

Optical microstructure and viscosity enhancement for an epoxy resin matrix containing multiwall carbon nanotubes

S. S. Rahatekar,¹⁾ K. K. K. Koziol,¹⁾ S. A. Butler,²⁾ J. A. Elliott,¹⁾
M. S. P. Shaffer,³⁾ M. R. Mackley,^{2),a)} and A. H. Windle¹⁾

¹⁾*Department of Materials Science and Metallurgy, University of Cambridge, CB2 3QZ, United Kingdom*

²⁾*Department of Chemical Engineering, University of Cambridge, CB2 3RA, United Kingdom*

³⁾*Department of Chemistry, Imperial College, South Kensington, London, SW7 2AZ, United Kingdom*

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Synopsis

This paper describes rheological measurements and associated optical microstructural observations of multiwall carbon nanotubes (MWCNTs) suspended in an epoxy resin matrix. The base epoxy resin was found to be essentially Newtonian, and the progressive incorporation of nanotubes enhanced the low shear rate viscosity of the suspension by nearly two decades. At higher shear rates, the suspension viscosity asymptotically thinned to the viscosity of the matrix alone. The low shear rate viscosity enhancement was correlated with the optical observations of interconnected aggregates of carbon nanotubes, which themselves were induced by the low shear conditions. Intermediate shear rates resulted in a reduction in the size of the aggregates. High shear rates appeared to cause near-complete dispersal of the aggregates. From these results it is conjectured that for this suspension, shear thinning is connected with the breaking of the interconnected networks between nanotubes and or aggregates of nanotubes, and not by nanotube alignment.
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I. INTRODUCTION

Carbon nanotubes are an exciting and fast developing class of material with a wide range of potentially interesting product applications relating to areas such as mechanical, electrical, and thermal property enhancement, (see for example Dresselhaus *et al.*, 1996; Treacy *et al.*, 1996; Lu, 1997; Harris, 2001). In order to manufacture products containing carbon nanotubes, the composite suspension has to be processed in some way, and both the rheology and the resulting microstructure of the product will have a significant effect on end user properties.

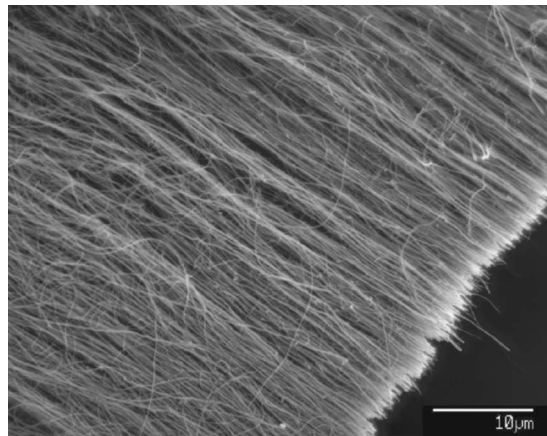
The work described in this paper is concerned with examining the rheology and optical microstructure of a model carbon nanotube system where the nanotubes are sus-

^{a)} Author to whom correspondence should be addressed; electronic mail: mrm5@cam.ac.uk

