technol., 61 (2001), 1899.
[3] LAU K.T. HUI D., Composites Part B: Engineering, 33 (2002), 263.
[4] NJUGUNA J., PIELICHOWSKI K., Adv. Eng. Mater., 5 (2003), 769.
[5] NJUGUNA J., PIELICHOWSKI K., Adv. Eng. Mater., 6 (2004), 204.
[6] ANDREWS R., WEISENBERGER M.C., Current Opinion Solid State Mater. Sci., 8 (2004), 31.
[7] BAUGHMAN R.H., ZHAKIDOV A.A., DE HEER W. A., Science, 297 (2002), 787.
[8] HARRIS P.J.F., Internat. Mater. Rev., 49 (2004), 31.
[9] Schaffer M. and Kinloch I.A., Comp. Sci. Technol., 64 (2004), 2281.
[10] VOIGT B., RYCHWALSKI, R.W., MCCARTHY D.M.C., DEN ADEL J.C., MARISSEN R., Polymer Composites, 24 (2003), 380.
[11] VOIGT B., ROUXEL D., MCQUEEN D.H., RYCHWALSKI R.W., Polymer Composites, 26 (2005), 144.

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