ANALYZING THE KINETICS OF FLOW-INDUCED STRUCTURE BUILD-UP IN CARBON NANOTUBE-EPOXY SUSPESNIONS

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1 Abstract
In this work, the kinetics of structure development upon cessation of shear flow is analyzed in MWCNT-epoxy suspensions under the influence of flow history, concentration and temperature. It has been shown that the structure reconstructs faster by increasing the concentration or temperature. Pre-shearing-rate becomes important only at very low concentrations.

2 Introduction
CNTs have been widely used to prepare polymer-nano-composites in order to enhance the physical properties of polymers, such as electrical conductivity, mechanical properties, thermal conductivity and thermal stability. To make multi-functional nano-composites, it is important to control their structure during processing and before they are set.

The suspension structure evolves under the influence of internal and external forces during and after processing. During flow, shear forces compete with Brownian forces; if the former become dominant, they induce flocculation at low shear rates [1, 2] and break the particle entanglements to form a more dispersed structure with some oriented particles in the flow direction at high shear rates [3, 4]. Right after shearing, the structure of CNT suspensions reconstructs under the influence of inter-particle interactions and Brownian forces [5]. In this article, the kinetics of structure evolution is analyzed upon cessation of shear flow and under the influence of pre-shear rate, temperature and concentration.

3 Materials
An epoxy EPON 828 (HEXIONTM Specialty Chemicals Inc.) with density of 1.16 (g/mL) and viscosity of 12.33 (Pa.s) at room temperate was used as the suspending medium. Multiwall carbon nanotubes (Cheap Tubes Inc.) with average length of 670 nm and outer diameter of 14.86 nm ($l/d \sim 45$) were dispersed in the epoxy at various concentrations using an EXAKT three roll mill at room temperature. More details about sample preparation are presented elsewhere [5].

4 Results and Discussion
4.1 Effect of Flow History and Concentration
Since the linear viscoelastic (LVE) measurements are non destructive, they are commonly used to study the microstructure of suspensions. On the other hand, we have previously shown that the elasticity of CNT suspensions stems from the presence of nanotubes in epoxy and originates mainly from the entanglements (inter- and intra-floc links) in nanotube clusters [6]. Hence, the storage modulus is a suitable rheological property for evaluating the evolution of structure.

Fig. 1 demonstrates the development of structure after pre-shearing at various rates for a 1 wt% suspension. Details about the experimental procedure is given in a previously published article [5]. It can be observed that the suspension structure and so its storage modulus increases upon cessation of flow. From this figure, the lower is the pre-shear rate, the higher is the storage modulus. A similar behavior can be observed at higher concentrations. However, the effect of flow history is more pronounced at lower concentrations [5]. Moreover, the storage modulus of suspensions evolves in an exponential trend that can be expressed in the following form [5], where G'_i and G'_∞ (Pa) are the storage moduli of the pre-sheared suspensions right after cessation of flow and 5000 s after cessation of flow, respectively. τ(s) is the time required for G' to reach 63% of its final value, G'_∞ and is called the characteristic time of the system. The lower τ(s) exhibits higher rate of structure build-up.

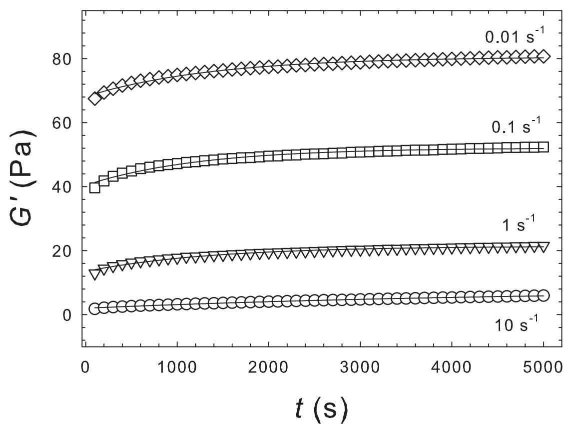

Fig. 1 Development of structure of a 1 wt% CNT – epoxy suspension after cessation of pre-shearing at different rates obtained at 1 rad/s and strain amplitude of 1.5%. The lines show the best fits of the experimental results with eq. (1).

