Viscosity of Bead Suspensions in Polymeric Solutions

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Synopsis

Viscosity measurements made by a cone-plate viscometer on polyisobutylene in decalin solutions at different concentrations and their corresponding glass bead suspensions with filler loadings up to 40% by volume are reported. The range of shear rate $\dot{\gamma}$ investigated is between 0.1 and 1000 sec^{-1}. The solutions show shear-thinning behavior, and the relative viscosity η_r of the slurries generally decreases with increasing shear rate. The results indicate two different types of mechanism, respectively at high and low shear rates. At low $\dot{\gamma}$, the relative viscosity can be correlated extending relations already well known for suspensions in Newtonian liquids which are based on the mechanism of aggregate disruption. The behavior at high $\dot{\gamma}$ values is believed to be due to the influence of the filler on the flow properties of macromolecules, in particular on relaxation time. Through a shifting procedure, an increase in relaxation time which depends on filler content and not on polymer concentration is shown.

INTRODUCTION

The rheological behavior of slurries in which the suspending medium is a non-Newtonian polymeric-fluid has recently been the object of large interest owing to increasing use of composite materials.

While the rheological properties of solid particulate composites can be fairly well predicted, the effect of filler on the viscosity–shear rate dependence, which is very important in the forming process of such polymeric systems, is not yet clear. In this work, viscosity measurements made by a cone-plate viscometer on polymeric solutions and their corresponding glass bead suspensions with filler loadings up to 40% by volume are reported.

In a previous paper,[1] the dependence of the viscosity η on shear rate $\dot{\gamma}$ for suspensions in non-Newtonian liquids was compared with that for suspensions in Newtonian liquids. For the latter slurries, the relative viscosity η_r (i.e., the ratio of the suspension viscosity to that of the medium at the same value of $\dot{\gamma}$) decreases with increasing shear rate toward an asymptotic value which is a function of filler content. To describe this concentration dependence, many correlations have been suggested in the literature,[2] starting from the one proposed by Einstein[3] in 1905.

The decrease in relative viscosity with the shear rate has been interpreted as due to the disruption of doublets[4] or aggregates of particles[5] and then to a further geometric redistribution of the filler in conditions of minimum energy dissipation. In particular, the data presented in reference 1 were correlated with the Kreiger-Dougherty equation.[4]

A similar dependence of relative viscosity η_r on shear rate has been found for suspensions in non-Newtonian polymeric solutions[1,6] and for particulate, filled melt polymers.[7]   This effect has tentatively been interpreted[1] by a mechanism analogous to the one active in suspensions of Newtonian liquids.   This dependence was correlated with a modified Krieger-Dougherty equation which takes into account the non-Newtonian character of the suspending medium.   However, the asymptotic η_r values obtained at high shear rate do not fit any of the existing equations used for slurries based on Newtonian liquids and are always lower than the predictable ones.

Therefore, in order to explain the behavior of such suspensions in polymeric liquids, a different mechanism, which will be discussed in analyzing the data presented here, must be invoked.

EXPERIMENTAL

The liquids used for the suspensions were solutions of polyisobutylene (Vistanex L 80) in decalin at concentrations of 2, 3, 4 and 5 g/dl, which are indicated in the text as PIB-2, PIB-3, PIB-4, and PIB-5, respectively.

The slurries were prepared with glass beads (Ballotini Europe 3000 CP/ 01) repeatedly washed with water to eliminate all mixed dust and extraneous matter, treated with warm, dilute hydrochloric acid to dissolve small amounts of iron particles present, and again washed with water to eliminate acidity.   After drying, beads having diameters less than 30 μ were separated by sieving.   This fraction, to be used for slurries, was finally degreased with isopropyl alcohol in a Soxhlet extractor and then resieved. The beads were mixed with the liquids under vacuum with the aid of a stirrer for about 15 min.

Viscosities in steady-shear flow were measured with a Weissenberg rheogoniometer (Model R 18, manufactured by Sangamo Controls Ltd.) with a cone diameter of 5 cm and a 2° angle.

Measurements were normally made at steadily increasing shear rates, but check runs were usually made at lower shear rates at the completion of a run to ensure that the results were reproducible.   In some cases, complete scans were also made at steadily decreasing shear rates.   In all cases there was good agreement between the initial and the check runs.   The temperature for all runs was 27°C.