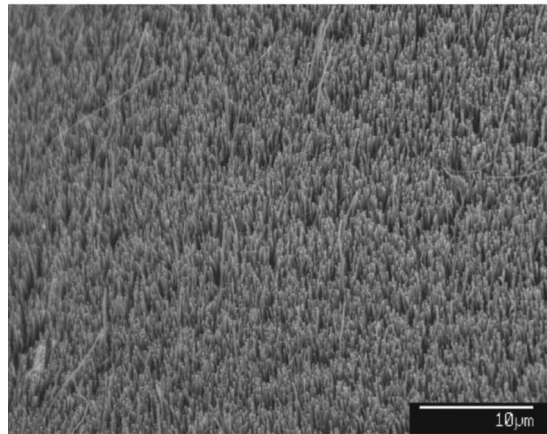
pended in an essentially Newtonian epoxy matrix. The particular carbon nanotubes considered in this paper were manufactured by a technique that gave initially aligned multiwall carbon nanotubes (MWCNTs) (Singh *et al.*, 2003). The flow behavior for a dispersion of this type of functionalized MWCNT in water has been described by Shaffer *et al.* (1999) and Kinloch *et al.* (2002) and viscosity enhancement was reported for nanotube loadings of between 0.4 and 9.5 vol %. In relation to other studies on nanotube suspension rheology, Potschke *et al.* (2002) and Abdel-Goad *et al.* (2005) have studied the rheology of MWCNTs dispersed in polycarbonate, where they reported a step change in viscosity for 2 wt % loading of MWCNTs in polycarbonate at low shear rates. The rheological behavior of MWCNTs in polypropylene, and their corresponding electrical properties as function of shear rate, have been studied by Kharchenko *et al.* (2004). Du *et al.* (2004) reported rheological and electrical properties of carbon nanotubes dispersed in PMMA, where they found that the rheological threshold for increase in the G' and G'' is smaller than the percolation threshold of electrical conductivity. Recently, Xu *et al.* (2005) again reported on the systematic development of viscoelasticity for carbon nanotubes in glycerol/water suspensions, and Shi *et al.* (2005) reported viscoelastic results for single-walled carbon nanotubes (SWNT) in uncrosslinked poly(propylene fumarate). Hough *et al.* (2004) investigated aqueous suspensions of surfactant stabilized single-wall carbon nanotubes. They found that the SWNT suspensions exhibit a rigidity percolation transition with an onset of solidlike elasticity at a volume of 0.26%. In terms of rheo-optic observations, Hobbie *et al.* (2003), and Lin-Gibson *et al.* (2004) have studied the optical anisotropy and elastic instability in MWCNTs dispersed in polyisobutylene, where some of their findings indicate orientation both along and transverse to the flow direction. Hobbie (2004) also developed a mathematical model for dispersed CNT orientation in a shear flow. For single-wall carbon nanotubes (SWCNT), Davis *et al.* (2004) report a range of different linear viscoelastic responses within a "superacid" matrix depending on whether the nanotubes were in a concentration regime associated with dilute, semidilute, biphasic, or liquid crystal behavior.

The dispersion technique used in this paper was developed for initially aligned MWCNTs in an epoxy resin by Sandler *et al.* (1999), where the goal of their work was to achieve an electrically conducting MWCNT/epoxy composite. In this paper, their dispersion technique was used to prepare material to study the flow behavior and microstructure of the suspension. Carbon nanotubes are semiflexible nanofilaments with a very high aspect ratio (around 600 for the tubes used in this study), and it might be expected that above a critical concentration they would show rheological characteristics related to entangled flexible, semirigid, or rigid polymer fluids. In some carbon nanotube studies the aspect ratio of the nanotubes has been obtained by direct scanning electron microscopy (SEM) or light-scattering techniques [see for example Kinloch *et al.* (2002) and Park *et al.* (2005)]; however, only limited information on fiber length and fiber distribution of lengths was available for the materials tested in this paper.

An objective of this paper was to compare the rheological behavior of MWCNT suspensions with their optical microstructure and establish similarities and differences between past work on other carbon nanotube and polymer systems. The paper starts by describing the production of the MWCNT materials used, and how the rheological experiments were carried out. Rheological experiments and the corresponding changes in the optical microstructures are then described. The paper concludes by discussing the interpretation of these results, and their implications for construction of a micromechanical model for MWCNT-filled epoxy resin systems.



(1a)



(1b)

FIG. 1. SEM micrographs of aligned multiwall carbon nanotubes (MWCNT) 99.9% purity, (OD: 40 nm, ID: 7 nm). (a) Plan view; (b) “end view.” For details on manufacture see Singh *et al.* (2003).

