

Viscoelastic properties of suspensions of non-colloidal hard spheres in a molten polymer

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We report an experimental study of suspension of solid particles suspended in a viscoelastic polymer matrix. A commercial entangled poly(ϵ -caprolactone was used as suspending fluid. The solid spheres are made of polymethylmetacrylate, and have a diameter of 15 μm , therefore their dimensions are non-colloidal. The volume fraction of the spheres in the polymer was varied in a range which allowed to explore both dilute and concentrated regime. The suspensions were prepared by solvent casting method and the efficiency of the dispersion was checked via electron scanning microscopy. We measured the rheological properties of the suspensions both in linear and nonlinear regime, with both dynamic and transient tests. The dependence of the linear viscoelastic moduli on the volume fraction of the suspended particles was investigated and the results compared with available theories, simulations and experimental data.

I. INTRODUCTION

Suspensions of hard spheres in liquid media are used in many consumer products, such as cosmetics, food, detergents, personal care, household and pharmaceuticals. Therefore, it is of crucial importance to understand the rheological properties of these systems, and the link between their structure and flow properties. The rheological properties of hard-sphere suspensions depend on several factors, such as viscoelasticity of the suspending fluid, and chemical nature, volume fraction, and size of the suspended particles^{1,2}. In particular, the size plays a key role in determining the dynamics of the particles. Above the colloidal range (1-100 nm), Brownian motion is negligible, and the dynamics are controlled by hydrodynamic interactions. The rheology of non-colloidal hard sphere suspensions is the subject of a vast literature³⁻⁹.

About a century ago, Einstein gave the first prediction for the bulk viscosity of a dilute suspension of rigid spheres in a Newtonian liquid¹⁰. He calculated that the effective viscosity η of the suspension obeys the following equation:

$$\eta = \eta_0(1 + 2.5\phi) \quad (1)$$

where η_0 is the shear viscosity of the matrix, and ϕ is the volume fraction of the suspended spheres. In Equation (1) it is assumed that the particles are monodisperse, and the distance between particles is much larger than the diameter¹⁰. Many experimental measurements can be found in literature¹¹⁻¹³, which have demonstrated that equation (1) can be verified only up to volume concentrations of approximately 5%. At higher concentrations, it is necessary to apply corrections. Batchelor calculated the viscosity of semi-dilute suspensions of hard spheres using statistical mechanics arguments¹⁴⁻¹⁶. In the case of pure hydrodynamic interactions (with absence of Brownian forces), and assuming a random particle distribution, the particle-particle interactions determine the presence of terms of second order in the expression for the stress tensor. Hence, the viscosity of the suspension is given by the

following equation:

$$\eta = \eta_0(1 + a\phi + b\phi^2) \quad (2)$$

the values of the parameters of equation (2) are $a=2.5$ and $b=7.6$ ¹⁶. However, the latter value of the second order parameter is obtained for purely irrotational flow only and, as a consequence, equation (2) describes the elongational viscosity, but not the shear viscosity. An approximate numerical result in the case of a solid suspension of rigid spheres of uniform size in shear flow yields $b=5.2$ ¹⁴. To date, exact predictions for the shear viscosity of suspensions of particles in dilute and concentrated regime are yet to be developed. Attempts to extend the work of Batchelor to higher volume fractions led to different values of the second order parameter, depending on model assumptions¹⁷⁻²¹. On the other hand, experimental validations of Batchelor's calculations can be found in literature²²⁻²⁵. Empirical models for the shear viscosity of nondilute suspensions, limited to the case of non-Brownian particles, have also been developed²⁶. However, predictions for the second order coefficient b in equation (2) become contradictory and dependent on model assumptions.

Several studies considered rigid particle suspensions as a special case of a liquid-liquid emulsion, where the droplets viscosity goes to infinity. Oldroyd²⁷ predicted that the coefficient b in equation (2) is equal to 2.5 for a Newtonian fluid in a Newtonian matrix. Such a value is smaller than Batchelor's exact calculation. Along similar lines, Choi and Schowalter²⁸ obtained the prediction $b=125/8$, using a cell model approach. A further level of complication in evaluating the second order parameter of equation (2) is considering a non-Newtonian suspending fluid. Experimental studies on suspension of hard spheres in viscoelastic liquids are hindered by the difficulty of properly suspending the particles in the matrix. This is the reason why the majority of the experimental works focused on fluids with low viscosity values, in which it is possible to disperse particles by hand mixing²⁸. Few studies used polymer melts as suspending fluids. In such systems the dispersion of the particles is usually performed at high temperatures or by using a co-solvent. In the first case, there is the risk of polymer degradation whereas, in the second case, it is often very difficult to eliminate co-solvent traces.