$$G'(t) = G'_i + (G'_\infty - G'_i)[1 - \exp(-t/\tau)] \qquad (1)$$

Using eq. (1) the kinetics of structure reconstruction can be analyzed. Fig. 2 represents the variation of τ(s) with the applied pre-shear rate for two suspensions of 1 wt% and 3 wt%. At low concentration of 1 wt% (and below the percolation threshold of 2 wt%), τ(s) and so the rate of structure build-up remains similar at low pre-shear rates up to 1 s^{-1}; however, by increasing the rate of pre-shearing, the kinetics of structure development slows down drastically as τ(s) increases to 2000 s for a pre-shear rate at 10 s^{-1} and 5000 s at 100 s^{-1}.

On the contrary, at higher concentration of 3 wt% (and above the percolation threshold), the characteristic time and so the rate of structure reconstruction remains approximately invariant with pre-shear rate. The observations of Fig. 2 can be explained by considering the influence of flow history on the structure, which was characterized previously [5] by the variation of the percolation threshold with pre-shear rate. It has been shown that pre-shearing at low rates results in the formation of more entanglements between nanotubes, which results in lower percolation thresholds up to 1 wt% when pre-shearing at 0.01 s^{-1} compared to 2wt% without pre-shearing [5]. This is in agreement with the flow-induced aggregation reported by Lin-Gibson *et al.* [1] in semi-dilute CNT suspensions. Upon the application of higher shear rates, some entanglements between nanotubes break down; this limits the formation of a percolated network to higher concentrations and shifts the percolation threshold to 2.5 wt% by pre-shearing at 100 s^{-1}.

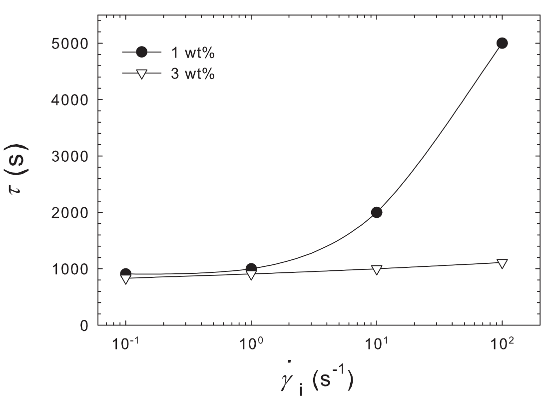

Fig. 2 Variation of the characteristic time of the structure build-up by pre-shear rate for 1wt% and 3 wt% suspensions at room temperature.

At low concentration of 1 wt%, the suspension structure is more fragile since no interconnected network is present; hence, the structure is more sensitive to the effect of flow history. Consequently, pre-shearing at low rates induces more entanglements between nanotubes; this results in faster structure build-up. By pre-shearing at higher rates, part of the nanotube entanglements break down and the rate of structure build-up slows down.

At higher concentration of 3 wt%, a strong interconnected CNT network is present which is relatively insensitive to the effect of flow history; thus, the rate of structure evolution remains independent of the flow history. From these results, it seems that the presence of a CNT network in the suspension facilitates the structure reconstruction in the absence of flow since the characteristic time decreases with increasing the concentration.

4.2 Effect of Temperature

In previous sub-section, it was shown that by increasing the inter-particle interactions via increasing concentration, the rate of structure build-up increases. The importance of inter-particle interactions can be further investigated by considering the effect of temperature.

Initially, the effect of temperature on the LVE properties of the suspensions was verified. To reduce this effect on the neat epoxy, the storage and loss moduli can be normalized by the complex modulus of the neat epoxy (G^*_s) at the same temperature. It has been shown that the reduced storage and loss moduli of the suspensions increase with increasing temperature [6]. Since the suspension elasticity stems from the presence of nanotubes, it can be concluded that the inter-particle interactions increase with increasing temperature. A similar increase in the reduced shear viscosity of the suspensions has been previously [5] observed with increasing temperature. Moreover, the time-temperature-superposition was verified at various concentrations by using the Arrhenius correlation. This reveals that although the inter-particle interactions increase with temperature, the particles remain dispersed in epoxy and no phase separation occurs.

