



## Macromolecular Nanotechnology

## The role of carbon nanotubes in both physical and chemical liquid–solid transition of polydimethylsiloxane



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## ABSTRACT

In this work we investigate the effect of the dispersion degree of as-received multiwall carbon nanotubes (MWNTs) in the liquid–solid transitions (LST) of polydimethylsiloxane (PDMS). The physical LST of the suspensions showed a strong dependence on the nanotubes dispersion degree due to the formation of an interconnected network as the dispersion time increased. These MWNTs acting as “effective physical cross-links” also influenced the dynamic viscoelastic properties, accelerating the chemical LST (or chemical cross-linking) and giving rise to an increase in the cross-linking density of the composite samples.

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## 1. Introduction

During the past decade, the liquid–solid transition (LST) in polymer materials have been extensively explored since it is a crucial technological point delimiting their processing conditions, properties and applicability [1]. Independently of the nature of the LST, i.e. physical or chemical, this phenomenon represents a change in the molecular mobility of the polymer matrix and can hence be easily followed by rheological measurements. One of the first systems to be analysed by rheology was a polydimethylsiloxane (PDMS), that presents a LST due to the chemical cross-linking of its chains and provides ideal model networks [2]. Furthermore, the excellent chemical and thermal properties of PDMS make it a widely used elastomer in commercial applications. However, it requires the addition of fillers in order to get a substantial improvement of its modulus and strength. The most common fillers added to PDMS are silica and titanium dioxide particles which have shown to provide a good mechanical reinforcement [3].

Current scientific interest on the use of nanofillers, and in particular carbon nanotubes, has been moderately investigated with PDMS showing mechanical reinforcement and increases in electrical conductivity [4–7]. The key-point for obtaining these enhanced properties stems from an effective dispersion and formation of a MWNT physical network in the PDMS polymer matrix prior and after its chemical cross-linking. Therefore, to attain this interpenetrating structure between filler and polymer, it is necessary to break apart the MWNT bundles and to stabilise the individual nanotubes in order to prevent their re-aggregation [8].

The use of rheological measurements has already been reported as an efficient method to understand the nanofiller dispersion degree [9–11]. A direct consequence of a homogeneous dispersion of MWNTs in a polymer matrix is the significant change in the viscoelastic properties [12–16]. Since the rheological parameters of a (nano)composite are correlated with the distribution of (nano)fillers within the polymer, measuring  $G'$ ,  $G''$  and  $\eta^*$  at different stages of the mixing process can provide information about the time necessary to achieve a suitable level of dispersion [9]. Recent studies have analysed the linear viscoelastic behaviour and re-aggregation mechanisms of semi-dilute

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suspensions of MWNTs/PDMS prior to the cross-linking process observing the formation of an elastic nanotube network [13,17]. Nevertheless, and to the best of our knowledge, the effect of fillers in the cross-linking process of PDMS has been generally overlooked until very recently when Esteves et al. [18] analysed the influence of micro-size garnet particles. The authors observed a slowdown of the overall cross-linking process due to a strong interaction of the particles with the catalyst. The influence of nano-size fillers and, in particular, of MWNTs with their ability to form an elastic network on the chemical LST of PDMS materials has not been investigated despite the fact that is one of the major factors that govern the ultimate properties of the resulting material. Hence, the influence of MWNT dispersion degree on the cross-linking reaction must be assessed in order to achieve and ensure good overall performances of the resulting elastomeric composites.

In summary, this study analyses both physical and chemical liquid–solid transition of semi-dilute MWNT/PDMS suspensions by measuring the linear viscoelastic and dynamic rheological properties, respectively, of the system.

## 2. Materials and methods

### 2.1. Materials

Multiwall carbon nanotubes (MWCNTs Thermally Purified) were kindly supplied by FutureCarbon GmbH. They were synthesised by chemical vapour deposition (CVD) with a mean diameter of 15 nm, an average length ranging from 5 to 50  $\mu\text{m}$  and a purity of 98%. A commercial poly(dimethyl)siloxane based formulation (PDMS RTV4420 A/B) supplied by BlueStar Silicones, was used as polymer matrix. This room temperature curing system consists of two components: Part A is a vinyl terminated polymer ( $\equiv\text{SiVi}$ ) together with a platinum catalyst, while Part B contains the pre-polymer ( $\equiv\text{SiH}$ ).