II. MATERIAL AND EXPERIMENTAL DETAILS

MWCNTs were synthesized in the Department of Materials Science in Cambridge using a method described by Singh *et al.* (2003) based on a chemical vapor deposition technique that allows production of highly aligned “carpets” of MWCNTs, as shown in the SEM micrographs in Fig. 1. The high initial alignment of the MWCNTs makes subsequent dispersal of the nanotubes relatively straightforward, as described by Sandler *et al.* (1999). This contrasts with other commercially available MWCNTs, which are highly entangled and can be difficult to disperse. The initially aligned MWCNTs were dispersed in pure epoxy resin (biphenyl-based epoxy, Araldite LY 556, Ciba, without addition of curing agent). The dispersion was carried out using a mechanical stirrer at 1000 rpm for 2 h at 25 °C. The MWCNTs were dispersed in epoxy with a degree of loading from 0.0035 to 0.5 wt %. In terms of nanotube length and diameter, transmission and scanning electron microscopy indicated that the average diameter of MWCNTs was 40 nm. The average length of MWCNTs, as estimated from SEM, was found out to be around 25 μm. Recent work by Huang *et al.* (2006) has shown that the way carbon

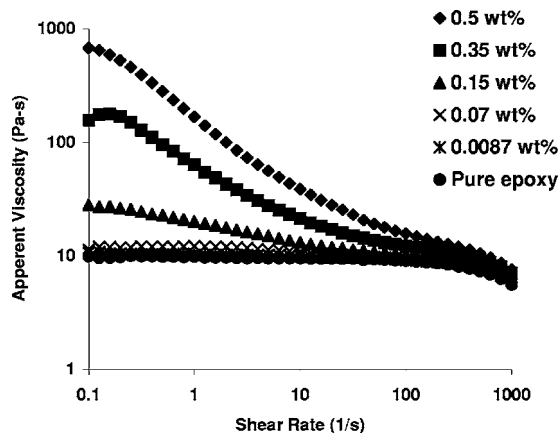


FIG. 2. The variation of apparent viscosity as a function of shear rate for a pure epoxy matrix and epoxy suspensions containing different wt % of MWCNT. The experiments were conducted at 25 °C.

nanotubes are mixed into a suspension can have a significant effect on the resulting rheology of the suspension. In this work the mixing condition was standardized and its effect was not explored.

Rheological measurements were carried out at temperatures of 25 °C to 80 °C, and made using a TA instruments ARES controlled strain rheometer fitted with 50 mm diameter parallel plates. A separation of 0.3 mm between the plates was used for all the experiments.

Optical observations were carried out using a Cambridge Shear System (CSS) microscope stage manufactured by Linkam Scientific Ltd. (Mackley *et al.*, 1999). This consists of two circular glass plates, the bottom of which can be rotated by means of a stepper motor. The gap between the plates can be accurately adjusted to as little as 10 μm . In this work the gap between the plates was set to 300 μm , the same as that used between the parallel plates for the rheology experiments. A sample of the MWCNT epoxy suspension was placed between the plates and sheared by rotating the bottom plate.

III. RESULTS

The base nanotube material is illustrated by two SEM micrographs in Fig. 1. The nanotubes consist of high aspect ratio fibers that have been manufactured in the unentangled state and are highly aligned. This assists in obtaining a relatively uniform dispersion of nanotubes within the pure epoxy matrix. The rheology of both the pure epoxy matrix and the nanotube suspensions is shown in Fig. 2 as a plot of apparent viscosity as a function of shear rate. The data were obtained using a forward shear rate sweep with a measurement time at each shear rate step of 10 s. The results show that the pure epoxy resin is essentially Newtonian at low and intermediate shear rates with a viscosity of about 10 Pa s. At high shear rates the matrix viscosity decreases; this may be caused by other factors such as shear-induced heating. The flow behavior of suspensions with 0.0087 and 0.07 wt % nanotube loading showed little deviation from the pure matrix. However, above this concentration, significant low shear rate viscosity enhancement was observed. Figure 2 shows the data obtained for further nanotube concentrations of 0.15, 0.35, and 0.5 wt % loading, and a progressive increase in the low shear rate apparent viscosity can be seen. For the case of 0.5 wt %, there is nearly a 70-fold increase in the low shear rate viscosity. For all three cases, progressive shear thinning occurs with

