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Gelation in carbon nanotube/polymer composites

Chenyang Liu[a], Jun Zhang[a], Jiasong He[a,*], Guohua Hu[b]

[a]*State Key Laboratory of Engineering Plastics, Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Zhongguancun, Beijing 100080, China*
[b]*Laboratory of Chemical Engineering Sciences, CNRS-ENSIC-INPL, 54001 Nancy Cedex, France*

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Abstract

The physical gelation in carbon nanotubes (CNTs)/polycarbonate composites was revealed by rheological analysis (Winter–Chambon method), based on the data reported by Paul [Polymer 43 (2002) 3247]. The gelation concentration c_g, the relaxation exponent n and the gel strength S_g characterizing the critical gel point for the composites are 1.6 wt%, 0.75 and 770 Pa s^n, respectively, which are comparable with those found for polymer gels. In fact, the gel points coincide with the percolation threshold of the electrical conductivity and the high strength in CNT/polymer composite applications. The new kind of physical gel originates from a combination of entanglement of CNTs and interactions between CNTs and polymer chains, instead of the chemical bonding or physical interactions in previous polymer gels.

Keywords: Physical gelation; Carbon nanotubes/polycarbonate composites; Rheological analysis

1. Introduction

Carbon nanotubes (CNTs) have attracted a great deal of interest due to their many potential applications [1]. One of them is the utilization of CNTs as nanoscale filler in CNT/polymer composites for structural or functional application. Incorporation of a small amount of CNTs into polymers can improve thermal conductivity [2], mechanical properties [3], and electrical properties [4] dramatically. It is interesting to correlate the structure of these CNT-filled composites with their peculiar properties. This paper reveals the physical gelation in CNTs/polymer composites by rheological analysis, based on the data reported by Paul [5].

2. Theoretical background of gelation rheology

Several reviews concerning polymer gels have been produced in the recent past [6–8], which elaborate the experiments, theory and application of polymer gel systems. Winter and Chambon [9–12] found experimentally that critical gels exhibited simple relaxation behavior following a power-law relaxation shear modulus:

$$G(t) = S_g t^{-n} \tag{1}$$

The gel strength S_g and the relaxation exponent n characterize the critical gel. The storage and loss moduli, G' and G'', of a critical gel also obey a scaling law with the same exponent, n :

$$G'(\omega), G''(\omega) \propto \omega^n \quad 0 < n < 1 \tag{2}$$

or

$$G''(\omega)/G'(\omega) = \tan\delta = \tan(n\pi/2) \tag{3}$$

The frequency-independence of the loss tangent in the vicinity of the gel point has been widely examined for chemical and physical gels [6–8], and also been employed to determine the gel point.

According to the theory of linear viscoelasticity of polymers, the dynamic moduli G' and G'' are given by

$$G'(\omega) = \omega \int_0^\infty G(t)\sin(\omega t)\mathrm{d}t \tag{4}$$

$$G''(\omega) = \omega \int_0^\infty G(t)\cos(\omega t)\mathrm{d}t \tag{5}$$

Therefore, the storage modulus, G', and the loss modulus,

* Corresponding author. Tel.: +86-10-6261-3251; fax: +86-10-6255-9373.
E-mail address: hejs@sklep.icas.ac.cn (J. He).

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G'', at the gel point are given by

$$G'(\omega) = G''(\omega)/\tan(n\pi/2) = S_g\omega^n\Gamma(1-n)\cos(n\pi/2) \quad (6)$$

where Γ is the gamma function. By knowing n, one can calculate S_g from G' or G'' at the gel point using Eq. (6).

