

# Flow activation volume of polystyrene/multiwall carbon nanotubes composites

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## ABSTRACT

We applied the rate theory of plastic deformation to evaluate the flow activation volume in polystyrene melts and in its composites with different concentrations of multiwall carbon nanotubes. The experiments consisted in the analysis of a perturbation induced to the melt by varying the shear rate of a monotonic test at a melt state with nearly constant viscosity. The variation consisted on the application of shear steps with lower shear rate during short-time intervals. The material's response to the perturbation allows a flow activation volume to be evaluated. For the pure polymer, the flow activation volume compares to the volume of a tube confining the chains, confirming the validity of tube model. Addition of nanotubes to the melt affects the melt response in the high temperature flow region, resulting in the development of a plateau in  $G'(\omega)$ . This plateau is linked to interactions of chains with nanotubes. However, the flow activation volume was not affected by the addition of nanotubes, suggesting that tube model holds also for composites of polymer melts with carbon nanotubes.

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## 1. Introduction

The rheological behaviour of composites involving polymers and nanoparticles has been studied for different combinations of polymer matrixes and nanoparticles alongside with the effect of nanoparticles addition on the composite's properties, such as thermal and electrical conductivity, among others [1,2]. The interest stems not only from the interesting and unusual phenomena observed [2–4], but also from the need to understand the effect of nanoparticles addition on the polymer flow behaviour [1,2,5]. From a practical point of view, rotational flow fields, such as shear flow, have been used to promote the orientation and dispersion of nanoparticles within the polymer matrix [6–8].

The high degree of aggregation between nanotubes was explained by their high cohesive energy, which was estimated to be  $\approx 36 RT$  for each nanometre overlap between nanotubes [6]. Among the unusual phenomena observed is the suppression of die-swell effect by addition of small concentrations of nanotubes ( $\phi \approx 0.01$ ), the strong shear thinning, the large negative normal stresses [2] and the drop in the viscosity of nanoparticle filled polymer melts [3,4]. This last result contradicts the Einstein's

equation for the viscosity of a liquid in which a large number of spheres are suspended in irregular distribution, which is

$$\eta^* = \eta(1 + 2.5\phi), \quad (1)$$

where  $\eta^*$  and  $\eta$  are the viscosities of the mixture and liquid, respectively, and  $\phi$  is the volume fraction of the spheres [9]. According to Eq. (1), the viscosity of the composite should always increase with the addition of nanoparticles. In fact, some authors [1,2], reported a systematic increase in the melt viscosity, even for very low concentrations of nanoparticles. The explanation for these different results is not clear. The interpretation of the viscosity decrease based on the increase in free volume and configurational changes, valid for mixtures of linear polystyrene chains and polystyrene nanoparticles, obtained by intramolecular crosslinking [4], do not seem to hold for composites of polypropylene and silica nanoparticles [3]. For the later composites, the selective adsorption of high molecular mass polymer chains on the surface of the nanofillers was provided as an explanation for the observed effect.

Another interesting phenomenon observed in these composites, related to the unusual phenomena described above, is the melt elasticity enhancement at the high temperature flow region. This elasticity increases by increasing the volume fraction of nanotubes added to the polymer matrix [1,2]. Concurrently with the emergence of this elasticity, it is found that Cox-Merz rule and the time–temperature superposition principle fail to apply.

In this work we propose to study the effect of this elasticity enhancement in the flow behaviour of the polymer and composite

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melts. For this evaluation, step-shear experiments were performed at different temperatures on the polymer melt and in composites with different concentrations of nanotubes. Conditions for the validity of these experiments are described in the results section. The experimental values of flow activation volume are fitted by an equation derived from the rate theory of plastic deformation [10] that allows a true flow activation volume to be evaluated. It is shown that this activation volume is one order of magnitude above the chain's physical volume and that it agrees, both for the polymer and composites, with the volume of a tube confining the chain motion.

According to the rate theory of plastic deformation, the activation volume is related to the distance needed for moving the flow segment from the reactant to the activated state. If the energy barrier for dislocation of flow segments in the flow direction in the absence of stress is  $\Delta G_0$ , then the strain rate resulting from a shear stress  $\tau$  is

$$\dot{\gamma}(\tau, T) = \dot{\gamma}_0 \exp[-(\Delta G_0 - \tau V^*)/k_B T], \quad (2)$$

where  $\dot{\gamma}_0$  is a constant,  $k_B$  the Boltzmann constant and  $T$  the absolute temperature. From this equation the flow activation volume (FAV) is expressed as

$$V^* = k_B T \frac{d \ln(\dot{\gamma})}{d \tau}. \quad (3)$$

If both forward and backward transitions over the energy barrier are considered, Eq. (2) may be written in the more general form as

$$\dot{\gamma}(\tau, T) = 2A \sinh[\tau V^*/k_B T], \quad (4)$$

where  $A = \dot{\gamma}_0 \exp[-\Delta G_0/k_B T]$ .