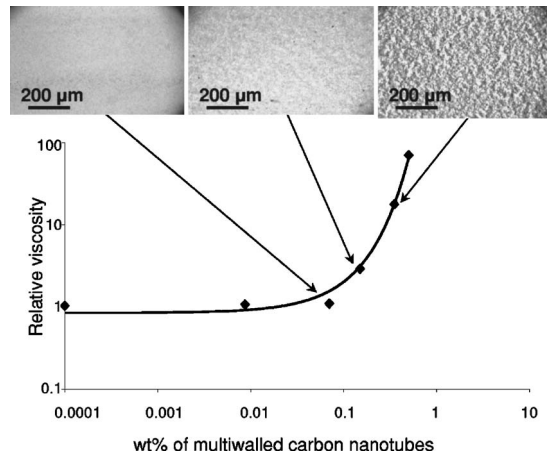


FIG. 3. The variation of “low shear rate” relative viscosity as a function of wt % MWCNT. Low shear rate corresponds to 0.1 s^{-1} . Experimental data as triangles, solid trend line. Micrographs show optical structure at different concentrations taken at shear rate 0.1 s^{-1} .

increasing shear rate and, in addition, the apparent viscosity at high shear rate approaches the asymptotic value of the pure matrix alone. The observed shear thinning behavior follows a Cross-type apparent viscosity curve (Cross, 1965) of the form given by Eq. (1), where the fluid changes from a high Newtonian viscosity at low shear rate through a power-law-type behavior to a lower limiting high shear rate Newtonian viscosity.

$$\eta_a = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{(1 + \alpha \dot{\gamma}^n)}. \quad (1)$$

In Eq. (1), η_0 and η_∞ are the limiting viscosities and α and n are fitting parameters (α and n were found to be 3.5 and 1, respectively, for 0.5 wt % of MWCNTs dispersion).

The way in which the low shear rate relative viscosity of the nanotube suspension changes with wt % concentration of tubes is shown in Fig. 3, together with typical optical micrographs of the observed textures. The graph shows the progressive increase in the low shear rate viscosity above a critical concentration, and the optical micrographs indicate that aggregates of carbon nanotubes are present. We believe that the rheology of the suspension could be linked to the aggregate size and the interconnections between the aggregates. The size of the aggregate structures of the nanotubes increases with increasing concentration and from the optical micrographs it is possible to estimate the area fraction that the aggregates occupy. At certain critical loading fraction the aggregates of the MWCNTs interact with each other, and form an interconnected network of aggregates. This network of interconnected aggregates offers resistance to deformation and hence an increase in viscosity is observed above this critical point.

The critical concentration at which the relative viscosity starts to significantly increase for carbon nanotube systems has similar values to that found for the critical concentration of polymer systems (Graessley *et al.*, 2004). A very small amount of carbon nanotubes is capable of occupying a large volume in the suspension (i.e., they have very high hydrodynamic volume) and from the data reported here the critical concentration for overlap of nanotube aggregates is of the order of 0.1 wt %. In this study we have not made a detailed investigation of the exact value of the critical concentration.

