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RELAXATION OF LOOSE AGGLOMERATES OF MAGNESIUM HYDROXIDE IN A POLYMER MELT

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ABSTRACT

The study of agglomerates of magnesium hydroxide badly dispersed in an olefinic polymer by means of oscillatory shear flow in the melt indicates that the agglomerates behave as a distinct phase. Optical and rheo-optical measurements carried out on these agglomerates also show that they are wetted by the melt and that they can be easily deformed under shear. However, the relaxation of shape in oscillatory shear is also the trace of the existence of an effective interfacial tension between the agglomerates containing high amounts of filler and the polymer matrix. The analogy with the behavior of polymer blends and the modeling by the Palierne model enables the calculation of such an interfacial tension. The surface free energy of magnesium hydroxide that can be calculated from this result by a simple mixing law is 95 mN m^{-1} . This value is compared with data from the literature on brucite and similar minerals.

INTRODUCTION

Magnesium hydroxide is widely used as flame retardant in olefinic polymers such as polyethylene, polypropylene and their copolymers. Upon heating, the strong endothermic dehydration reaction which occurs at 580 K with water as a product makes it particularly efficient for the improvement of fire resistance properties of plastic materials. Nonetheless, this efficiency is only interesting provided that other technological properties such as mechanical resistance are not impaired by side-effects connected to the bad dispersion of the mineral in the organic medium especially regarding the occurrence of agglomerates.

In a previous work [1], we studied the dispersion mechanism of a single agglomerate of magnesium hydroxide immersed in a molten polymer matrix and subjected to shear. At low shear stress, erosion was the main mechanism responsible for the dispersion while when the shear stress increases, the mechanism switches to rupture. This has been reported many times in the literature and for various fillers mostly for particle agglomerates with high cohesive strength. In the case of magnesium hydroxide the cohesion is much less therefore, the transition occurs at lower shear stress in comparison to silica or carbon black for example. This is partly due to the high porosity of the agglomerates. Because of this porosity, the molten polymer is able to infiltrate the space between the elementary particles. For this reason, it was observed that the rupture of agglomerates occurs upon shearing in a ductile manner, with a large deformation of the wetted agglomerates before breaking. This means that for infiltrated agglomerates, the stress criterion is not meaningful enough and that a “new” criterion mixing stress and strain such as energy must be used instead.

The fact that an infiltrated agglomerate behaves as a separate phase with internal cohesion that differs from that of the matrix implies that this phase must have its own surface properties. The modification of the surface tension of polymers by mineral or organic fillers has already been reported. The issue is generally addressed in view of the compatibilization of polymer blends by fillers that, in particular conditions, may locate at the interface between the phases. This is an extension of phenomena already reported in low viscosity liquids where such emulsions are often referred as Pickering emulsions [2] when colloidal particles are used. These particles act to reduce the coalescence of droplets but reduction of interfacial tension is not the only mechanism [3]. In the case of highly viscous liquids, the situation seems more complex since both reduction of interfacial tension and hindering of coalescence are reported. Ellias et al. [4] found that depending on their hydrophilic or hydrophobic nature, silica particles may act by one and the other mechanism in PS/PP blends. Hydrophilic silicas were preferentially located in the PS phase and reduce the interfacial tension from 2.15 until to 0.085 mN m⁻¹. On the contrary in this study, hydrophobic silicas were either located at the interface preventing coalescence or in the PP phase without effect

on the interfacial tension. According to the same authors [5-7], in PP/EVA blends, silica particles decrease the effective interfacial tension independent from the nature of the surface of the silica, hydrophobic (from 0.92 to 0.18 mN m⁻¹) or hydrophilic (from 0.75 to 0.30 mN m⁻¹). The hydrophilic silicas remain within the EVA phase whereas the hydrophobic silica stays in the EVA phase or migrate to the interface depending on the viscosity of the EVA. Effects of silica in SBR/NBR elastomer blends were also reported [8]. Hong et al. [9] showed an interfacial tension reduction in PBT/PE/clay nanocomposite from 57.6 to 1.4 mN m⁻¹. Similarly, the apparent interfacial tension of PE/PA blends, drops from 10 mN m⁻¹ to 4.5 mN m⁻¹ by addition of 1% of cloisite C30B and tends to a value of 3 mN m⁻¹ for 2% and 4% of added clay [10]. In similar cases with PS/PP [11], the reduction of the interfacial tension has been attributed mainly to the preferential location of the clay at the interface. In other cases, it was supposed to be due to penetration of the polymer chains in the space between layers in the case of lamellar organo-clays in PS/PP blends [12], in PS/PEMA [13] or PC/PMMA blends [14-15]. In these situations however, interfacial tension is an apparent property that should rather be considered as a property of the filler-polymer system than a property of the polymer couple.