With results of the step-shear experiments we evaluate an experimental, or apparent, flow activation volume (FAV),  $V_e$ ,

$$V_e = k_B T \left[ \frac{d \ln(\dot{\gamma})}{d \tau} \right]_{T, DefMech}, \quad (5)$$

under the assumption that the deformation mechanism of the monotonic test remains unaltered by the shear steps. Experimental – apparent – ( $V_e$ ) and true ( $V^*$ ) FAV are different. A relationship between them is obtained by inserting Eq. (4) into (5). The result is

$$V_e = \frac{\cosh(\tau V^*/k_B T)}{\sinh(\tau V^*/k_B T)} \frac{\partial(\tau V^*)}{\partial \tau}, \quad (6)$$

Assuming that for very large values of  $\tau$ ,  $\partial V^*/\partial \tau = 0$ , the above equation may be written as

$$\frac{V_e}{k_B T} = \frac{V^*}{k_B T} \coth(\tau V^*/k_B T) = \alpha \coth(\tau \alpha), \quad (7)$$

where  $\alpha = V^*/k_B T$  is the only fitting parameter to the experimental data.

## 2. Experimental

### 2.1. Samples and sample preparation

Properties of the atactic polystyrene used are presented in Table 1. The glass transition temperature evaluated from DSC scans at 10 °C/min, preceded by a cooling at the same rate, was 91 °C. Other values indicated in Table 1 were obtained from Refs. [11,12]. Table 1 shows also values for the volume of a tube confining the chain ( $V_{tube-Mn}$ ), the volume of a chain ( $V_{chain-Mn}$ ) and the volume of one Kuhn monomer ( $V_k$ ). Procedures for evaluating these volumes from data in Table 1 are presented below.

### 2.2. Rheology experiments

The step-shear experiments were performed in a Physica MCR 300 rheometer (Paar Physica) with parallel plate configuration (plate diameter 25 mm diameter and gap size set to 0.7 mm for all experiments) and cone-and-plate configuration (plate diameter 25 mm and cone angle 2°). Results obtained with this configuration are provided as supplementary material. These experiments were preceded by all recommended calibrations. A set of reference experiments were performed under nitrogen atmosphere with the flow rate recommended by the manufacturer and compared with similar experiments performed in the presence of air, to check for differences between them. A set of five experiments with different samples were performed for each condition. A few experiments with exceptionally different results, which could result from slippage or other experimental artifacts, were rejected. Samples for rheological experiments were prepared from pellets melted at 200 °C and injected into a mould with a Thermo scientific Mini Jet II injector. Mould temperature was set to 100 °C, injection pressure was 400 bar during 13 s, and second pressure was 200 bar during 4 s.

### 2.3. Preparation of composites

Multiwall carbon nanotubes (MWCNT) reference N7000 (Nanocyl) with average diameter and length of 9.5 nm and 1.5  $\mu$ m, respectively, containing 90% pure carbon and 10% of metal oxides (mainly alumina), were directly mixed with the polystyrene melt in a Brabender mixer (Plastograph EC) at 180 °C during 30 min at 100 rpm. It was shown that this procedure leads to samples with good dispersion of nanotubes within the polymer matrix [8,13]. Different concentrations of nanotubes were used for preparing the composites: 1.25 wt%, 5 wt% and 15 wt%. Collected samples were heated at 200 °C and injected into a mould following the procedure described above for polystyrene.

The homogeneity in the distribution of nanotubes was ascertained by microscopic observation of sections obtained from the prepared samples. As stated by others, this technique assesses only very large agglomerates and does not give information of dispersion at the submicron scale [8]. Despite this shortcoming, it is often used for providing information on the aggregation state [13]. Results at the supplementary material show that the size and distribution of agglomerates of nanotubes compares with those

**Table 1**

Molecular characteristics of the polystyrene used in this work: weight average molecular weight ( $M_w$ ), z average molecular weight ( $M_z$ ), polydispersity index ( $M_w/M_n$ ), molecular weight between entanglements ( $M_e$ ), molecular weight of the Kuhn monomer ( $M_k$ ), length of the Kuhn monomer ( $l_k$ ), volume of a tube confining a chain with molecular weight of  $M_n$  ( $V_{tube-Mn}$ ), physical volume of a chain with molecular weight  $M_n$  ( $V_{chain-Mn}$ ), the volume of one Kuhn monomer ( $V_k$ ) and the packing length ( $p$ ). Data extracted from references [11] and [12].