Following Einstein's and Batchelor's approach, the complex

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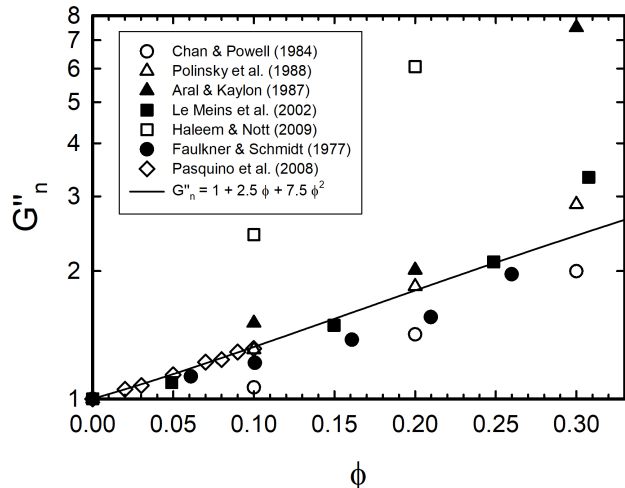


FIG. 1. Experimental data from literature of normalized viscous modulus as a function of the spheres volume content.

modulus of hard sphere suspensions in viscoelastic matrix can be expressed as a series expansion in the volume fraction of particles:

$$G^* = G_0^* (1 + a\phi + b\phi^2) \quad (3)$$

Palierne²⁹ demonstrated, by hydrodynamic calculations, that the value of a in equation (3) is equal to 2.5 for dilute suspensions of solid spherical particles. Conversely, an exact calculation of the parameter b has not been attempted and, to date, only empirical estimations are available^{30,31}.

Figure 1 shows an updated graph, based on figure 6 of D'Avino et al.³², which reports the most relevant experimental results on suspensions of non colloidal spheres in different matrices. More specifically, Figure 1 reports the effect of the particles content on the viscous modulus of a viscoelastic matrix in linear regime for various systems^{25,33–38}. Although they all agree that the viscous modulus increases with increasing particle volume fraction, the trend differs from one study to the other. Apart from the aforementioned works, it is Mall-Gleissle et al.³⁹ and Tanner⁸ have focused on similar systems, measuring mainly tangential and normal bulk stresses in shear flow, with no information on the viscoelastic moduli.

Computer simulations have also been performed to investigate the rheological behavior of suspensions. Considerable attention has been reserved to the behavior of Brownian particles (Brady 2001 and more) and to the flow of disk particles, mainly in Newtonian fluids. Less attention has been paid to suspensions of non-colloidal particles. The work of Schaik et al. and D'Avino et al.^{32,40}, using different numerical methods, reached the same results, i.e. the elastic modulus in the linear regime have the same dependence on the volume fraction of the viscous modulus, and is the same of the Newtonian loss modulus.

This paper investigates the rheological behaviour of spheres of non-colloidal size (diameter bigger than $1\mu\text{m}$) suspended

in a polymer melt matrix. Volume fractions up to 30% were used, thus exploring both the semidilute regime and the concentrated regime. A good dispersion of particles in the polymer matrix is proven by microscopy experiments. Rheological experiments were performed in a way to understand the reinforcement effect due to the presence of a solid filler in the polymer sample. The experimental results are compared with predictions of existing theories, in particular those based on purely hydrodynamic calculations, simulations and experiments.