RESULTS AND DISCUSSION

In Figures 1 and 2, the viscosity η of the PIB solutions used and their corresponding glass bead suspensions at volumetric filler loadings Φ of 0.1, 0.2, 0.3, and 0.4, respectively, is plotted versus the shear rate $\dot{\gamma}$.

An analysis of these curves shows that the relative viscosity of the suspensions increases with decreasing shear rate depending on the polymer and filler content.   For the PIB-2 data (Fig. 1), it can be observed that for a curve at fixed filler loading the increase of relative viscosity with decreasing shear rate is generally stronger in the $\dot{\gamma}$ values corresponding to the New-
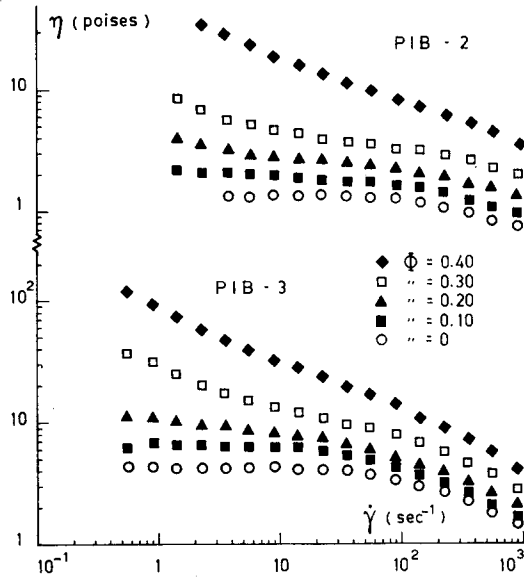
Fig. 1. Viscosity vs. shear rate for PIB-2 and PIB-3 slurries at different volumetric filler loadings.
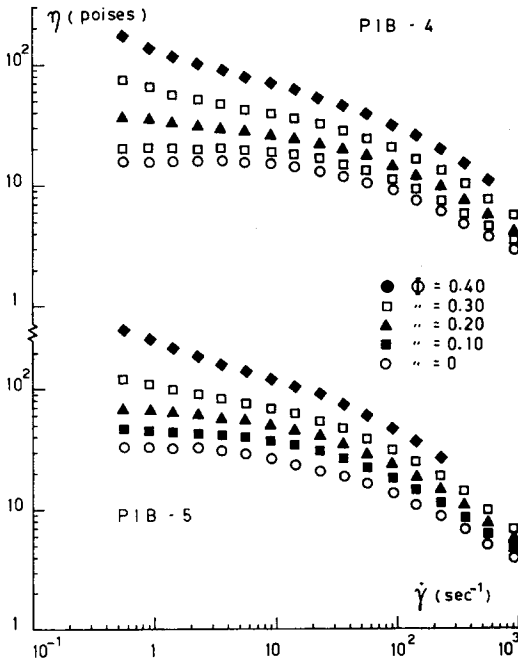

Fig. 2. Viscosity vs. shear rate for PIB-4 and PIB-5 slurries at different volumetric filler loadings.
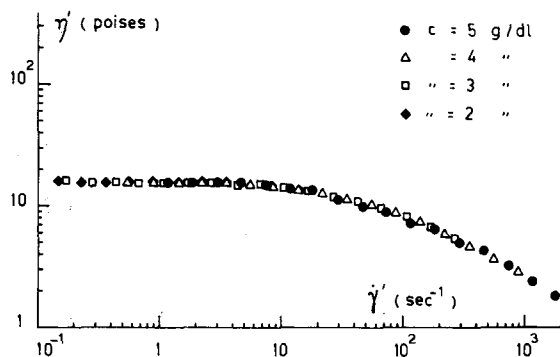
Fig. 3. Master curve, reduced viscosity vs. reduced shear rate, for unfilled
PIB solutions at reference concentration of 4 g/dl.

tonian (constant viscosity) zone of the suspending medium, and then there is
a change in the curvature.   This sharp enhancement of viscosity at low $\dot{\gamma}$
is more evident as the filler content increases and disappears with increasing
polymer concentration, until for the PIB-5 suspensions it can be hardly
noticed for $\Phi = 0.4$.