	$M_w$ (kg/mol)	$M_z$ (kg/mol)	$M_w/M_n$	$M_e$ (g/mol)	$M_k$ (g/mol)	$l_k$ (Å)	$V_{tube-Mn} \times 10^{-6}$ (Å <sup>3</sup> )	$V_{chain-Mn} \times 10^{-5}$ (Å <sup>3</sup> )	$V_k \times 10^{-3}$ (Å <sup>3</sup> )	$p$ (Å)
aPS	205.0	298.0	2.1	14,800	710	18	2.88	1.75	1.27	3.92

reported in other works, for composites obtained under similar conditions. The analysis of the dispersion state of nanotubes is usually done by indirect methods involving electrical conductivity measurements and analysis of the melt response to small amplitude oscillations in the viscoelastic linear regime [1].

### 3. Results

The different behaviour of polystyrene and its composites with MWCNT at the high temperature flow region is illustrated in Fig. 1a and Fig. 1b. They present small amplitude oscillatory shear results obtained at 210 °C in a controlled stress rheometer at the viscoelastic linear regime with a constant stress of 600 Pa. The viscoelastic linear limit was evaluated by stress scan experiments at the same temperature with an oscillation frequency of 10 Hz. Its value is around 1000 Pa.

Results in these two figures are well known and common for composites with different matrixes [1,2]. Polystyrene results are indicated by lines, solid and dashed, for  $G'(\omega)$  and  $G''(\omega)$ , respectively. Increasing the content of nanotubes to 1.25 wt% decreases slightly both  $G'(\omega)$  and  $G''(\omega)$ . This effect is more evident for the complex viscosity results – see the inset in Fig. 1b. Similarly to results of other works, also for this polymer and for this low concentration of nanotubes, we observed a behaviour contrary to the one predicted by Einstein's Eq. (1). One possible reason for the viscosity decrease may be explained, as in the work of Mackay et al. [4], by an increase in the free volume, originated by the chain ends not interacting with the nanotubes. The alternative explanation proposed by Sachin et al. [3] considers the selective adsorption of high molecular mass polymer chains on the surface of the nanotubes. We discuss this issue further in the discussion section.

An elastic plateau in the high temperature flow region becomes evident for the composite with 5 wt% of nanotubes. The percolation threshold limit for electrical conductivity in MWCNT and polystyrene composites was estimated to be around 4 wt% [14]. This percolation threshold depends on the method used in the preparation of the composite. Values of ~1.25 wt% were evaluated for composites prepared by mixing the nanotubes in a solution of polystyrene [15] and the appearance of solid-like behaviour was also detected at this low concentration of nanotubes. It appears that a link may exist between the percolation threshold for electrical conductivity and the onset of a well-defined elastic plateau at the flow region. However, this elasticity is not simple to understand. It was shown by Pötschke et al. [1] that the transition from liquid-like to solid-like behaviour strongly depends on temperature and that

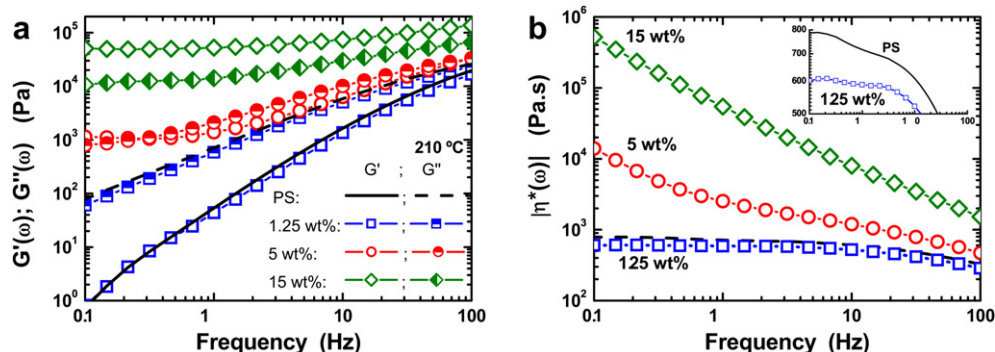
at higher temperatures it occurs for much lower concentrations of nanotubes.