II. MATERIALS AND METHODS

Poly(ϵ -caprolactone) CapaTM 6800 (henceforth coded as PCL) with an average molecular weight of 120 kDa and a polydispersity index of about 1.7 was supplied by Perstrop Holding AB, Sweden. PMMA spheres (Spheromers CA15 from Microbeads) were used as fillers. They have a volume average particle diameter of about $14\mu\text{m}$ and a density of $1.3\text{g}/\text{cm}^3$. Polymeric beads were preferred to the more widely used glass beads to reduce the medium-particle density difference, thus minimizing settling phenomena. Details of the bead size distribution are reported elsewhere²⁵. The suspensions were prepared via the solvent casting method, by using dichloromethane. Such solvent completely dissolves the PCL matrix, and avoids softening the PMMA fillers. The PCL was dissolved in dichloromethane for about 2 hours. Then, the right amount of particles was added to the solution. The solution containing the polymer and the particles was stirred for 12 hours in a controlled environment, which allowed for a slow evaporation and, consequently, a good dispersion. After that, the samples were left few days at 40°C in a vacuum oven, in order to eliminate residual traces of the solvent. The solutions were weighed at different times, in order to track the evaporation of the solvent. By using the procedure described above, suspensions of PMMA beads with volume fractions ranging from 0% to 30% were prepared. Rheological measurements were performed on an ARES rheometer (TA instruments, USA) equipped with a force-rebalance transducer (2KFRTN1), and a convection oven for thermal control. As measuring geometries, we used 8mm and 25mm parallel plates for dynamic measurements. For steady flow measurements at low rates we used a 25 mm cone and plate geometry, with a cone angle of 0.1 rad and a truncation of $53\mu\text{m}$. Concerning the start-up shear tests, we used a cone-partitioned plate geometry with an inner diameter of the plate of 6mm ^{45,46}. The gap used for parallel plates was approximately 1 mm. To facilitate the loading of the sample between the plates of the rheometer, disks samples of 25mm or 8mm diameter were prepared by using a hydraulic press (Carver Inc, ACS group) and a hole punch. Nitrogen atmosphere was used at high temperature, in order to avoid polymer degradation. The dispersion of the particles in the matrix was assured via microscopy, by analyzing a piece of each sample, after the use of the hydraulic press. SEM pictures are shown in Figure 2. Optical measurements were performed with a Leo-Cambridge S440 microscope. SEM experiments were

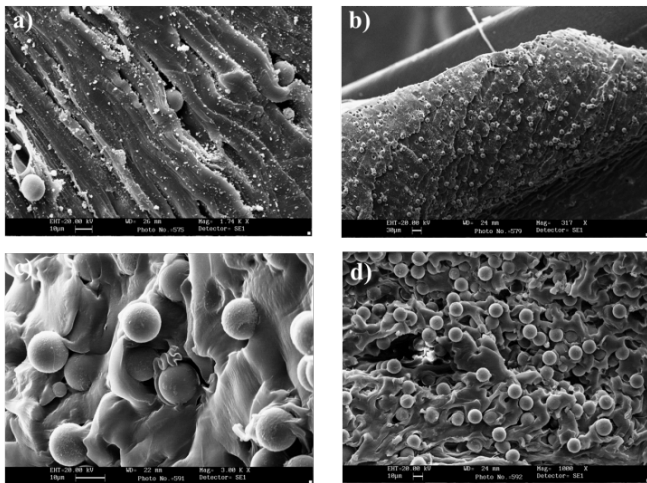


FIG. 2. SEM pictures of PMMA spheres in PCL with volume fractions: a) 7%; b) 10%; c) 15%; d) 30%.

performed by attaching the samples on specific Al stubs and by covering them with Au through a sputter. The acceleration tension (EHT) is 20.00 kV for all the samples. The working distances (WD) are 26, 24, 22 and 24mm for a,b,c and d images, respectively.

III. RESULTS AND DISCUSSION

Dynamic measurements were performed on the polymer matrix and the prepared suspensions in the temperature range 60-120°C. Figure 3 reports the mastercurve of the pure polymer at the reference temperature $T_{ref} = 120^\circ\text{C}$. The time-temperature superposition (TTS) principle was used to build the dynamic master curves. The rheological behaviour of the matrix is typical of an entangled polymer in the terminal flow regime. The relaxation time at 120°C, evaluated as the inverse of the crossover frequency, is approximately 0.01 s. The plateau modulus is not directly accessible from the mastercurves reported in Figure 3 because measurements at higher frequencies or lower temperatures are limited by instrument compliance and crystallization, respectively. The relatively high polydispersity index of the PCL used here determines the non-terminal slopes for the elastic modulus at low frequency. Polydispersity is also reflected in the broad transition from the terminal region to the elastic plateau region, which corresponds to a broad spectrum of relaxation times.