3. Results and discussion

Recently, Paul and co-workers [5] have studied the rheological behavior of multiwalled CNT/polycarbonate (PC) composites. This is the first preparation of CNT/polymer materials in kilogram quantity produced by using conventional melt extrusion. Their main objectives are to investigate the effect of the nanoscale fillers on processing properties by using rheological behavior at high frequencies, and to obtain information about the percolation of the CNT within the composites by using rheological behavior at low frequencies. In their study, the viscosity curves for pure PC and CNT/PC composites containing 0.5 and 1 wt% nanotubes have a Newtonian plateau at low frequencies. Whereas above 2 wt% nanotubes loading, the viscosity curves exhibit a strong shear thinning effect in the frequency range studied, as shown in Fig. 1(a) (Fig. 2 of Ref. [5]). Moreover, Fig. 1(b) (Fig. 4 of Ref. [5]) shows that for PC composites containing less than 2 wt% nanotubes G' is expected to decrease to zero at low frequency. While at 2 wt% nanotubes loading a low-frequency horizontal plateau in G' has appeared and beyond 5 wt% nanotubes G' is nearly independent of frequency. A similar result can be found in a more recent research [13]. This is one of typical rheological features of physical gelation [6–8]. Therefore, in the present study, Winter–Chambon method will be used to determine the gel point of the CNT/PC composites.

The frequency dependence of the loss tangent during the gelation process is depicted in Fig. 2 by using data presented in Ref. [5]. As expected, at a certain nanotubes concentration between 0.5 and 2 wt%, tan δ should be independent of frequency, so gel point should be between 0.5 and 2 wt% nanotubes loading. In the pregel regime, tan δ decreases with increasing frequency, as typical for a viscoelastic liquid. In the postgel regime, a moderate increase of tan δ appears with increasing frequency, indicating a dominating elastic response of the sample.

This method, i.e. the frequency-independence of tan δ for characterizing gelation, can also be applied in an alternative way for determining accurately the gel point without a gelling system exactly at the gel point. The gel point can be determined by the observation of a frequency-independent value of tan δ obtained from a multifrequency plot of tan δ versus nanotube concentration. This type of plot is shown in Fig. 3. The general trend is a steady decrease in the loss tangent with increasing nanotube concentration, with the decrease most pronounced for the lowest measurement

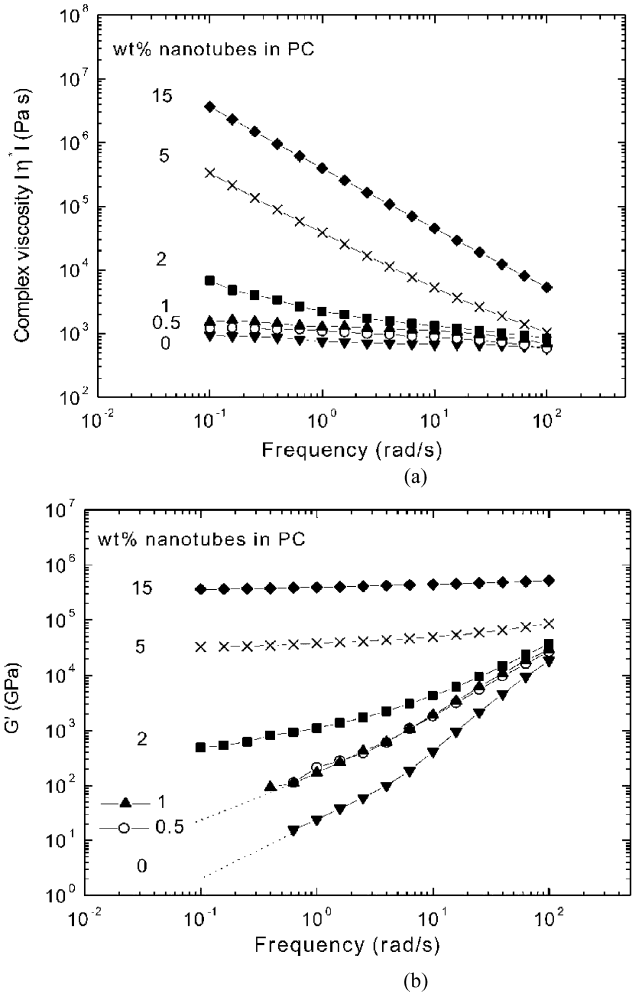

Fig. 1. Complex viscosity $|\eta^*|$ (a) and storage modulus G' (b) of nanotube filled polycarbonate at 260 °C. (Paul DP, et al. Polymer 2002;43:3247. Figs. 2 and 4).

