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A rheological analysis of interactions in phenoxy/organoclay nanocomposites

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Abstract

Novel oscillatory flow results of phenoxy/organoclay nanocomposites are analysed considering the blocking effect of nanostructure on polymer chain mobility. The modification provoked by this hindering effect on loss tangent spectrum is investigated. The study of three different systems, involving a pristine montmorillonite and two montmorillonites modified with one alkyl tail and two alkyl tails, respectively, leads to conclude that polymer–alkyl repulsive interactions play the most important role in the chain mobility obstruction process. Our results suggest that polymer–alkyl interactions increase with temperature.

Keywords: Nanocomposites; Organoclay; Phenoxy; Mechanical relaxation; Chain mobility

1. Introduction

It is well known that polymer–nanoparticle interactions determine the dispersion level of nanoparticles in the polymer matrix, which in turn is directly correlated to the rheological and mechanical properties of the system. Depending on the interaction between the components, different morphologies can be formed. In the case of functionalized nanoparticles, three different types of interactions have to be considered, involving the following components [1,2]: the particle surface, the interfacial component (organic substitution of the particle surface) and the matrix polymer chains. For chemically modified montmorillonites, four situations can be envisioned in polymer-based nanocomposite preparation [3–5]: (a) The polymer chains remain separated from the montmorillonite layers. (b) The polymer chains are intercalated between the clay layers, resulting in an alternate structure. (c) The polymer chains break the structure of the clay and layered silicates are exfoliated and dispersed in the polymer matrix. (d) Montmorillonites are not exfoliated neither intercalated by polymer chains, but remain as tactoids forming an effective network within the polymer matrix.

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The mechanical properties of nanocomposites are to a great extent determined by the particle dispersion level. However, as the rheological behaviour in the terminal zone is concerned, longer experimental times are involved and the different types of polymer–nanoparticle interactions can play a more crucial role than the dispersion level. Consequently, the rheological properties of polymer-based nanocomposites have deserved an intensive scientific interest in the last quinquennium. In particular, the oscillatory or dynamic flow of unmodified and organically modified montmorillonite nanoparticles mixed with polycarbonate [3], EVA copolymer [4], polyethylene [5], polypropylene [6], polyamide [7] and poly(butylene terephthalate) [8] have been investigated. Similar studies have been carried out for carbon nanotubes dispersed in polycarbonate [9,10], polypropylene [11], polyamide [12], polyurethane [13] and poly(methyl methacrylate) [14]. The results we present in this paper refer to phenoxy/montmorillonite nanocomposites. Poly(hydroxy ether of bisphenol A), plainly called phenoxy (Ph), has been rarely used as a polymer matrix [15,16]; to our knowledge no rheological results of phenoxy-based nanocomposites have been reported in the literature. However, this is a rheologically interesting polymer because it can be processed in the interval 165–250 °C and its high activation energy of flow gives rise to a wide range of viscosities. From a more general point of view, phenoxy is an adequate matrix for producing polymer nanocomposites, because its pendent hydroxyl group makes it very prone to chemical interactions with polar groups of organically modified clays. Our work is focused on the effect of nanoparticle/polymer chain interactions on the terminal viscoelastic zone.

2. Experimental

In this study the same matrix is employed to prepare all nanocomposites: a commercial poly(hydroxy ether of bisphenol A), received from Union Carbide, with weight average molecular weight $M_w = 50{,}700$ and number average molecular weight $M_n = 18{,}000$. Cloisite Na$^+$ (pristine montmorillonite) and two different types of organically modified montmorillonites (organoclays), manufactured by Southern Clay Products, are used: the first clay is Cloisite 30B (C30B), treated with a surfactant (MT2EtOH) having the chemical structure: methyl, tallow, bis(2-hydroxyethyl), quaternary ammonium chloride, as it is shown in Fig. 1a. The other organoclay, Cloisite 20A (C20A), is treated with a surfactant (2M2HT) having the chemical structure dimethyl, dehydrogenated tallow, quaternary ammonium chloride (Fig. 1b). In this figure, N$^+$ denotes quaternary ammonium chloride, T denotes tallow consisting of 65% C18, 30% C16 and 5% C14 and HT denotes dehydrogenated tallow. The amount of surfactant is 32 wt% in Cloisite 30B and 35 wt% in Cloisite 20A, and in both cases 100% of the Na$^+$ ions in natural montmorillonite have been exchanged. Note that Cloisite 30B has two hydroxyl groups and one tail, and Cloisite 20A has two tails.