The TTS principle was also applied on the polymer suspensions. The dynamic moduli of some representative suspensions are shown in Figure 4(a). Incorporating particles in the polymer matrix induces a reinforcement effect, with both viscous and elastic moduli increasing with increasing volume fraction of particles. Interestingly, the dependence of the loss factor upon frequency is nearly identical for the different suspensions and the pure polymer, indicating that the relaxation time remains roughly the same. In other words, adding spheres to the polymer matrix induces mainly a vertical shift

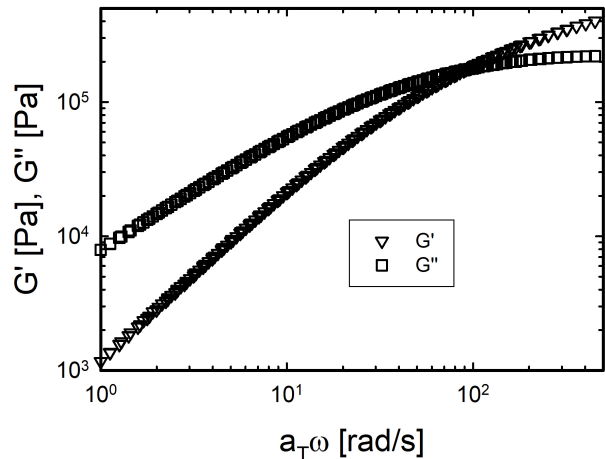


FIG. 3. Linear viscoelastic moduli of the pure polymer matrix at 120°C

of the viscoelastic moduli, suggesting that the relaxation dynamics of the different suspensions are similar. Such a scenario is corroborated by the fact that the dependence of the horizontal shift factors on the volume fraction of the spheres suspended in the molten polymer is weak (Figure 4b). We note that the temperature is far above the melting temperature of the PCL. Approaching the melting temperature of PCL, the horizontal shift factor for the suspensions is expected to deviate from that of the pure polymer, although there is not a systematic behavior with increasing particle volume fraction. The Williams-Landel-Ferry equation (WLF fit) has been used to fit the whole set of experimental data. The best fit through data is obtained with the values of the two constants equal to $c_1 = 2.37$ and $c_2 = 227^\circ\text{C}$, (solid line in Figure 3(b)). Such values are in agreement with previous literature⁴¹.

As mentioned above, the terminal flow regime, where $G' \propto \omega^2$ and $G'' \propto \omega$ is not attained in dynamic experiments. This means that the Newtonian plateau of the complex viscosity could not be measured based on the dynamic mastercurves. On the other hand, measurements at temperatures higher than 120°C were hindered by polymer degradation and torque resolution of the instrument. Therefore, dynamic tests could not be pushed further. However, in order to check how the viscoelastic properties of the matrix are affected by the addition of hard spheres, it is important to access the zero shear viscosities of the suspensions. For this purpose, it is also helpful to verify the agreement between dynamic and steady flow properties, that is, the applicability of the Cox-Merz rule^{42,43}. To this end, besides dynamic tests, start-up shear experiments were also performed both in linear and nonlinear regime. At low rates, a simple cone-and-plate geometry was sufficient to measure the zero shear viscosity. At higher rates, nonlinear effects can occur, particularly edge fracture, which can invalidate rheological tests. In order to prevent experimental artifacts caused by edge fracture, we used a cone-partitioned plate geometry to measure the steady state viscosity. Figure 5, reports both transient and dynamic data for the pure polymer and a sus-