At the concentration of 5 wt% of nanotubes,  $G''(\omega)$  becomes lower than  $G'(\omega)$ . Increasing the nanotubes concentration to 15 wt%, an additional increase in the  $G'(\omega)$  relative to  $G''(\omega)$  is observed. This behaviour may result from the increased density of interactions between polymer chains and the nanotubes. The differences between the two components of complex modulus are more evident at this concentration. Concurrently with this behaviour, and in agreement with published results [16], an increase in the shear thinning effect is observed by increasing the concentration of the nanotubes – Fig. 1b.

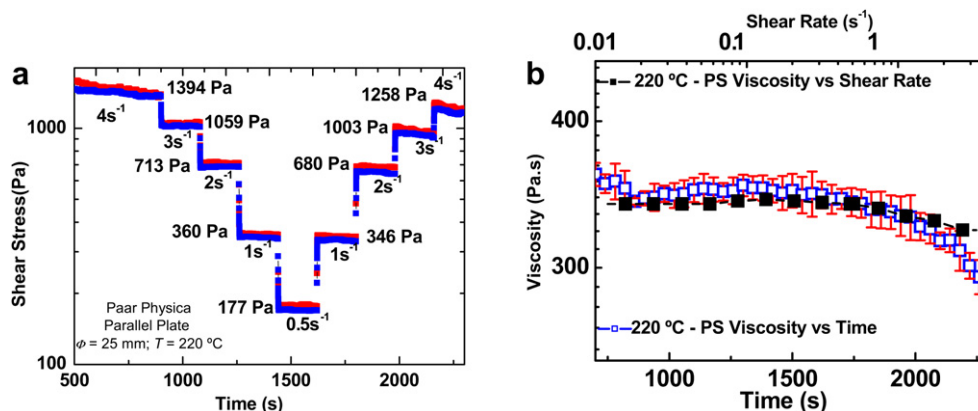
The analysis of the results in Fig. 1a and b raises several questions, which to our knowledge, were not fully answered so far. The first question relates to the physical nature of the elastic plateau at the high temperature flow region that increases in value by increasing the concentration of nanotubes. The second question relates to the effect of high temperature elasticity in the flow behaviour of polymer melts. The third one concerns the conciliation of the enhancement in the elasticity with the strong shear thinning observed for samples with higher concentration of nanotubes. Another question, related to the first one, is about the appearance of the solid-like behaviour for lower concentration of nanotubes at higher melt temperatures. In this work we answer the second question and discuss some of the other questions in the discussion section.

To answer the second question, we planned a set of step-shear experiments in polymer melts and their composites with different concentration of nanotubes. With results of these experiments we evaluated a flow activation volume (FAV).

The experimental evaluation of FAV in processes involving plastic deformation requires transient experiments. The purpose of these experiments is observing the type of response induced by a small perturbation to a monotonic test. In the flow of polymer melts a possible monotonic test consists in shearing the melt at constant shear rate – the start-up of shear experiment or shear stress growth experiment [17,18]. In these experiments, the shear stress, or melt viscosity, initially increases, goes through a maximum, the yield stress of the melt, decreases and stabilizes at a constant value in a steady-state. The initial behaviour, up to the viscosity stabilization, is non-linear. The final behaviour, the viscosity stabilization, is linear only if flow remains Newtonian, i.e. if the applied shear rate is small. Otherwise, due to the shear thinning character of polymer melts, or its enhancement in composites with nanotubes, small shear rate variations would induce significant changes in the melt viscosity that may change



**Fig. 1.** Small amplitude oscillatory shear results for polystyrene and the composites with MWCNT performed with a constant stress of 600 Pa at 210 °C. All results were obtained within the high temperature flow region. (a) Variation of the elastic and dissipative components of the complex modulus with the oscillation frequency. Note the shift between  $G'(\omega)$  and  $G''(\omega)$  at the concentration of 5 wt% of nanotubes. (b) Complex viscosity variation with the oscillation frequency. The inset shows the difference in the viscosity between the pure polymer and the composite with 1.25 wt% of nanotubes. Note the increased shear thinning behaviour at higher concentrations of nanotubes.