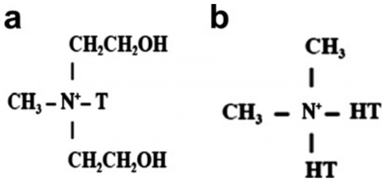

Fig. 1. (a) Chemical structure of Cloisite 30B. (b) Chemical structure of Cloisite 20A. T denotes tallow consisting of 65% C18, 30% C16 and 5% C14 and HT denotes dehydrogenated tallow. Cloisite 30B has one tail and two hydroxyl groups, and Cloisite 20A has two tails (see text).

To prepare the nanocomposites, pure polymer was dried in a vacuum oven at 80 °C for 14 h. Nanocomposites were obtained by melt blending using a Collin ZK25 co-rotating twin-screw extruder-kneader. The barrel temperature was 190 °C and the rotation speed 150 rpm. The amount of clay varies from 2 to 8 wt%.

A phenoxy/SWNT (single wall carbon nanotubes, prepared by the arc discharge method) nanocomposite was also compounded for comparison purposes.

After drying pelletized nanocomposites and getting specimens by compression moulding (4 min at 190 °C and 100 bar), rheological measurements were carried out using an Advanced Rheometric Expansion System (ARES, Rheometric Scientific) with a parallel-plate fixture (25 mm diameter) to conduct dynamic frequency sweep experiments of the nanocomposites, measuring the loss tangent as a function of angular frequency (ω), covering an interval from 0.0628 to 94.2 rad/s at 170–230 °C. The differences found between data obtained from low to high or from high to low frequencies, were absolutely irrelevant. In accordance, the occurrence of polymer degradation or non-equlibrium in nanoclay orientation is disregarded.

3. Results and discussion

In Fig. 2 the storage modulus, G', and the loss tangent, $\tan\delta$, are displayed as function of frequency to show the alteration of the terminal viscoelastic zone when a certain amount of filler (in this case 4% Closite 20A organoclay) is added to the phenoxy matrix. Similar results are obtained for phenoxy/Cloisite Na^+ and phenoxy/Closite 30B nanocomposites. The strong reduction of the frequency dependence of G' observed for 4% Closite 20A nanocomposite at low frequencies (Fig. 2a) is attributed to the formation of a three-dimensional structure, as has been typically reported and discussed in the literature [6–8]. However, the appearance of a low frequency $\tan\delta$ maximum, as such observed in Fig. 2b, has not deserved practically any attention. To our knowledge, only Devendra et al. [5], for polyethylene/montmorillonite nanocomposites and Pötschke [10], for carbon nanotubes dispersed in polycarbonate, have shown a similar $\tan\delta$ trend, but disregarded any interpretation of the data. What we propose in this paper is to gain insight on the polymer chain–nanoparticle interactions, analysing $\tan\delta$ results like those shown in Fig. 2b. Our interpretation of the results is based on the mobility restrictions imposed by nanoparticules to polymer chains.

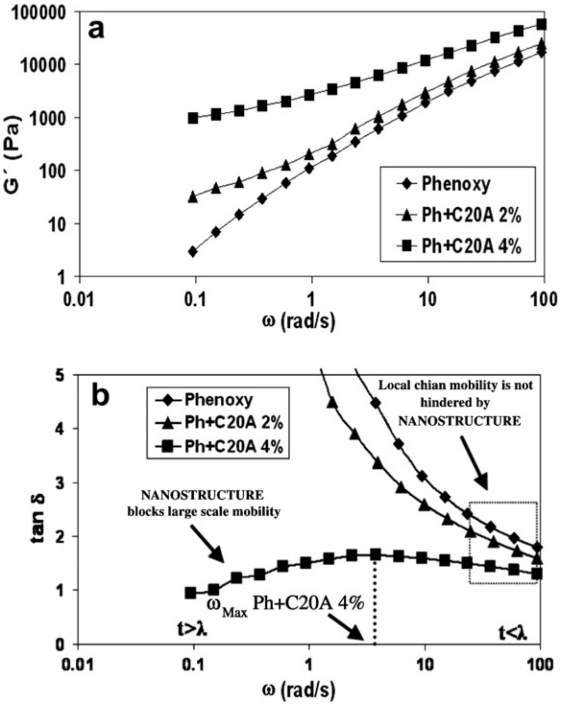

Fig. 2. Dynamic viscoelastic functions for pure phenoxy and the indicated phenoxy/organoclay nanocomposites at $T = 230\,°C$: (a) Storage modulus as a function of frequency. (b) Loss tangent as a function of frequency. For phenoxy and Ph+C20A2% samples, the loss tangent increases continuously as frequency is decreased (data at low frequencies are not included to shorten the scale). The mechanical relaxation ($\tan\delta$ maximum) observed for Ph+C20A 4% nanocomposite is attributed to the built up nanostructure. See Fig. 2 and the text for the physical meaning of λ characteristic time.