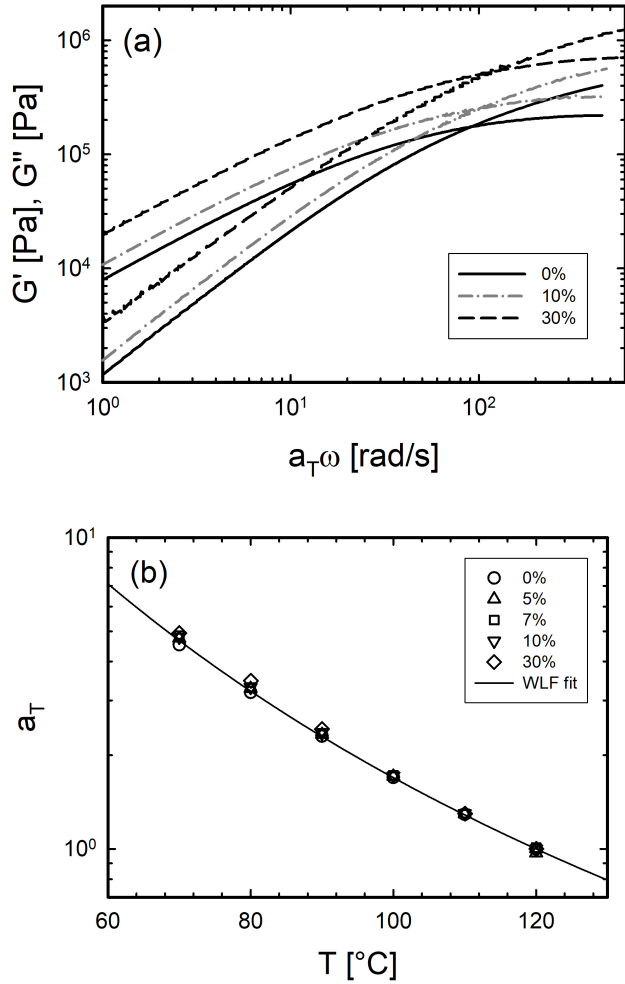


FIG. 4. (a) rheological mastercurves of the hard sphere suspensions at different volume fractions. (b) horizontal shift factors used to build the mastercurves.

suspension with a volume fraction of $\phi = 0.25$ in hard spheres. The steady state viscosity obtained with the cone-and-plate geometry overlaps well with the data obtained with the cone-partitioned plate tool. In addition, the steady state viscosity values obtained in start-up shear experiments are numerically equivalent to those of complex viscosity when the shear rate is equivalent to the frequency. This observation demonstrates the applicability of Cox-Merz rule for both the pure polymer and the suspensions and provides confidence in comparing dynamic and steady data. The dynamic tests in linear regime are not affected by flow instabilities and, as such, they are useful to understand the non-linear behavior too.

Figure 6 reports the steady state viscosity as function of the shear rates for some representative samples of the investigated suspensions. As expected, at very low rates the Newtonian regime is approached, with the viscosity independent on the strength of flow. The steady state data confirm the trend observed from the dynamic data of figure 4: at increasing volume fraction of the solid fillers, the zero shear viscosity of the

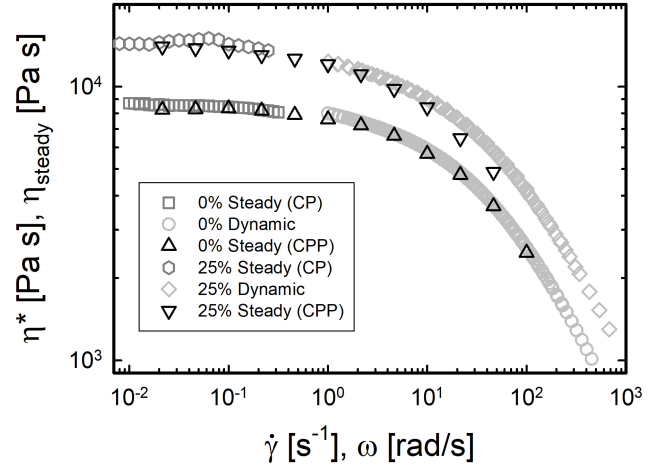


FIG. 5. Overlay between steady and complex viscosity for the pure polymer matrix. Reference temperature is 120°C.