In this paper, we report about the apparent interfacial tension that may exist between a polymer melt and the same melt filled with a mineral component. In particular, it was observed that when a mineral such as magnesium hydroxide is badly dispersed in a melt of polyethylene-octene where it forms wetted agglomerates, these agglomerates behave as a distinct phase from the rheological point of view. In particular, they deform in oscillatory shear flow and show a shape relaxation similar to that observed in polymer blends. Such a behavior can be modeled by the Palierne model and owing to the fitting, an apparent interfacial tension between the loose agglomerates and the melt can be determined. The value of free surface energy of the mineral that can be calculated from the interfacial tension is discussed in view of data of the literature regarding the surface energy of minerals commonly used as fillers in polymers.

It is worth noting that in most of the studies mentioned before, the particles were nanometer in scale, at least in one dimension. In particular, for the studies dealing with silica, the primary particles were nanometer in scale with aggregate dimensions ranging from 10 to 100 nm and mostly around 10 nm. In the present work, the primary particles are sub-micronic and agglomerates are hundred times larger. Though the dispersion problems should clearly be discussed in a multi-scale approach, the mechanisms that lead to the infiltration of the polymer in the agglomerates are not discussed in details since they were addressed in a previous paper [1]. Therefore, the present paper assumes that continuum-scale models can be applied.

EXPERIMENTAL

Materials

Magnesium hydroxide Mg(OH)₂ Hydrofy® (Nuova Sima) was dispersed in an ethylene-octene copolymer Engage® 8401 (Dow Chemicals). Magnesium hydroxide is natural and non-treated with a uniform shape factor. The size of the particles measured on the powder in a Mastersizer®2000 device using a 3 bar gas flow showed 10 vol-% of elemental particles having a diameter lower than 0.67 μm, 50 vol-% of particles having a diameter lower than 2.90 μm and 10 vol-% of particles having a diameter higher than 7.85 μm. Therefore, these are the minimum sizes that can be achieved by mechanical dispersion. The distribution of sizes is given on Figure 1. The olefinic copolymer contains 30% of octene co-monomer, its weight average molecular weight is 70000 g/mol with a polydispersity of 2. The rheological behavior is Newtonian until 1 s⁻¹ and the zero-shear viscosity at 140°C is 1250 Pa.s.

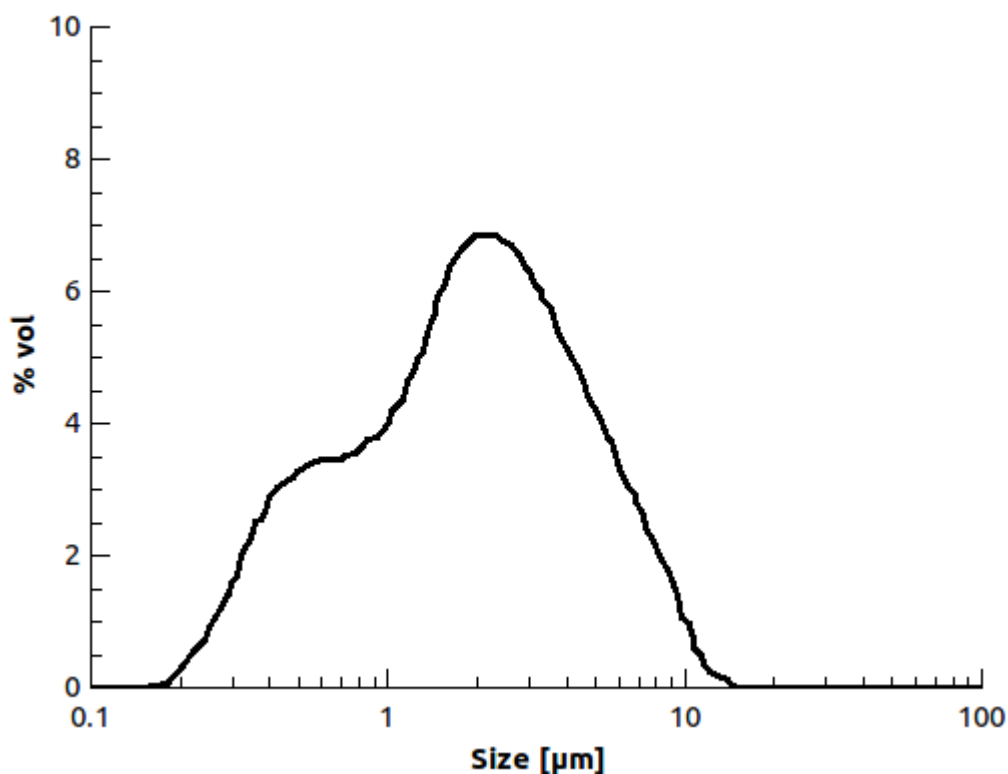


Figure 1: Particle size distribution for magnesium hydroxide particles.