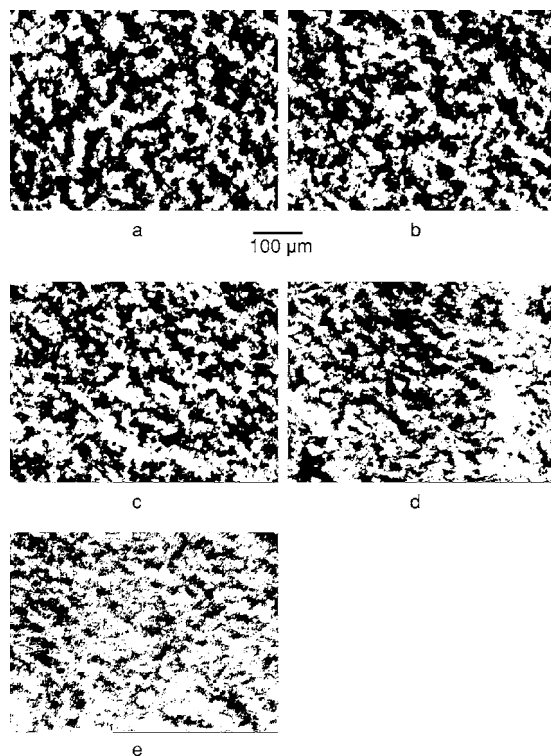


FIG. 4. Binary images of optical micrographs showing nanotube aggregate size (black region) as a function of the shear rate for 0.35 wt % MWCNTs suspension. (a) 1 s^{-1} ; (b) 5 s^{-1} ; (c) 10 s^{-1} ; (d) 50 s^{-1} ; (e) 100 s^{-1} .

The optically observed nanotube aggregate size was found to be sensitive to the applied shear rate, as shown in Fig. 4 for the 0.35 wt % nanotube suspensions for a series of different shear rates. As the shear rate is increased, the size of the aggregates decreases and the level of interconnection between aggregates also appears to decrease (implying that the MWCNT aggregates seem to be broken down under shear into a more uniform dispersion). This effect is difficult to capture with still photographs and is more easily seen from video sequences. The photographs shown in Fig. 4 were taken immediately after shear at the appropriate shear rate. The photographs are then converted into binary images using IMAGE J software (<http://rsb.info.nih.gov/ij/>). The experimental observations indicate that the shear thinning behavior of the nanotube suspension is related to the size and state of interconnection of the nanotube aggregates.

Unlike some polymer solutions, the behavior of this material appeared to show little hysteresis. Figure 5 shows the results obtained from successive shear rate sweeps. In the first experiment the shear rate was increased from 0.1 to 1000 s^{-1} . This was immediately followed by a second experiment where the shear rate was decreased from 1000 to 0.1 s^{-1} . As can be seen, the data superimpose well. In this case the time duration at each shear rate was 10 seconds and, perhaps surprisingly, was long enough for a dynamic equilibrium situation to be achieved at each respective shear condition. Optically, it was also observed that the aggregate texture adjusted quickly to a particular shear condition, suggesting that at any shear rate a dynamic equilibrium exists in relation to both size and interaction level between nanotube aggregates. The optical effect is illustrated in Fig. 6, where a series of three aggregate structures is shown. In Fig. 6(a), the aggregate structure

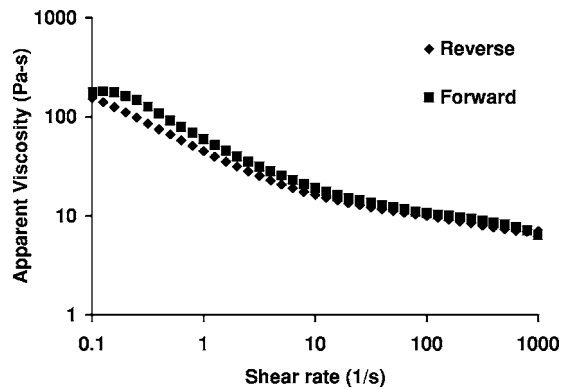


FIG. 5. The variation of apparent viscosity as a function of shear rate for a forward and reverse sweep steady-state shear rate experiment with 0.35 wt % MWCNTs. The experiment was conducted at 25 °C.

for a shear rate of 0.1 s^{-1} is shown. The shear rate was then increased to 200 s^{-1} and, in Fig. 6(b), a substantial change in texture can be seen. In Fig. 6(d), the shear rate has then been reduced to a low value of 0.5 s^{-1} and the optical texture returned to close to that of Fig. 6(a). At high shear rates, the aggregates are broken down to a small size, which causes shear thinning. However, when a low shear rate is applied, the motion causes a buildup of the aggregates [Fig. 6(d)]. The slow mechanical movement during low shear causes the MWCNTs to aggregate. It was also observed that if no shear was applied after shearing, the aggregate texture did not change, even after waiting for 1 hour [Fig. 6(c)]. It is conjectured that shear-induced aggregation of carbon nanotubes is responsible for viscosity enhancement at low shear rates, and that intermediate or high shear rates result in the progressive breakdown of interaction between nanotube aggregates.