A significant aspect of the viscoelastic spectrum of an amorphous polymer of high molecular weight is the presence of a loss tangent minimum, after the transition from glasslike to rubberlike state. This general behaviour is depicted in Fig. 3. According to the classical explanation based on entanglements coupling (still currently admitted), the loss tangent should pass through minimum separating motions within entanglement strands and motions across entanglement loci. As stated by Ferry [17], the loss is minimal because the period of oscillation is long compared with the longest relaxation time of an entanglement network strand, but short compared with times for entanglement slippage motions. The presence of a nanostructure in the amorphous polymer matrix alters considerably the viscoelastic behaviour in the terminal zone. A clarifying example of the terminal zone modification is seen in the viscoelastic pattern of block copolymers, envisaged by Kossuth [18], an adaptation of which is shown in Fig. 3 in terms of the loss tangent. Besides the minimum associated to entanglements, a second $\tan\delta$ minimum is noticed at a lower value of frequency, disclosing the existence of a mechanical relaxation denoted by an intermediate $\tan\delta$ maximum. The appearance of the lowest frequency $\tan\delta$

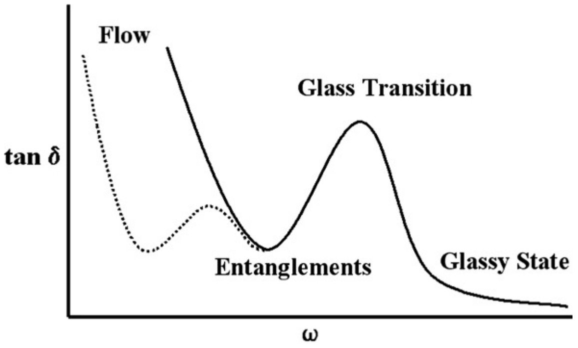

Fig. 3. General trend of the loss tangent as a function of frequency: continuous line shows the viscoelastic behaviour of an amorphous polymer. Dotted line shows the modification of the terminal zone due to the presence of a nanostructure in the polymer matrix.

minimum is a result of the formation of a three-dimensional structure.

Considering the general frameworks depicted in Fig. 3, the times involved in our experiments of Fig. 2 are longer than the relaxation time for entanglement slippage motion or disengagement time in tube and reptation model [19]. This leads to a predominantly viscous response of the material characterized by a $\tan\delta$ increase without limit, provided that chain mobility is not hindered by other kind of interactions, such as those arising, for instance, from microphases (in the case of block copolymers) or nanoparticles. The rheological consequences of the hindering effect of organoclay nanoparticules are seen in Fig. 2b. At high frequency values, the trend observed for pure phenoxy and nanocomposites indicates that motions across entanglements are possible in spite of the presence of nanoparticles. However, at low frequencies, the mobility of the chains is considerably reduced for 4% organoclay nanocomposite, giving rise to an increase of the elastic response, since losses decrease as ω tends to zero. Therefore, the $\tan\delta$ maximum, $(\tan\delta)_{\mathrm{Max}}$, observed in Fig. 2b marks a certain limit in the mobility of polymer chains in a nanocomposite. A characteristic time, λ, of a relaxation process is defined taking the inverse of the frequency at which $(\tan\delta)_{\mathrm{Max}}$ occurs. That is to say, $\lambda = 1/\omega_{\mathrm{Max}}$. At a given temperature, the chain mobility which requires times larger than λ ($t > \lambda$, which implies the low frequency zone is hindered. However, the chain mobility level involving times shorter than λ ($t < \lambda$, corresponding to the high frequency zone is not obstructed.

The general viscoelastic behaviour depicted in Fig. 3 and the reflections on the results shown in Fig. 2b must be analysed considering the existence of three physical networks in polymer nanocomposites [10]: (a) Chain entanglements-polymer network, (b) combined polymer–nanoparticle network, and (c) organoclay–organoclay network.