The appearance of the viscosity–shear rate curves at low $\dot{\gamma}$ values is
similar to that for suspensions in Newtonian liquids, and the reduction of
the viscosity enhancement effect with increasing polymer concentration can
be explained by simultaneous increase in the viscosity of the suspending
medium.[1]   Viceversa, the subsequent decrease of relative viscosity in the
non-Newtonian zone cannot be interpreted as was done for the Newtonian
liquids, i.e., as the tendency toward an asymptotic value, because for the
largest $\dot{\gamma}$ values investigated, the relative viscosity η is lower than the as-
ymptotic value for suspensions in Newtonian liquids and becomes more so as
the polymer and filler concentration increase.

These results indicate, as already mentioned, that two different types of
behavior, respectively at low and high shear rates, i.e., in the Newtonian
and non-Newtonian zone of the suspending solution, are active, as also
observed by Matsumoto et al.[8]   Of course, it is possible that these two ef-
fects overlap for some values of filler and polymer concentrations.

In Figure 3, a master curve of reduced viscosity η' versus reduced shear
rate $\dot{\gamma}'$ obtained with a double shift procedure,[9–11] assuming as reference
curve that for $c = 4$ g/dl, is reported.   In this plot, the reduced variables
are defined as

$$\eta' = a_\eta \cdot \eta \qquad \dot{\gamma}' = a_{\dot{\gamma}} \cdot \dot{\gamma} \tag{1}$$

where a_η and $a_{\dot{\gamma}}$ are the vertical and horizontal shift factors, respectively.
Obviously, a_η is defined as

$$a_\eta = \frac{\eta_{0,4}}{\eta_0} \tag{2}$$

where η_0 is the zero-shear viscosity of the solutions used and $\eta_{0,4}$ is the zero-
shear viscosity of PIB-4.

TABLE I
Shift Factors for Master Curves at Fixed Φ Values
and Zero-Shear Viscosity of PIB Solutions

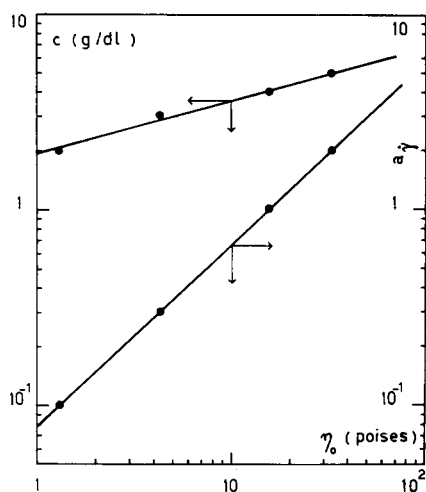| c, g/dl	η_0, poises	$\phi = 0$		$\phi = 0.10$		$\phi = 0.20$		$\phi = 0.30$		$\phi = 0.4$	
		a_η	$a_{\dot\gamma}$	a_η	$a_{\dot\gamma}$	a_η	$a_{\dot\gamma}$	a_η	$a_{\dot\gamma}$	a_η	$a_{\dot\gamma}$
2	1.3	12	0.1	11.5	0.1	12	0.1	11.1	0.1	9	0.1
3	4.3	3.6	0.3	3.5	0.3	4	0.3	3.8	0.3	3.8	0.3
4	15.6	1	1	1	1	1	1	1	1	1	1
5	32.8	0.475	2	0.45	2	0.44	2	0.46	2	0.46	2

Fig. 4. Horizontal shift factor and polymer concentration vs. zero-shear viscosity of unfilled PIB solutions.

These η_0 values are reported in Table I and logarithmically plotted versus the polymer concentration c in Figure 4. From the straight line drawn through the experimental data, it can be noticed that, in the range of concentrations investigated, η_0 is almost proportional to $c^{3.8}$. Analogously (Fig. 4), the $a_{\dot\gamma}$ values are plotted versus η_0, and a straight line correlates the experimental points, furnishing