Steady-state shear rate experiments were carried out for 0.35 wt % of MWCNTs at 25 °C and 80 °C, as shown in Fig. 7. At low shear rates the contribution to the viscosity of the suspension was predominantly from the aggregates of MWCNTs and the low shear viscosity was little affected by the temperature. At high shear rates, when MWCNTs aggregates are broken, viscosity is controlled by the matrix and in this case the limiting high shear viscosity is very temperature dependent. This type of behavior has been reported before for different systems and mostly from complex viscosity measurements (Abdel-Goad *et al.*, 2005; Xu *et al.*, 2005).

The viscoelastic properties of the nanotube suspensions are also of interest, although at this stage we have not investigated them fully at present. Figure 8 shows that the base epoxy matrix alone is essentially Newtonian with the complex viscosity being independent of angular frequency. Figure 8 also shows the linear viscoelastic response of the 0.35 wt % MWCNTs suspension. Data were collected down to an angular frequency of 0.01 rad s^{-1} , which is a decade lower than the minimum steady shear rate, and there the complex viscosity curve shows that, even at 0.01 s^{-1} , the low shear rate Newtonian plateau is still not fully developed and G' is still dominant, thereby indicating the presence of very long relaxation times. It is possible that a Newtonian zero shear rate plateau does not exist for this material. The data in Fig. 8 also show that at high frequencies, unusually for viscoelastic fluids, G'' dominates. We believe this to be a consequence of the high Newtonian matrix viscosity dominating in this region of the frequency domain. A number of other authors have reported viscoelastic properties of different carbon nanotube suspensions and our data in general are consistent with their overall behavior [see for example Abdel-Goad *et al.* (2005); Xu *et al.* (2005); and Huang *et al.* (2006)].

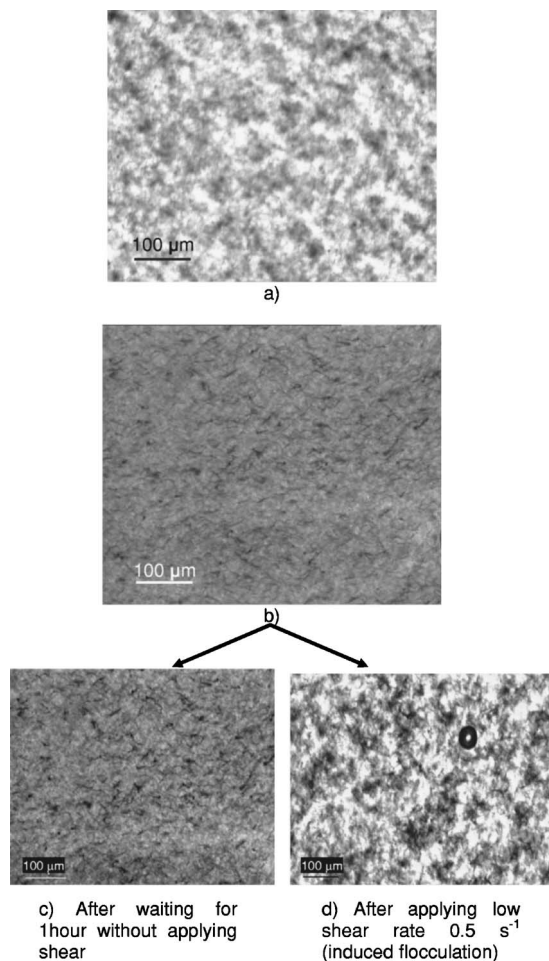


FIG. 6. The deflocculation during forward shear rate sweep (a) 0.1 s^{-1} ; (b) 200 s^{-1} ; (c) 200 s^{-1} after waiting for 1 h; (d) low shear-induced flocculation during reverse sweep 0.5 s^{-1} .