Interaction between adjacent aggregates can lead to a particle network structure, but interactions between clay particles and polymer chains are more likely to occur at low clay contents. The effect of two types of interactions, entanglements and polymer–nanoparticle interactions, should be noticed in the terminal zone. In the molten state, the chain mobility required to achieve slippage motions across the entanglement loci is acquired at low short times, corresponding to the oscillatory experiments carried out at our highest frequencies. According to the results of Fig. 2, entanglement slippage motions are accomplished, even in the eventual presence of a polymer–nanoparticle network (4% sample). However, motions which imply distances larger than the strands between particle/polymer interaction points require times $t > \lambda$ and are, therefore, blocked, provoking the $\tan\delta$ decrease as frequency increases.

In Fig. 4, the $\tan\delta$ results of four phenoxy nanocomposites based in three different organoclays and SWNTs are presented. The analysis of the results obtained, respectively, with phenoxy/Cloisite Na^+, phenoxy/Cloisite 20A and phenoxy/Cloisite 30B nanocomposites can help to gain insight on the origin of the polymer–nanoparticle interactions. As it has been reported in two papers published by Gurmendi et al. [15,16], of our research institute (POLYMAT), on the same phenoxy/organoclay systems prepared under the experimental conditions described in Experimental part, Cloisite 30B is better dispersed than Cloisite 20A, and the latter better than Cloisite Na^+. This higher dispersion level is attributed to the two hydroxyethyl groups of Cloisite 30B which make it polar, leading to a stronger interaction with the polar phenoxy matrix. This should lead to a more efficient blocking effect of Cloisite 30B on polymer chains and, consequently, to a shorter λ characteristic time than for Cloisite 20A. Actually chain mobility at short times is very similar for both systems, as deduced by the practically equal $\tan\delta$ values at high frequencies (Fig. 4). But $(\tan\delta)_{\mathrm{Max}}$ shifts to a lower frequency value for phenoxy/Cloisite 30B nanocomposite, indicating that the blocking effect of Cloisite 30B

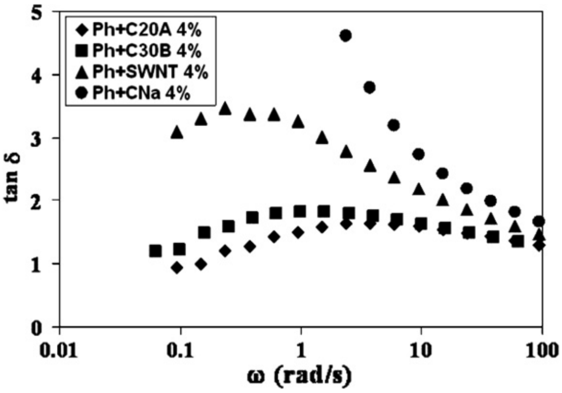

Fig. 4. Analysis of the mechanical relaxation of the terminal zone for 4% phenoxy/Cloisite 20A, phenoxy/Cloisite 30B and phenoxy/SWNT nanocomposites at $T = 230$ °C.

is delayed (larger λ value), although more polymer–organoclay interactions should be expected for this system. This unexpected result, which is also observed for other concentrations and temperatures (not shown), must be interpreted within the framework of a thorough analysis of phenoxy–organoclay interactions. Our reflections are based on the role played by alkyl tails on the interactions of the polymer chains with the organoclay platelets, disclosed recently by Fornes et al. [2] for nanocomposites based on Nylon 6. Besides platelet–platelet attractions, interactions between the polymer and the silicate pristine surface, as well as polymer–alkyl repulsive interactions, are considered. The number of alkyl tails plays a crucial role in the density of these interactions. Increasing the amount of alkyl tails provokes a reduction of polymer–silicate contacts, but an increase of polymer–alkyl interactions. Regarding the organoclays considered in our work, we recall that Cloisite 20A has two alkyl tails and Cloisite 30B only one. Therefore the more efficient blocking effect of Cloisite 20A (as noticed in Fig. 4) leads to suggest that the mobility of polymer chains is hindered by the alkyl tails of the organoclays. That is to say, polymer–alkyl repulsive interactions play a more important role than interactions between the polymer and the silicate surface in the obstruction of polymer chains mobility. Significantly enough, no mechanical relaxation is observed for the nanocomposite based in pristine montmorillonite, although this could also be due to the poorly reached dispersion level.