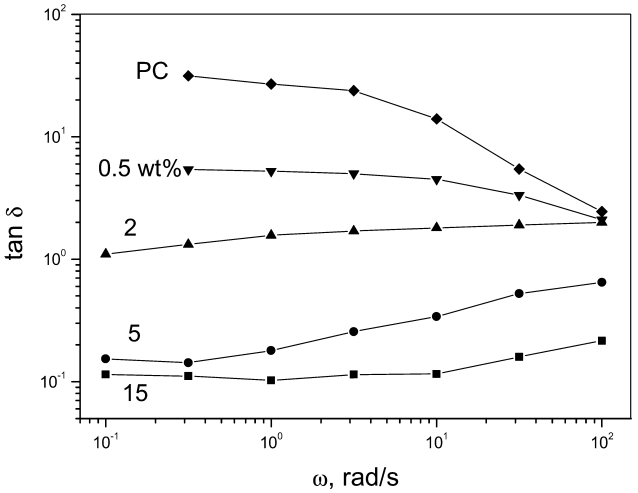

Fig. 2. The loss tangent tan δ as a function of frequency ω for the CNT/PC composites.

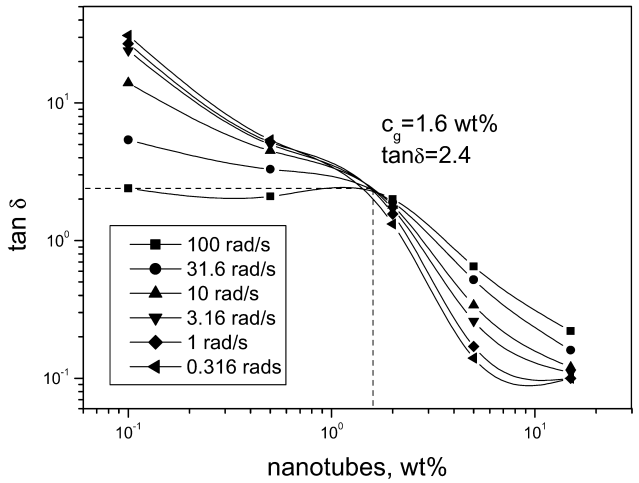

Fig. 3. The loss tangent tan δ as a function of nanotubes concentration for the CNT/PC composites.

frequency. The cross point in this plot results in a value of tan δ becoming frequency independent at a particular gelation concentration c_g, and is defined as the gel point. For the CNT/PC composites presented in Ref. [5], $c_g = 1.6$ wt% and tan $\delta = 2.4$. The critical exponent n is 0.75 calculated from the gel point by using the relation in Eq. (3).

The physical nature of a gelling system at the gel point can be described by the gel strength S_g defined by Eq. (1). This implies that S_g is related to the physical strength of the gel network at the gel point. We are able to take the advantage of Eq. (6) that suggests the existence of a crossover of G' and $G''/\tan(n\pi/2)$ at the gel point: the value of G' at the gel point should be obtained by plotting G' and $G''/\tan(n\pi/2)$ against nanotube concentration, and then S_g would be easily calculated. This kind of plot is shown in Fig. 4 for the CNT/PC composites. Since the system at the gel point obeys the frequency-independence of tan δ, all crossover points appear quite well at the gel point of $c_g = 1.6$ wt%,