**Fig. 2.** Results of step-shear experiments with atactic polystyrene at 220 °C with the parallel plate configuration, plate diameter of 25 mm and gap size of 0.7 mm. (a) Start-up of shear with a constant rate of 4 s<sup>-1</sup> during 800 s (strain of 3200 s.u.) until the attainment of a well-defined steady-state. The monotonic test was perturbed with the following shear steps: 3 s<sup>-1</sup>, 2 s<sup>-1</sup>, 1 s<sup>-1</sup>, 0.5 s<sup>-1</sup> and up again. The time duration of each step was 180 s. (b) Variation of viscosity with time during the perturbation of the monotonic test. Open squares show the average result of three different experiments. The error around the mean is indicated. Filled squares show the viscosity variation with shear rate. The melt was initially sheared with constant rate of 4 s<sup>-1</sup> during 800 s – same strain as in (a). After this shearing, a controlled shear rate was performed from 4 s<sup>-1</sup> to 0.01 s<sup>-1</sup>.

the flow mechanism. The key assumption in these experiments is that the flow mechanism is not affected by the transient experiments. It should be stressed that the fulfilment of this assumption is better achieved if the monotonic test conducts the melt to a steady-state and if perturbations are applied only in this state.

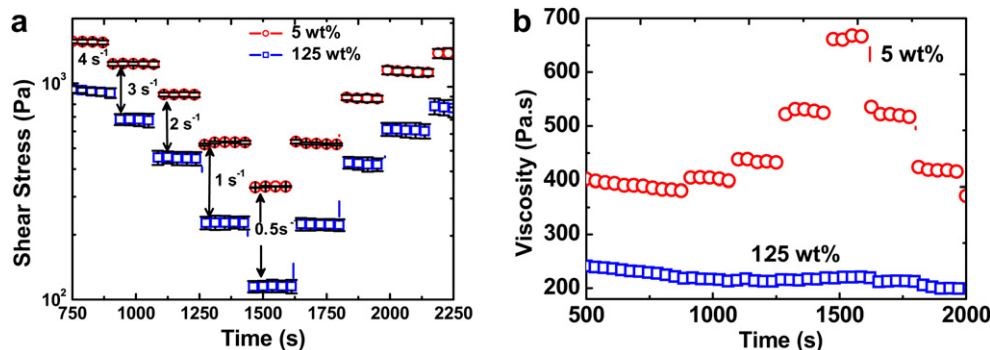
Fig. 2a shows results of step-shear experiments for polystyrene. The protocol followed was based on results of previous works where the strain needed to establish a steady-state at different melt temperatures was evaluated [18]. For aPS, in the temperature range between 200 °C and 240 °C, this strain varies from ~8000 s.u. to ~2000 s.u. At 220 °C, the melt was sheared with a constant rate of 4 s<sup>-1</sup> during 800 s (strain of 3200 s.u.). This monotonic test was perturbed by steps with lower shear rates (3 s<sup>-1</sup>, 2 s<sup>-1</sup>, 1 s<sup>-1</sup>, 0.5 s<sup>-1</sup>, and then up), each one with a time duration of 180 s. The average stress at each step is indicated in Fig. 2a. The highest difference in the average stress values occurs for the shear rate of 4 s<sup>-1</sup>, and it is around 10%.

The variation of melt viscosity during the transient experiments is presented in Fig. 2b (open squares). Viscosity changes during the whole transient experiment are less than 10% around the mean value. This variation suggests that the flow mechanism was unaffected by the monotonic test. The similarity of stress values for perturbations induced at the same rate shown in Fig. 2a confirm this assessment. Further confirmation of these melt viscosity values was made by controlled shear rate experiments at the same melt temperature, shown by filled squares in Fig. 2b. The melt was

initially sheared with a constant rate of 4 s<sup>-1</sup> during 800 s (similarly to the step-shear experiments). This initial shearing was then followed by a controlled shearing from 4 s<sup>-1</sup> to 0.01 s<sup>-1</sup>.