The case of a different nanocomposite, phenoxy/SWNT, in which the carbon nanotubes are not chemically modified, is also considered in Fig. 4 for comparison purposes. The mechanical relaxation, loss factor maximum, is also observed, but the associated λ characteristic time is larger than for organoclays, indicating that non functionalized SWNTs are less prone to block polymer chains than organically modified montmorillonite.

The influence of temperature through the investigated low frequency mechanical relaxation is shown in Fig. 5a. The maximum shifts to higher frequencies as temperature increases. This is attributed to the mobility of the polymer chains which augments with temperature and, therefore, the blocking effect of polymer–nanoparticle interactions should be noticed at shorter times. Such a variation of chain mobility is given by the viscosity dependence on temperature. In the range of temperature considered in our work, well above the glass transition temperature of the phenoxy polymer matrix, an Arrhenius-like dependence is observed,

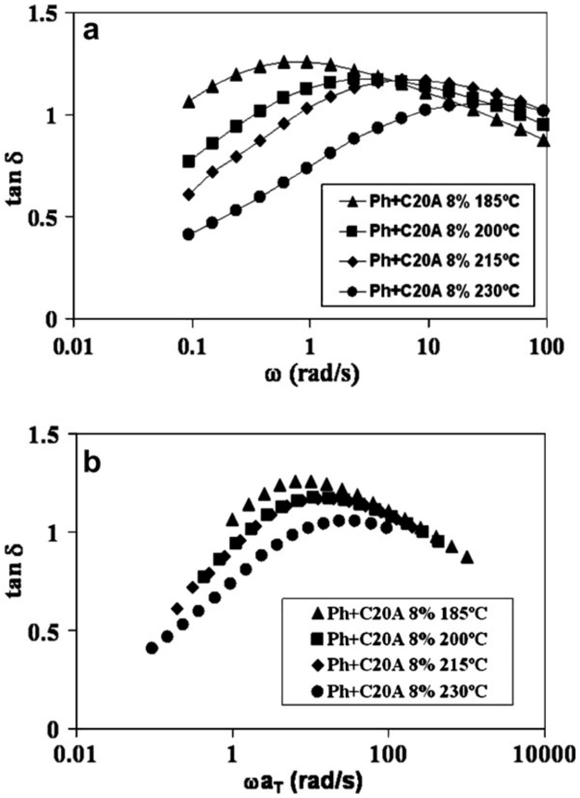

Fig. 5. Effect of temperature on the mechanical relaxation observed in the terminal zone, for 8% phenoxy/Cloisite 20A nanocomposite: (a) Results at different temperatures. (b) Horizontal shift of the data using the reduced variable ωa_T (see text). Reference temperature $T_0 = 230$ °C. It is observed that $(\tan\delta)_{\mathrm{Max}}$ is not shifted to the same position for all temperatures.

$$\eta(T) = B\,\mathrm{e}^{(E_a/RT)} \tag{1}$$

where the activation energy of flow is $E_a = 101$ KJ/mol K. An horizontal superposition of the data of Fig. 5a could be expected using the reduced variable (ωa_T), where the shift factor $a_T = \eta(T)/\eta(T_0)$ accounts for the effect of temperature on chain mobility. A certain superposition of data is observed at high frequencies in Fig. 5b. However, the results show that the relaxation times (inverse of the frequency at which $(\tan\delta)_{\mathrm{Max}}$ occurs) are not shifted to a single value: Therefore it should be an intrinsic effect of the temperature on the polymer–nanoparticle interactions. Since a_T corrects the effect of temperature on chain mobility, the shorter relaxation times, $\lambda = 1/\omega_{\mathrm{Max}}$, observed as temperature increases, indicate that even with the same capacity of the chains to move, a shorter time is required to block their motion at high temperatures. This implies that interactions between modified clay and polymer chains, in particular polymer–alkyl repulsive interactions, are promoted as temperature increases.

4. Conclusion

The rheological results of phenoxy-based nancomposites, involving a pristine montmorillonite and two montmorillonites modified with one alky tail and two alkyl tails, respectively, are interpreted considering the hindering effect of the nanostructure on polymer chain mobility. It is concluded that polymer–alkyl repulsive interactions, rather than interactions between the polymer and the silicate surface, obstruct mobility. According to our interpretation of the experimental results, polymer–alkyl interactions increase with temperature.

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