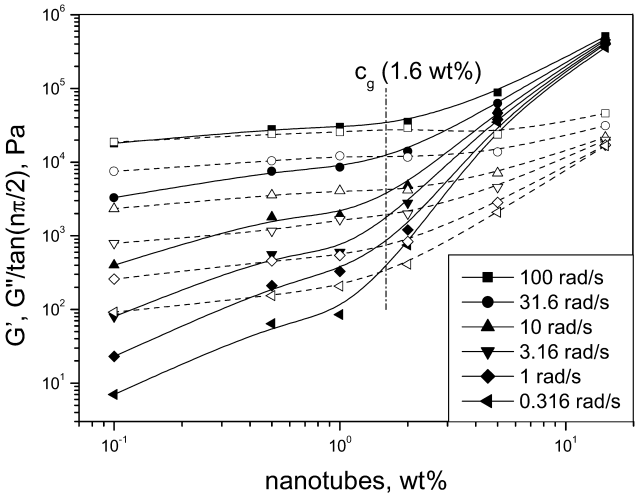

Fig. 4. Plots of G' (solid) and $G''/\tan(n\pi/2)$ (open) against nanotube concentration for the CNT/PC composites.

which is consistent with that obtained by using the frequency-independence of tan δ in Fig. 3. Using the values of G' at crossover points and Eq. (6), we obtained the value of $S_g = 770$ Pa s^n.

The results obtained by using the Winter–Chambon method on these data reveal a new kind of physical gel in the CNT/polymer composites. These values, the relaxation exponent n of 0.75 and the gel strength S_g of 770 Pa s^n, are comparable with those found for polymer gels [6–8]. For comparison, consider the equivalent values of 0.5–0.8 and 10^3–10^4 Pa s^n tabulated for HDPE melts with a level of long chain branching [14]. Windle et al. [15] reported that the viscosities increased dramatically above a critical concentration of around 0.5 and 1 vol% for the aqueous dispersion of nanotubes and bromine-shortened nanotubes, respectively. These thresholds are similar to the gel point of CNT/PC composites, by considering that the corresponding volume concentration of 1.6 wt% is 1.1 vol% according to the material densities [5], while Paul also reported that the conductivity percolation threshold was between 1 and 2 wt%.

The long-range connectivity in a polymeric material may arise from chemical bonding or physical interactions [6–8]. Chemical bonding results in the chemical gelation when covalent bonds connect polymer chains into a three-dimensional network. In contrast, physical gelation occurs when physical interactions, (such as crystallization, hydrogen bonding, phase separation, helix formation, etc.) connect the chains. Two factors should be responsible for this gelation behavior in CNT/polymer composites. One is the entanglement of the CNT themselves, resulted from their very large aspect ratios and intrinsic random curvature of these defective nanotubes [15,16]. The other is the interaction between the polymer chains and CNTs [17], although this interaction is non-covalent. A research based on molecular simulation suggests [18] that the interfacial adhesion is significantly higher than most carbon fiber-reinforced polymer composite systems. At the percolation threshold, an interconnecting structure of nanotubes is formed, which is similar to interpenetrating polymer networks. Because the mutual constraint of this structure hinders straightforward relaxation of the polymer chains, the increase in the storage modulus may be of the order of 10^4 or more, as shown in Fig. 1(b).

The gelation of CNT/polymer shown in Paul's paper originates from a combination of entanglement of CNTs and interactions between CNTs and polymer chains, instead of the chemical bonding or physical interactions in previous polymer gels. For this kind of CNT/polymer gels, it can be expected that the gel point, the gel strength S_g and exponent n will strongly depend on the aspect ratios of CNTs, dispersion of CNTs within polymer matrix and the interactions between CNTs (functionalized or not) and the

polymer matrix (polar or non-polar). It is interesting to investigate them in depth in the future.

4. Conclusions

By using Winter–Chambon method, the gel point for CNT/PC composites have been accurately determined based on the data of Ref. [5]. The gel strength S_g and exponent n obtained are comparable with those found for polymer gels. In fact, the gel points coincide with the percolation threshold of the electrical conductivity and the high strength in CNT/polymer composite applications. Therefore, the determination of gel point by rheological method is of significance to the control of the physical properties and the processability of these new materials, and useful as a characterization technique for the dispersions and alignments of nanotubes.

Acknowledgements

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