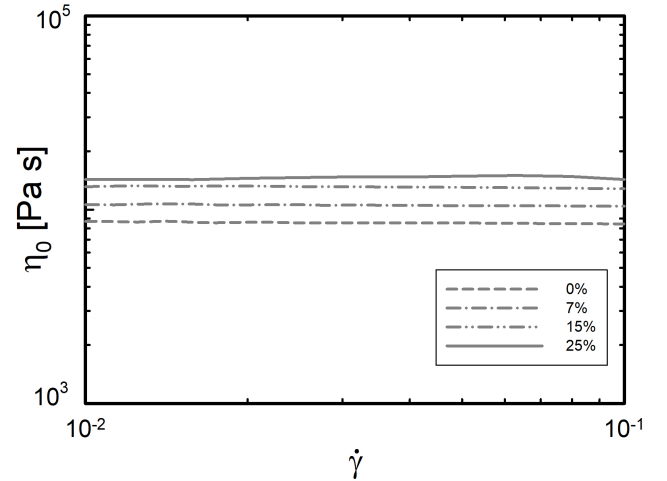


FIG. 6. Steady viscosity curves for suspensions with the solid content shown in the legend. Reference temperature is 120°C.

suspension increases.

The increment of the rheological properties (viscoelastic moduli and viscosity) depend on particle concentration. A way to evaluate such increment is to normalize the rheological parameters with respect to the polymer matrix. Following Pasquino et al.²⁵ the nondimensional parameters considered are:

$$G_n'' = \frac{G''}{G_0''} \quad (4)$$

$$G_n' = \frac{G'}{G_0'} \quad (5)$$

$$\eta_n = \frac{\eta}{\eta_0} \quad (6)$$

where G''_0 , G'_0 and η_0 are the viscous modulus, elastic modulus and viscosity of the polymer matrix, respectively. The normalized quantities highlight the reinforcement effect given to the polymer matrix due to the presence of the suspended spheres. As mentioned above, the reinforcement effect induces a shift of the mastercurves which is virtually only vertical. Therefore the normalized parameters could be evaluated at an arbitrary frequency of the spectrum. Figure 7 reports the normalized quantities defined in equations (4), (5) and (6) as functions of the volume fraction. The normalized viscoelastic moduli the suspensions are evaluated at different frequencies in the range [1,10] rad/s. The data shown in Figure 7 are averaged values of the different ratios obtained at different frequencies. The small errors bars indicate that, at least in this frequency range, the curves are vertically shifted, of an equal factor, whatever frequency is considered. For the viscosity, we consider both the zero-shear viscosity value and the predicted values obtained by fitting the complex viscosity curve. The small error bars confirm the conjecture according to which the reinforcement affects the dynamics to a minimal effect. The normalized viscosity of Figure 7(c) is calculated as an average of steady state data. Quadratic polynomial equations were used to fit the data. The result of the fitting procedure is reported in the panels of Figure 7 as lines (dashed, dotted and continuous lines are referred to the viscous modulus, the elastic modulus, and the viscosity, respectively). To fit the data, the first term of the polynomial equation was fixed at 2.5, as previously discussed (see introduction). The fits are described by the following equations:

$$G'_n = 1 + 2.5\phi + 8.1\phi^2 \quad (7)$$

$$G''_n = 1 + 2.5\phi + 7.4\phi^2 \quad (8)$$

$$\eta_n = 1 + 2.5\phi + 6.9\phi^2 \quad (9)$$

where equation (7), (8) and (9) refer to the viscous modulus, elastic modulus, and viscosity, respectively. The quadratic term of the polynomial expansion is very similar for both dynamic and steady rheological quantities. The average value of the three parameters is $b = 7.5 \pm 0.6$. Such value is very close to the predicted value found by Batchelor.

Figure 8 shows the comparison between the fit through our experimental data (dark grey line) and the Batchelor prediction (dashed black line). The dotted line represents Einstein's prediction, limited to the dilute regime, and the dot-dashed line represents recent simulations by D'Avino et al.³² and numerical calculations by Schaik et al.⁴⁰. The plot demonstrates a good agreement between our data and Batchelor's prediction, and confirms a weaker dependence of the rheological properties on the volume fraction for concentrations higher than 20%, if compared to recent numerical predictions^{32,40}.