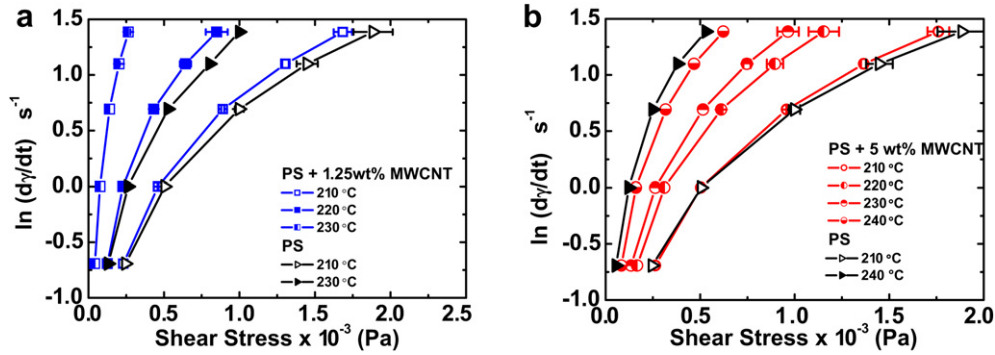
Comparable experiments, following the protocol described for the experiments depicted in Fig. 2a, were performed for the composites with nanotubes. Fig. 3a and b show the results obtained for 1.25 wt% and 5 wt% of nanotubes. Due to their poor reproducibility, results for the composites with 15 wt% of nanotubes are not shown. The lower viscosity of the composite with 1.25 wt% is confirmed again in Fig. 3b.

A significant difference in these results with respect to those obtained for the pure polymer is the change in the viscosity of the composite with 5 wt% of nanotubes during the transient experiments. This is explained by the strong shear thinning illustrated in Fig. 1b, which is also probably the reason for the experimental difficulties found in the step-shear experiments for the composite sample with higher concentration of nanotubes. Despite the viscosity variation during the transient experiment, we consider that the basic assumptions of the rate theory of plastic deformation still remain valid for this composite (5 wt%) and that the flow mechanism remains unperturbed by the shear steps. Those assumptions are the microscopic reversibility and the principle of detailed balance. Since both shear stress and viscosity return to their previous values after the perturbation, we presuppose the fulfilment of the above assumptions.



**Fig. 3.** Results of step-shear experiments with the composites of atactic polystyrene and MWCNT at 220 °C. The experimental setup was the same as in Fig. 2. (a) Start-up of shear with a constant rate of 4 s<sup>-1</sup> during 800 s (strain of 3200 s.u.) until the attainment of a well-defined steady-state. The monotonic test was perturbed with the following shear steps: 3 s<sup>-1</sup>, 2 s<sup>-1</sup>, 1 s<sup>-1</sup>, 0.5 s<sup>-1</sup> and up again. The time duration of each step was 180 s. (b) Variation of viscosity with time during the perturbation of the monotonic test. Open squares indicate the results obtained for 1.25 wt% of nanotubes and circles those for 5 wt% of nanotubes.





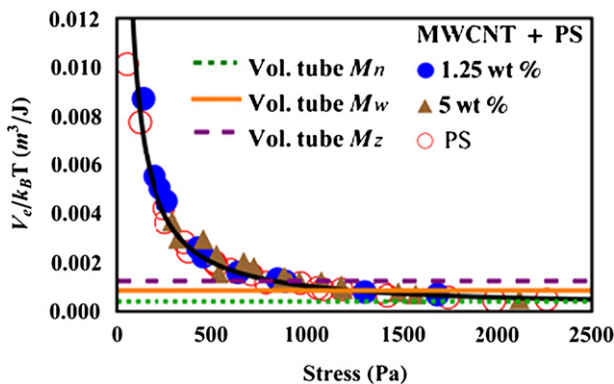
**Fig. 4.** Variation of the logarithm of the shear rate as function of the shear stress for polystyrene and the composites. (a) Composite with 1.24 wt% of MWCNT. (b) Composite with 5 wt% of MWCNT. In both figures results obtained for PS are indicated with triangles – open triangles for the lowest temperature and filled triangles for the highest temperature.

Representation of data in Figs. 2a and 3a according to Eq. (5) is shown in Fig. 4a and b for the composites with 1.25 wt% and 5 wt% of nanotubes, respectively. Results obtained for polystyrene at the lowest and highest temperature of the set of experiments represented in Fig. 4a and b are indicated with triangles (open and filled). The slope of these curves at each shear stress value is  $V_e/k_B T$ .

Fig. 5 shows the experimental values of FAV evaluated for the polymer and composites obtained by applying Eq. (5) to the results of Fig. 4. The fit of these results with Eq. (7) is also shown. We note that this equation has only one adjustable parameter. Clearly, the variation of experimental flow activation volume with the shear stress is well described by the rate theory of plastic deformation. The value obtained for the  $\alpha$  parameter was  $3.357 \times 10^{-4} \text{ m}^3/\text{J}$ , which yields a flow activation volume at  $T = 240^\circ\text{C}$  of  $2.378 \times 10^6 \text{ \AA}^3$ . This value is much larger than the physical volume of the chain, which is one order of magnitude below (see Table 1). Volumes higher than the physical volume of the chain have to be considered for explaining this large value obtained. We note that results similar to those of Fig. 5 are described in the literature for the plastic deformation of metals [10,19]. However, in the later case, much lower values for the flow activation volume were obtained.