$$a_{\dot\gamma} = 0.075 \cdot \eta_0^{0.94}. \tag{3}$$

In Figures 5 and 6, the master curves for the four filler loadings tested are reported. The master curve at fixed Φ is obtained with the superposition of the part of the η–$\dot\gamma$ plots corresponding to the non-Newtonian zone of the relative unfilled solution, assuming as reference curve that of $c = 4$ g/dl. As can be seen from Table I, the vertical shift factors a_η at a fixed Φ are within 10% of the value for Φ = 0, with the exception of the one for Φ = 0.4 and $c = 2$ g/dl, and the $a_{\dot\gamma}$ (the horizontal shift factors) values are equal to those for Φ = 0.
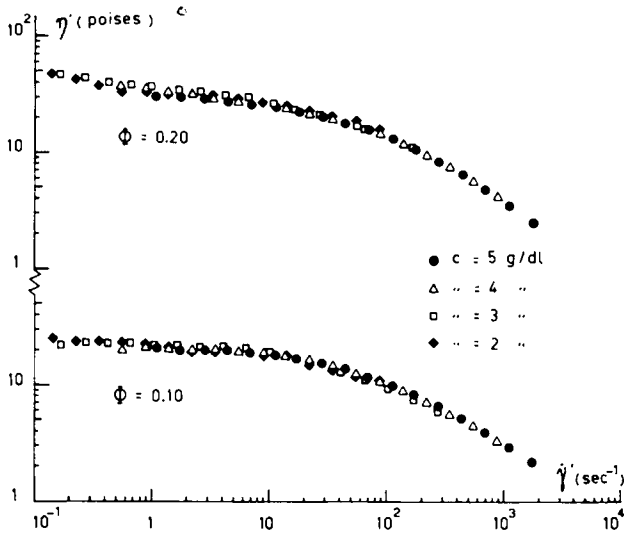
Fig. 5. Master curves, reduced viscosity vs. reduced shear rate, for slurries at volumetric filler contents of 0.10 and 0.20 and at a reference polymer concentration of 4 g/dl.
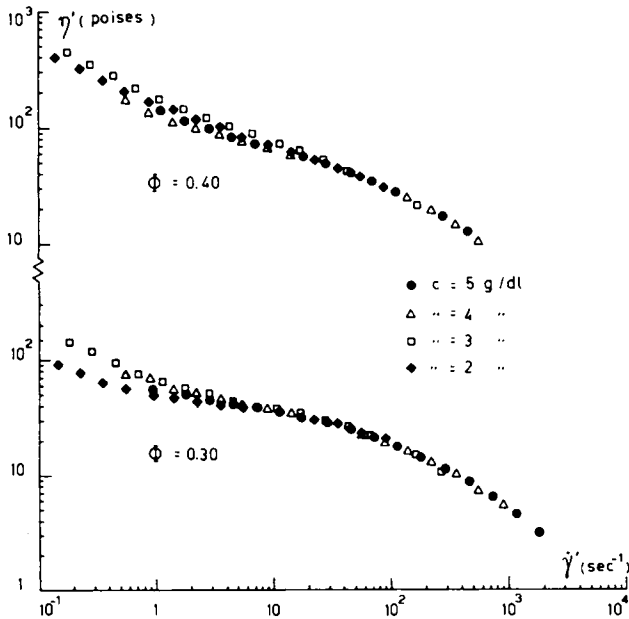

Fig. 6. Master curves, reduced viscosity vs. reduced shear rate, for slurries at volumetric filler contents of 0.30 and 0.40 and at a reference polymer concentration of 4 g/dl.
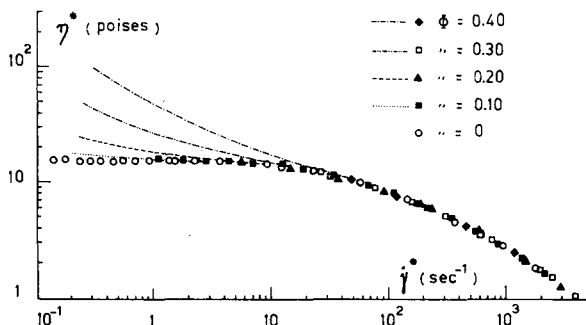
Fig. 7. General master curve, reduced viscosity vs. reduced shear rate, for slurries of glass beads in PIB solutions with reference curve of unfilled-PIB-4. Sample points are reported.

Therefore, if $\tau_{c,\phi}$ is the relaxation time for a suspension at a given Φ in a solution at a concentration c and $\tau_{c,0}$ is the one relative to an unfilled solution at the same polymer concentration c, then (9–11):

$$a_{\dot\gamma} = \frac{\tau_{c,0}}{\tau_{4,0}} = \frac{\tau_{c,\phi}}{\tau_{4,\phi}} \tag{4}$$

where the index 4 is referred to the PIB-4, which is the reference solution for all master curves. Equation (4) leads to

$$\tau_{c,\phi} = A_{\dot\gamma} \cdot \tau_{c,0}. \tag{5}$$

The factor $A_{\dot\gamma}$ independent of polymer concentration is a function of Φ; in fact, it is possible, for every Φ, to obtain a corresponding value of $A_{\dot\gamma}$ through the superposition of the master curves previously obtained at different Φ on that of unfilled solutions.