Finally, it should be noted that for higher concentration micrographs shown so far, there is no optical evidence to indicate that shear has induced alignment of the nanotube aggregates. At lower concentrations ($0.035 \text{ wt } \%$), however, there was clear evidence for alignment; this effect is shown in Fig. 9. When the fraction of MWCNTs is very low they do not form macroscopic aggregates, as shown in Fig. 9(a) for the suspension of $0.035 \text{ wt } \%$ MWCNT. This is because at low volume fraction the nanotubes are significantly further apart from each other and are not able to diffuse through the epoxy resin to form macroscopic aggregates. When a small amount of shear force is applied then MWCNTs become aligned in the direction of shear as shown in Fig. 9(b).

IV. DISCUSSION AND CONCLUSIONS

This paper has reported both rheological and optical microstructural observations on an epoxy resin matrix containing multiwall carbon nanotubes (MWCNTs). Due to the particular method used to manufacture the MWCNTs, it was found that dispersion of the nanotubes within the matrix was relatively straightforward. However, even with efficient

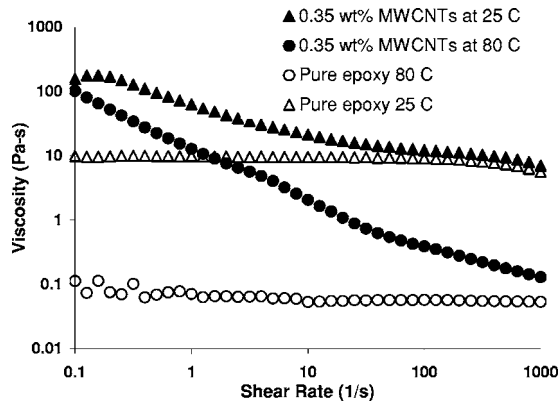


FIG. 7. The variation of apparent viscosity as a function of shear rate for a pure epoxy matrix (Newtonian) and a 0.5 wt % MWCNT epoxy suspension (shear-thinning) at 25 °C (triangles) and 80 °C (circles).

dispersion, aggregation of the nanotubes was a key microstructural feature. At nanotube concentrations of below 0.1 wt %, no significant viscosity enhancement was observed, and at low or zero shear rates, isolated clusters of nanotube aggregates were seen optically. Below the critical concentration of MWCNTs, if the shear rate was increased to around 10 s^{-1} , no significant viscosity change was observed although shear alignment of the nanotubes was observed.

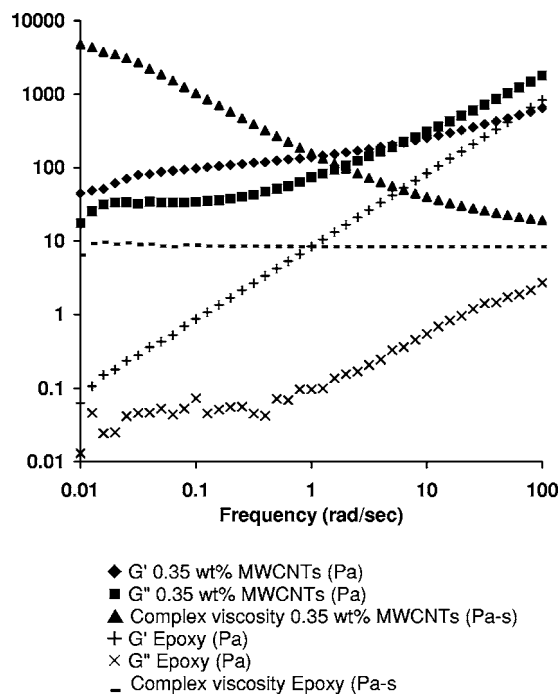


FIG. 8. The variation of the complex viscosity and the elastic and viscous moduli as a function of the oscillatory shear frequency for (a) pure epoxy resin (— complex viscosity, +G', ×G''). (b) 0.35 wt % loading of MWCNT (▲ complex viscosity, ◆ G', ■ G'').