Physically meaningful volumes in polymer melts, higher than the volume of a chain, are those of a tube confining the chains with different molecular weight. The volume of a tube confining a chain with molecular weight  $M$  is

$$V_t = \pi \frac{a^3}{4} Z = \frac{\pi}{4} \frac{M_e^{1/2}}{M_k^{3/2}} \cdot l_k^3 \cdot M, \quad (8)$$



**Fig. 5.** Variation of the flow activation volume with the shear stress for polystyrene and the composites. Black line is the fit of the experimental data obtained with the equation derived from the rate theory of plastic deformation, Eq. (7). Horizontal lines show the values of  $V/k_B T$  for the volume of a tube confining the chains with  $M_n$  (short dash),  $M_w$  (solid) and  $M_z$  (long dash).

where  $a$  is the tube diameter defined as  $\langle a^2 \rangle = n_{k,e} \cdot l_k^2$ ;  $n_{k,e}$  is the number of statistical chain segments between entanglements, each one having a length equal to one Kuhn monomer ( $l_k$ );  $Z$  is the number of entanglements in the chain defined by the ratio  $M/M_e$ , where  $M_e$  is the molecular weight between entanglements;  $M_k$  is the molecular weight of the Kuhn monomer.

The physical volume of the chain was evaluated from the definition and experimental values of the packing length. The packing length [11] is defined as

$$p = \frac{V_{\text{chain}}}{\langle r^2 \rangle_0} \quad (9)$$

where  $V_{\text{chain}}$  is the physical volume of the chain and  $\langle r^2 \rangle_0$  the average square distance of the unperturbed chain.

#### 4. Discussion

Fig. 5 demonstrates that the experimental flow activation volume of polystyrene and the composites superimpose in the same curve. This curve was fitted by Eq. (7) derived from the rate theory of plastic deformation. The true flow activation volume is clearly that of a tube confining the chain. Although there is some uncertainty in the experimental flow activation volumes evaluated at large stress values, the result obtained for this specific polymer suggests that true FAV is determined by a tube confining chains with lowest molecular weight, those of  $M_n$ . Validity of this assessment will be tested in future works with model polymer samples of lower polydispersity.

Since similar flow activation volumes were evaluated for the polymer and composites, regardless the concentration of nanotubes, we concluded that low frequency elasticity illustrated in Fig. 1 didn't affect the volume swept by the flow segment. For understanding this result, a detailed analysis of the interactions between polymers and nanotubes, or similar surfaces, is required.

Molecular dynamics simulations are a good source for providing details of these interactions. Despite results of more recent works, we focused our attention on the work of Liao and Li [20]. They performed molecular dynamics simulations of polystyrene molecules with different length interacting with graphene and provided information for the strength of these interactions. It was found that the adhesion energy between random coils of polystyrene and a much larger graphene surface decreases with the chain molecular weight, stabilizing at a value of 0.22 eV (21.22 kJ/mol) for a chain with 80 repeated units, around half the molecular weight between entanglements.

The interaction energy of 21.22 kJ/mol is relatively high, almost five times the melt thermal energy at  $200^\circ\text{C}$ , and much higher than

the interaction energy involving a loop and chain of polystyrene, which is  $\approx 1.8$  kJ/mol at the same temperature [21]. This energy results from van der Waals and electrostatic interactions. For a carbon nanotube-polystyrene system with no chemical bonding, it was found, in addition, that besides van der Waals and electrostatic interactions, two additional sources of interaction result from the mismatch in the coefficient of thermal expansion of the nanotubes and PS, and the radial deformation of nanotubes induced by atomic interactions. Liao and Li considered also that these last two factors “may be more important in governing the interfacial characteristics in MWCNT/PS systems”.

These results provide some quantitative support to a qualitative model proposed by Pötschke et al. [1]. This model considers that blending of polymers with nanotubes results in the formation of three networks: 1) a temporary polymer network formed by entanglements, 2) the carbon nanotube network and 3) a combined carbon nanotube-polymer network. To explain the elastic plateau in  $G'(\omega)$ , it was assumed that the “connection of polymer chains to the carbon nanotubes is much more stable than the entanglements of the polymer chains”, i.e. the relaxation time of polymer-nanotube interactions is longer than the reptation time of polymer chains.