This general master curve is plotted in Figure 7 as reduced viscosity η^* versus reduced shear rate $\dot\gamma^*$, defined by

$$\eta^* = A_\eta \cdot \eta' = A_\eta \cdot a_\eta \cdot \eta \tag{6}$$

$$\dot\gamma^* = A_{\dot\gamma} \cdot \dot\gamma' = A_{\dot\gamma} \cdot a_{\dot\gamma} \cdot \dot\gamma$$

where A_η and $A_{\dot\gamma}$ are the shift factors in the vertical and horizontal directions, respectively.

In Table II, the $A_{\dot\gamma}$ values obtained at different filler contents are reported. From this table, it can be observed that, for all suspensions, the $A_{\dot\gamma}$ values are bigger than unity, which means that the flow curves of the suspensions show a non-Newtonian behavior stronger than that of the unfilled solutions. In Table II also, the $\bar\eta_r$ values defined as $(A_\eta)^{-1}$ are reported. These are the ratios of the reduced viscosity η' for a given Φ value and that for $\Phi = 0$ at the same value of $\dot\gamma^*$. Therefore, $\bar\eta_r$ represents the asymptotic value obtained when the mechanism active in the Newtonian zone vanishes and the other effect discussed above is not present. This

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TABLE II
Shift Factors for General Master Curve

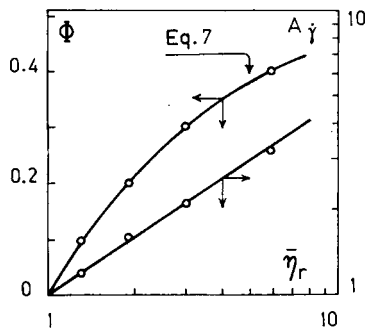|	$\phi = 0$	$\phi = 0.10$	$\phi = 0.20$	$\phi = 0.30$	$\phi = 0.40$
$\bar{\eta}_r$	1	1.3	1.9	3	5.9
$A_{\dot\gamma}$	1	1.2	1.6	2.1	3.2

Fig. 8. Horizontal shift factor $A_{\dot\gamma}$ and filler content Φ vs. relative viscosity $\bar{\eta}_r$.

interpretation is confirmed by the data reported in Figure 8, in which the $\bar{\eta}_r$ values are well correlated by the Eilers equation[12]:

$$\bar{\eta}_r = \left(1 + \frac{1.25\ \Phi}{1 - \Phi/\Phi_m}\right)^2 \tag{7}$$

with $\Phi_m = 0.62$.[1]

In Figure 8, also the $A_{\dot\gamma}$ values are logarithmically plotted versus $\bar{\eta}_r$ and can be correlated by a straight line with the equation

$$A_{\dot\gamma} = \bar{\eta}_r^{0.68}. \tag{8}$$

Recalling that $A_{\dot\gamma}$ represents the ratio between the relaxation time of the slurrie with a filler volume loading Φ and that of the relative unfilled solution, eq. (5), eq. (8) seems to indicate that enhancement of relative viscosity due to the filler causes an increase in relaxation time of the macromolecules. This effect is analogous to the one obtained by increasing the polymer concentration of the solution and represented by eq. (3). In this case, however, it has been shown[9,10] that the entanglements between molecules increase with polymer concentration, and therefore it is reasonable to assume that this effect will thus be more marked. The presence of entanglements in the solutions used is suggested by the fact that the zero-shear viscosity, η_0, is roughly proportional to $c^{3.8}$.