IV. CONCLUSIONS

We investigated the rheological properties of non-colloidal suspensions of solid spheres of PMMA in a PCL matrix. The suspensions were prepared via solvent casting method and the homogeneity of the dispersion was demonstrated via mi-

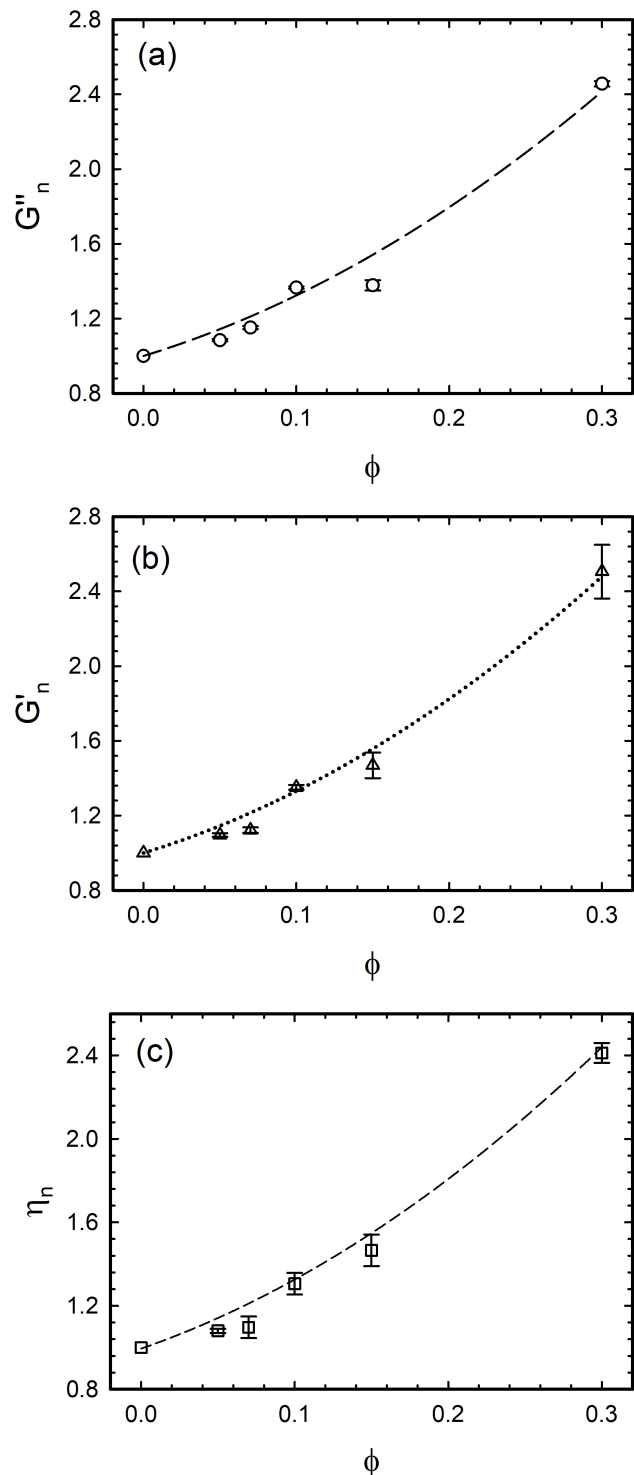


FIG. 7. Normalized rheological parameters as functions of the volume fraction of spheres: a) viscous modulus; b) elastic modulus; c) viscosity. Lines are best fits of the data.

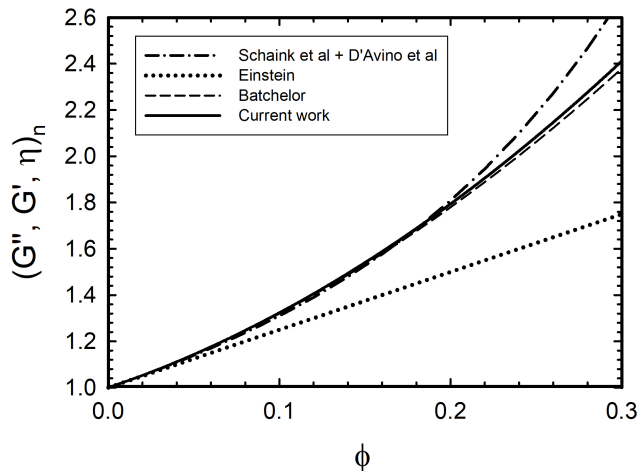


FIG. 8. Normalized rheological parameters as functions of the volume fraction of spheres: a) viscous modulus; b) elastic modulus; c) viscosity. Lines are best fits of the data.