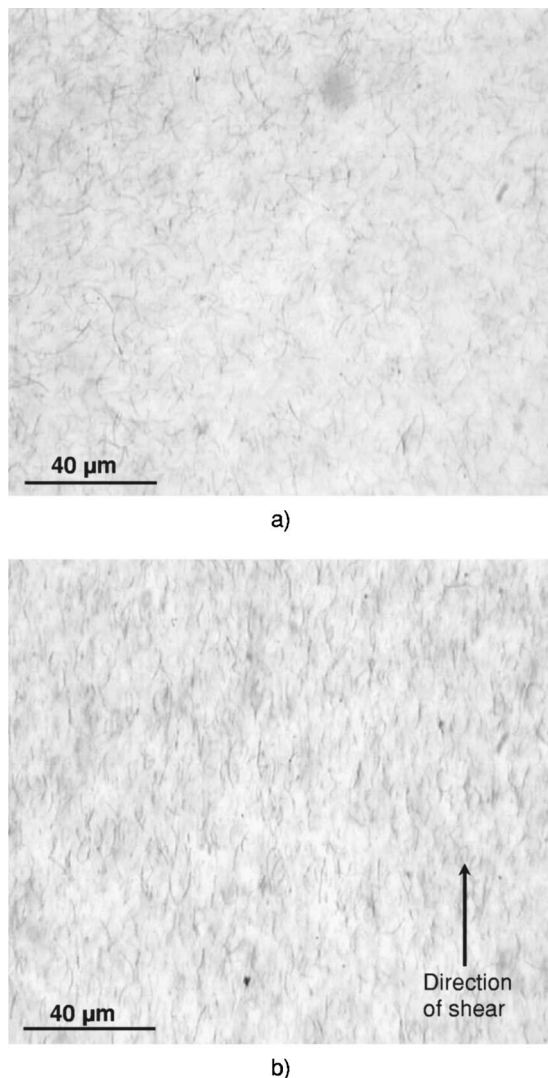


FIG. 9. Shear alignment of 0.035 wt % MWNCT suspensions: (a) 0 s^{-1} ; (b) 10 s^{-1} . The direction of applied shear was vertical in the photographs.

Above a 0.1 wt % concentration of nanotubes, there was a progressive increase in the zero shear rate viscosity with increasing suspension concentration, and a matching increase in nanotube aggregate interaction was observed. At intermediate shear rates, shear thinning of the suspension was observed with the viscosity approaching an asymptote of the pure resin at high shear rates. The shear thinning behavior follows that of a Cross equation, where the suspension viscosity changes from a high zero shear rate Newtonian value, through a power-law index at intermediate shear rates, to a lower high shear rate Newtonian value. Optical observations indicated that the shear thinning behavior was correlated with a “disentanglement” of nanotube aggregates and not shear-induced alignment of the nanotubes. It is conjectured that the mechanism for low shear viscosity enhancement is related to nanotube aggregate interaction above a certain concentration of nanotubes, and that the shear thinning behavior is a consequence of shear-induced de-

flocculation of MWCNTs. In the case of single-wall carbon nanotube suspensions, percolation concepts between individual carbon nanotubes have been used to model critical concentration behaviour (Hough *et al.*, 2004). In our case it may also be possible to use percolation modeling, but the percolation between aggregates of carbon nanotubes as well as individual nanotubes will need to be considered.

A key finding of the paper is that low shear rate motion “mechanically” induces aggregation formation and aggregate interaction of the nanotubes, whereas high shear rate motion causes aggregate size and interaction reduction. In both cases, however, Brownian motion appears to play little or no part in the dynamics of the aggregates. Shear alone causes microstructural changes.

It is clear that further experimental rheological and microstructural observations need to be carried out on this new and interesting class of material. It should then be possible to construct a micromechanical model to describe the zero shear rate viscosity enhancement and the materials’ viscoelastic response together with its striking nonlinear shear thinning behavior.

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