With the type of superposition procedure done, also the data corresponding to the initial part of the flow curves, i.e., the ones relative to the Newtonian zone of the unfilled solutions, draw together sensibly, as can be seen from Figures 5 and 6. This is so because the horizontal shifts $a_{\dot\gamma}$ are almost proportional to η_0, eq. (3), and, as already observed, the $\dot\gamma$ dependence of η in the initial part of the flow curves is lower as the solution viscosity is higher, at a given Φ.
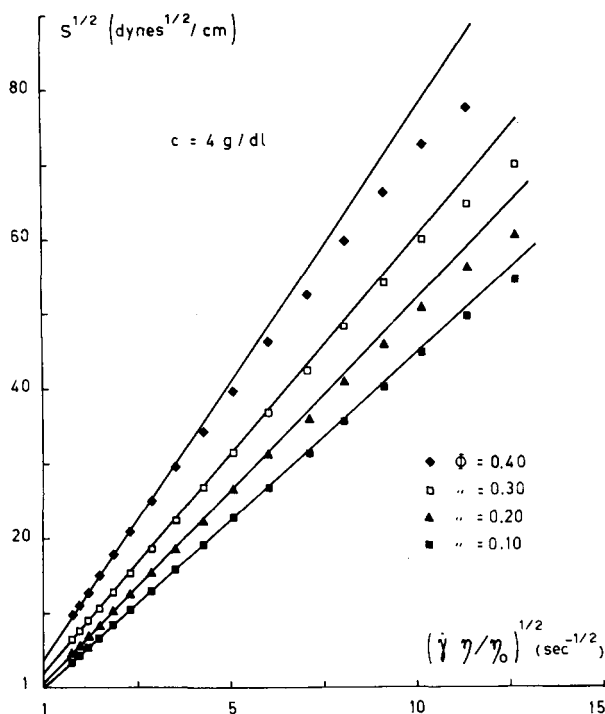
Fig. 9. Plot of $S^{1/2}$ vs. $(\dot{\gamma}\eta/\eta_0)^{1/2}$ for suspensions of 4 g/dl PIB in decalin and glass beads at different volume contents.

In Figure 7, the average curves for the initial zone at various Φ values are reported. Those corresponding to $\Phi = 0.1$ and 0.2 approach the curve for $\Phi = 0$ before the beginning of the non-Newtonian zone, showing that the mechanism of aggregate disruption is completely exhausted before the second mechanism begins. At $\Phi = 0.3$, the asymptote is reached almost at the beginning of the non-Newtonian zone, while for $\Phi = 0.4$, there is an overlap of both effects and the master curve presents a flex point with a nonhorizontal tangent. Nevertheless, also at this value of Φ, $\bar{\eta}_r$, is well correlated by the Eilers equation (Fig. 8).

The differences of the a_η values at various Φ values reflect the uncertainty on the separation of the two mechanisms for each curve, besides the experimental errors. The data relative to the Newtonian zone can be correlated with the existing equations for suspensions in Newtonian liquids, eventually corrected for the non-Newtonian behavior of the suspending medium.[1,8]

In Figure 9, an example of this type of correlation for the data relative to the PIB-4 suspensions is shown. The data are plotted in the form requested to compare with the Casson equation modified to take into account the non-Newtonian behavior of the suspending medium[8]:

$$S^{1/2} = K_0 + K_1 \left(\dot{\gamma}\, \frac{\eta}{\eta_0} \right)^{1/2} \tag{9}$$

where S is the shear stress in the suspension at a given $\dot{\gamma}$; and η and η_0 are, respectively, the viscosities at that given $\dot{\gamma}$ and at zero shear, for the suspending liquid (in this case, PIB-4). For a Newtonian liquid, $\eta = \eta_0$ and eq. (9) becomes the equation originally proposed by Casson.[5]

Figure 9 shows that it is not possible to correlate all the data at a fixed Φ with a straight line as expected by eq. (9), but that it can be done only for few initial points up to $\dot{\gamma}$ values slightly above the Newtonian zone of the suspending solution. Data which are not on the straight line are those influenced by the mechanism discussed in the present paper; and, in fact, these have been used for the shifting procedure.

This mechanism was not observed previously[1] for the absence of the initial part of the curve due mainly to the different microbead dimensions. In fact, while in reference 1 the maximum diameter of microspheres was 44 μ, here it is 30 μ, and the effects derived by the disruption of filler aggregates are very sensitive to the particle dimensions, as pointed out also by other researchers.[13,14,15]

In conclusion, the data reported in this work confirm the existence of two different mechanism in suspensions based on polymeric solutions which are active in the range of low and high shear rates, respectively. The latter, in the case of fairly concentrated polymeric solutions, as those studied here, appears as an increase in the relaxation time of the solution and is a function of the volumetric filler loading and not of the polymer concentration of the suspending liquid.

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