scopy techniques. We have evaluated the effect of increasing the volume fraction of particles in the polymer matrix by means of linear and non-linear rheology. Rheological properties of the suspensions were measured in a temperature range in which the PCL is molten and the PMMA spheres remain solid. We found that the viscoelastic moduli as well as the steady viscosity of the suspensions increase when the solid particles content increases. The reinforcement effect by solid particles translates into a vertical shift of the viscoelastic moduli towards larger values. The spectrum of relaxation times of the PCL matrix does not seem to be affected by the addition of the spheres, at least in the observed temperature range, as confirmed by the horizontal shift factors. We analyzed the results in terms of normalized rheological properties, both dynamic and steady, and compared them with hydrodynamic calculations for extensional viscosity^{14,15} and recent numerical studies^{32,40}. We found that our data are in good agreement with the theoretical predictions and show a weaker dependence on volume fraction if compared with numerical studies^{32,40}.

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Appendix A: Start-up shear tests

Start-up shear tests were performed with a cone-partitioned plate geometry in order to avoid artefacts caused by edge fracture at high shear rates. Figure 9(a) reports the transient viscosity as a function of time for the pure PCL polymer whereas Figure 9(b) shows data for the suspension with $\phi = 0.25$.

Shear rates from 0.0215 s^{-1} to 100 s^{-1} were used. The steady viscosity value corresponding to each shear rate is taken as the arithmetic average over the steady state portion of the reported curves.

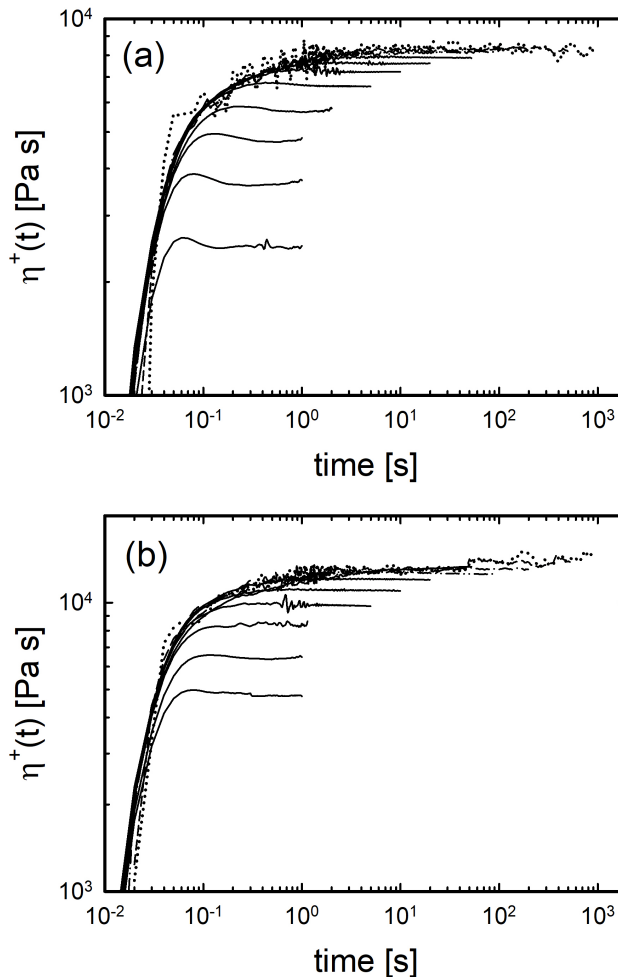


FIG. 9. (a) Start-up shear tests on pure PCL and (b) start-up shear tests on the suspension with $\phi = 25\%$. The tests are performed at 120°C for both samples. Shear rates from top to bottom: 0.0215 , 0.0464 , 0.1 , 0.215 , 0.464 , 1 , 2.15 , 4.64 , 10 , 21.5 , 46.4 , 100 s^{-1} . The latter rate is not attained for the suspension.

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