### 2.2. Preparation of MWNT/PDMS suspensions

Given that the basis of the work is on the quality of the prepared suspensions special attention must be paid on how to prepare the aforementioned suspensions. It is well known that the most common and widely used dispersion techniques for suspensions in a low–medium viscosity material are “high-shear” mixing and ultrasonication [19]. The latter is able to release higher power and is quite efficient to separate MWNT agglomerates, but it also may cause a considerable damage in MWNT structure due to the violent cavitation [20,21]. To evaluate the possible breakage of the MWNTs during mixing, Huang et al. [9] calculated the shear stress applied to MWNTs mixtures as follows:

$$\sigma \approx \frac{\eta R \omega}{h} \quad (1)$$

where  $\eta$  is the polymer viscosity,  $\omega$  is the angular frequency of the mixer,  $R$  and  $h$  are the radius and the gap of the vessel employed. They obtained a shear stress of 1 MPa, which compared to the tensile stress of single and

multiwall carbon nanotubes of about 200–900 MPa [22–24], indicated a low level of nanotube breaking. Applying this analysis to our system, we obtained an applied shear stress of about 5 MPa, which is again considerably lower than the tensile stress of MWNTs. Hence, we selected the high shear mixing protocol to avoid major damages to our MWNTs. We should point out that MWNTs concentration was kept constant along this study since the aim of this work is to clarify the influence of MWNTs dispersion degree on both physical and chemical LST of the raw polymer.

Samples of 10 g total weight with 0.5 wt.% of MWNTs were prepared by directly adding the nanotubes into the  $\equiv\text{SiH}$  pre-polymer. The dispersion time was then chosen as the variable parameter and, hence, MWNTs were mechanically mixed (Ika Mixer) at 2400 rpm for different times ( $t = 2, 4, 6,$  and  $24$  h). Changes in the microstructure of the suspensions were studied measuring the linear viscoelastic properties immediately after the desired dispersion time.

### 2.3. Preparation of MWNT/PDMS composites

MWNT/PDMS cross-linked composites were obtained by mixing  $\equiv\text{SiVi}$  pre-polymer with the suspensions previously prepared in a ratio 1:1. After stirring the mixture for 2 min, the pasty suspensions were degassed in a vacuum oven at 30–50 mbar for approximately 10 min to remove air bubbles formed during mixing operations. Films with an average thickness of about 0.5 mm were prepared by mould casting and then cured at room temperature for 24 h before swelling and microstructural characterisation.

### 2.4. X-ray photoelectron spectroscopy (XPS)

The chemical composition of MWNTs was evaluated by X-ray photoelectron spectroscopy (XPS). Photoelectron spectra were acquired with a VG Escalab 200 R spectrometer equipped with a hemispherical electron-analyser and a Mg  $K\alpha$  ( $h\nu = 1253.6$  eV) non-monochromatic X-ray source. The O1s and C1s signals were scanned using the binding energy (BE) of C1s core-level peak at 284.9 eV as reference.

### 2.5. Rheological measurements

The rheological properties were measured on a stress-controlled rheometer (TA Instruments Advanced Rheometer AR1000). Experiments were performed at room temperature using parallel plate geometry (gap = 500  $\mu\text{m}$ ) with a 20 mm upper corrugated plate. Stress sweep tests (frequency kept constant at 1 Hz) were carried out to monitor the extent of each sample's linearity. After the sample's linear viscoelastic region was defined, dynamic oscillation frequency sweeps were performed at the terminal region (0.01–10 Hz) to monitor the state of the MWNT dispersion. Isothermal curing runs with constant shear frequency (1 Hz) in the linear viscoelastic regime were also performed to determine the influence of the cross-linking reaction on the viscoelastic properties.

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