The effect of temperature on the structure evolution of the suspensions can be verified by keeping the temperature constant during pre-shearing and structure build-up. The storage modulus of the reconstructed structure G'_∞ was obtained 5000 s after cessation of pre-shearing at different pre-shear rates and temperatures ranging from 15 to 45 ^{o}C. Fig. 3 reports the reduced G'_∞ for a 3 wt% suspension. From this figure, the reduced storage modulus increases with increasing temperature.

By considering the variation of characteristic time τ(s) with temperature at various pre-shear rates and concentrations, the effect of temperature on the kinetics of structure build-up can be analyzed. Fig. 4 presents the results for 1 wt% and 3 wt% suspensions.

It can be observed that at low concentration of 1 wt%, the effect of temperature becomes important at relatively high pre-shear rates ($\dot{\gamma}_i > 1$ s^{-1}), where the characteristic time decreases significantly with temperature revealing a faster structure build-up.

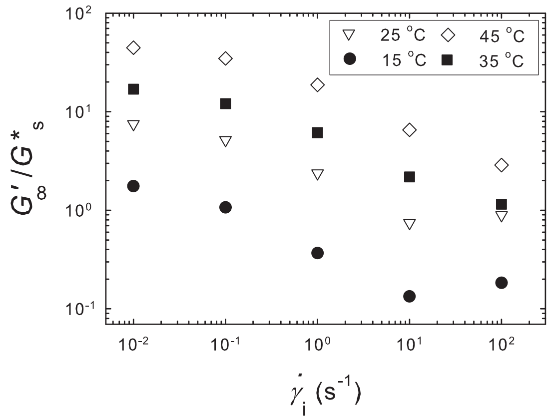

Fig. 3 Effect of temperature on the reduced storage modulus of a 3 wt% suspension as a function of pre-shear rate. G^*_s is the complex modulus of the neat epoxy.

At the highest pre-shear rate of 100 s^{-1}, the characteristic time of this suspension decreases more than four times upon a 20^{o}C increase in temperature.

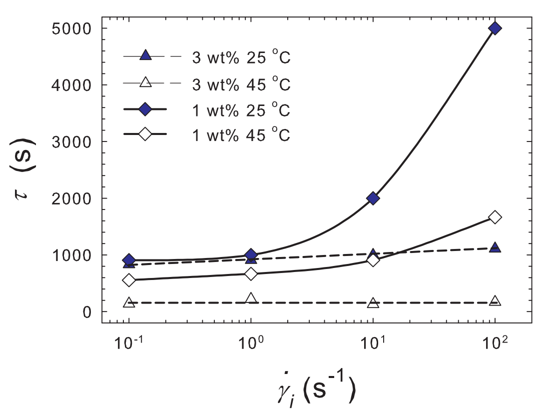

Fig. 4 Variation of the characteristic time τ(s) for 1 wt % and 3 wt % suspensions as a function of the pre-shear rate.

A similar effect of temperature on the kinetics of structure build-up is evident at higher concentration of 3wt%, except that in this case, since the suspensions structure is more entangled, the rate of structure build-up is influenced similarly by the effect of temperature at various pre-shear rates.

5 Summary

In this work, the effect of pre-shear rate, concentration and temperature was quantitatively analyzed on the kinetics of the flow-induced structure reconstruction in CNT-epoxy suspensions. Using the characteristic time of the system, it was shown that the inter-particle interactions play a significant role in structure reconstruction of suspensions upon cessation of flow. Moreover, by increasing the concentration or temperature and so the inter-particle interactions, the rate of structure build-up increased.

At relatively low concentrations, it was observed that the characteristic time significantly increased with increasing rate of pre-shearing; thus the rate of structure build-up diminished. However, at higher concentrations where an entangled CNT network was formed, the rate of structure evolution at rest remained almost independent of the pre-shear rate.

6 Acknowledgement

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7 References

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