The flow activation energy of polystyrene is  $\approx 90$  kJ/mol. Its value for the composite with nanotubes is impossible to determine due to the failure of time–temperature superposition. The relative strength of polymer-nanotube ( $>21.22$  kJ/mol) and polymer–polymer (1.8 kJ/mol) interactions explains in principle the physical nature of the elastic plateau at the flow region. The coexistence of these interactions with the similar values evaluated for the flow activation volume value may be understood if they are represented by a “solid-like” network connecting chain segments in random conformational sequences – the combined carbon nanotubes-polymer network of Pötschke et al. [1].

Invoking again the principle of microscopic reversibility, we assume that, at steady-state, chain segments detached from the nanotubes as a result of shear flow are compensated by the attachment of other chain segments of similar length. For a polymer with a specific molecular weight, the average number of chain segments interacting directly with the nanotubes should remain constant during flow in a steady-state, depending only on the nanotubes concentration, and of course, on their dispersion within the matrix. Hence, higher concentration of nanotubes would imply more frequent interactions with chain segments, explaining therefore the higher values obtained for the elastic plateau.

An alternative explanation for the morphology at the interface between polymers and nanotubes implies considering flow units composed by the nanotube and the attached polymer chains. If this was the case, the experimental flow activation volume of the composites would not superimpose with the values obtained for the polymer, as we found in Fig. 5. This explanation is therefore excluded.

We will discuss with more detail in a future work the issue of interactions between polymer chains and nanotubes at the high temperature flow region. The increase in the number of interactions between chains and nanotubes may result from two factors: an increase in the concentration of nanotubes or an increase in the polymer molecular weight. A composite of a high molecular mass polymer and low concentration of nanotubes should behave similarly as a composite of a low molecular weight polymer and a higher concentration of nanotubes. A set of detailed experiments within the viscoelastic linear regime at the flow region will be presented in future work. Results of these experiments will provide quantitative support to the key ideas expressed in the model of Pötschke et al. [1], allowing a deeper understanding of the elasticity

of nanotube-polymer composites at the flow region. It is our view that experiments with composites of model polymer chains and nanotubes could provide useful information for better understanding the flow mechanisms in polymer melts.

Less frequent interactions of polymer chains with carbon nanotubes may be at the source of the lower viscosity shown by the composites with 1.25 wt% of nanotubes. A viscosity decrease may easily be understood by a free volume increase. However, the selective adsorption of high molecular mass polymer chains, presented as an alternative explanation for that effect, does not necessarily disagrees with a free volume increase. The later effect may imply the former. In composites with low concentration of nanotubes, carbon nanotube-polymer interactions are less frequent, involving with more probability chains of high molecular weight. Because of these interactions, longer chains interacting with the nanotubes are expected to be less entangled with other chains, when compared to chains of similar length in the melt. Fluctuations of the chains resulting from the thermal (Brownian) motion of the segments may be estimated by a fluctuation amplitude  $-\delta L/L = Z^{-1/2}$ , where  $L$  is the length of the primitive chain,  $\delta L$  the fluctuation and  $Z$  the number of entanglements in the chain [22,23]. Less entangled chains have higher fluctuation amplitude which originates an increase in the free volume.

## 5. Conclusions

The experimental flow activation volume of polymer melts and composites with carbon nanotubes was evaluated by transient experiments. In these experiments, a monotonic test at steady-state was perturbed by shear steps. We assumed that perturbations induced by the shear steps left the flow mechanism unchanged. An average stress value at each shear step was evaluated, and it was shown that the stress variation of the apparent flow activation volume follows the rate theory of plastic deformation.

The true flow activation volume for polymer melts and composites was evaluated by fitting the single parameter equation derived from the theory to the experimental results. It agrees with the volume of a tube confining the polymer chain and it is one order of magnitude higher than the physical volume of the chain, and far below the volume of a nanotube.

In a way similar to the entanglements in polymer melts, the coexistence of these flow units (volume of a tube confining the chains) with the elasticity observed in composites at the high temperature flow region was explained assuming that, at steady-state, the chain segments detaching from nanotubes are compensated by an equal number of chain segments attaching to the nanotubes. Our results suggest that interactions with an energy higher than  $>21.22$  J/mol are created and destroyed during flow at steady-state.

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## Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.09.028.

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