Mixing

Two set of samples were prepared. In the first set, samples containing 0 to 60 wt-% (0 to 33.5 vol-%) of filler were prepared in the same mixing conditions. The desired amount of powder was

dispersed in the matrix in a Haake Rheomix batch mixer at 140°C. The polymer granules and the powder were previously tumble-blended during 5 minutes before feeding then blending was carried out at 32 rpm (approximately 16 s^{-1}) during 10 minutes. In all cases, the actual content of filler was checked by weighting the amount of minerals left after one hour at 700°C using the decomposition reaction of the magnesium hydroxide. No significant loss of mineral can be noted.

The second set of samples was prepared in the same way but only 10 wt-% of powder (3.6 vol-%) was used and the mixing time was varied from 2 to 10 minutes. In the selected shear rate and temperature conditions, the shear stress within the polymer matrix is less than 20 kPa. According to our previous work [1] on diluted systems, the main dispersion mechanism is erosion for agglomerates with diameters below 80 μm . For larger diameters, this mechanism switches to a rupture mechanism.

State of dispersion

The state of dispersion of the filler was analyzed by SEM microscopy coupled with X-ray analysis of the magnesium element in a Hitachi S3000N microscope. Observations were performed on cryo-fractured samples after coating with Au-Pd alloy at 15kV. Mapping of the magnesium in the sample was used to assess the state of dispersion. Acquisition time was about 20 min for a $100\mu\text{m} \times 100 \mu\text{m}$ typical picture. The pictures were then treated using the imageJ software. The observed pictures were threshold and binarized, eventually including some despeckling. All images presented in this paper show the mapping of magnesium (in black) in the matrix (in white) without effects of the topography of the samples.

In addition, direct observations of the individual agglomerates and of the reduction of size during shearing were obtained in the counter-rotating transparent rheometer developed by Seyvet and Navard at CEMEF [16-17]. Particles were disposed in between two polymer films with less than 1 mm thickness and then between two 40 mm glass plates rotating in opposite directions in the rheometer. The observations of an immobile particle were made with an optical microscope coupled with a video camera at 140°C.

Rheological behavior

Measurements in oscillatory shear flow were performed at 140°C in a Paar-Physica MCR301 rheometer using a plate-plate geometry with a diameter of 25 mm and a gap of 1.5 mm. Frequency sweeps were carried out in the range 0.01 rad/s to 100 rad/s. The maximum strain amplitude was chosen to operate within the linear viscoelastic conditions. The strain values range from 1% for the pure polymer to 0.01% for the highly filled materials. For each composition, the experiments were repeated three times and reproducibility was good. In particular, no slip could be detected even at

high filler loadings and the phase angle signal was stable.

RESULTS

Evidence of agglomerates at all concentrations from the hydrodynamic interactions

Figure 2 shows the trace of agglomerates of magnesium hydroxide obtained from the SEM pictures after X-ray mapping of the magnesium in the first set of samples with 0 to 33.5 vol-% of filler. After threshold and binarization, the image displays some areas with large concentration of magnesium that correspond to the agglomerates. In this polymer matrix, though the residence time in the mixer was long for these samples, the dispersion efficiency is limited due to the low viscosity of the melt. These agglomerates are thus made of elementary particles surrounded by the polymer but the shear stress is not high enough to induce the breaking of the agglomerates especially if their size becomes too small [1]. Our previous work on very diluted systems, and particularly the derivation of the relation between the critical stress and the size (Equation 2), show for the shear stress generated in the mixing conditions (20 kPa), the particles with diameter larger than 80 μm cannot be broken. Of course the situation might be clearly more complicated in concentrated systems since collision-induced breaking can also occur. In this previous work, we have shown an evidence of the penetration of the melt inside the agglomerates through the observation of the effect of the hydrodynamic contribution of the filler to the overall rheological behavior of the polymer filled with various amounts of magnesium hydroxide. Indeed, the function $\psi(C)$ describing the hydrodynamic interactions can be obtained from the storage and loss moduli measured in oscillatory shear in the form proposed by Krieger and Dougherty [18]:

$$\psi(C) = \left(1 - \frac{KC}{C_M}\right)^{-[\eta]C_M} \quad (1)$$

Where $[\eta]$ is the intrinsic viscosity of the particles,

C_M is the maximum packing fraction,

In this equation, we have added the K parameter to account for the effective volume that is actually occupied by the particles if they are infiltrated by the matrix [19]. This accounts for the amount of polymer that is trapped between the elementary particles into the agglomerates. For dense spherical particles with uniform sizes, the packing fraction is 0.62, $[\eta]$, $C_M = 2$, and $K = 1$ [19]. On the opposite, when polymer is entrapped between the elemental particles in the agglomerate, the effective volume is larger and $K > 1$.

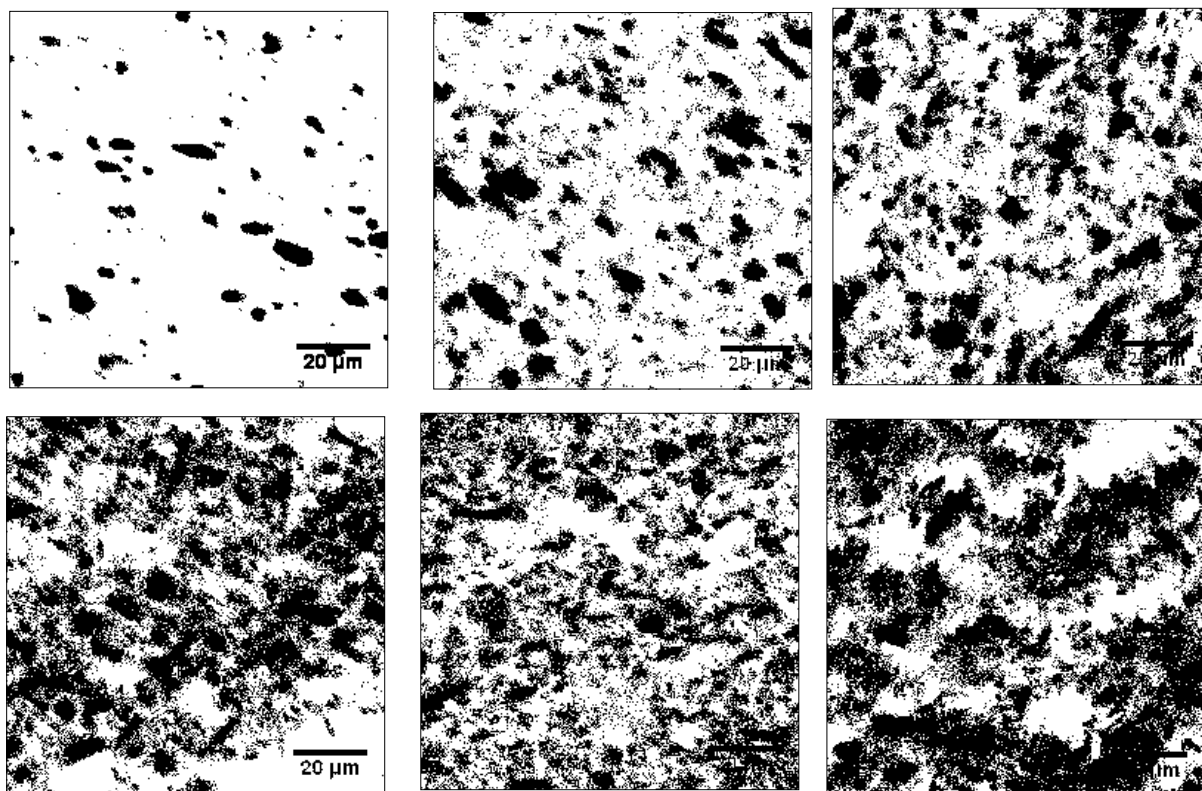


Figure 2: Threshold X-ray mapping of magnesium on SEM images showing the dispersion of magnesium hydroxide (in black) in the polymer matrix (in white). From left to right and top to bottom, volume fraction is: 0.036, 0.077, 0.126, 0.183, 0.252, 0.335.

The agglomerates are responsible for various viscoelastic phenomena that are reflected on the rheological behavior of the filled systems, including drastic changes of the linear viscoelastic response of the molten materials. Figure 3a and b show the results of oscillatory experiments on samples containing increasing amounts of filler between 0 and 60 wt-% (volume fraction $C = 0$ to 0.335) that have also experienced a long mixing time in the internal mixer, which is supposed to improve the dispersion quality and to reduce the amount of agglomerates.

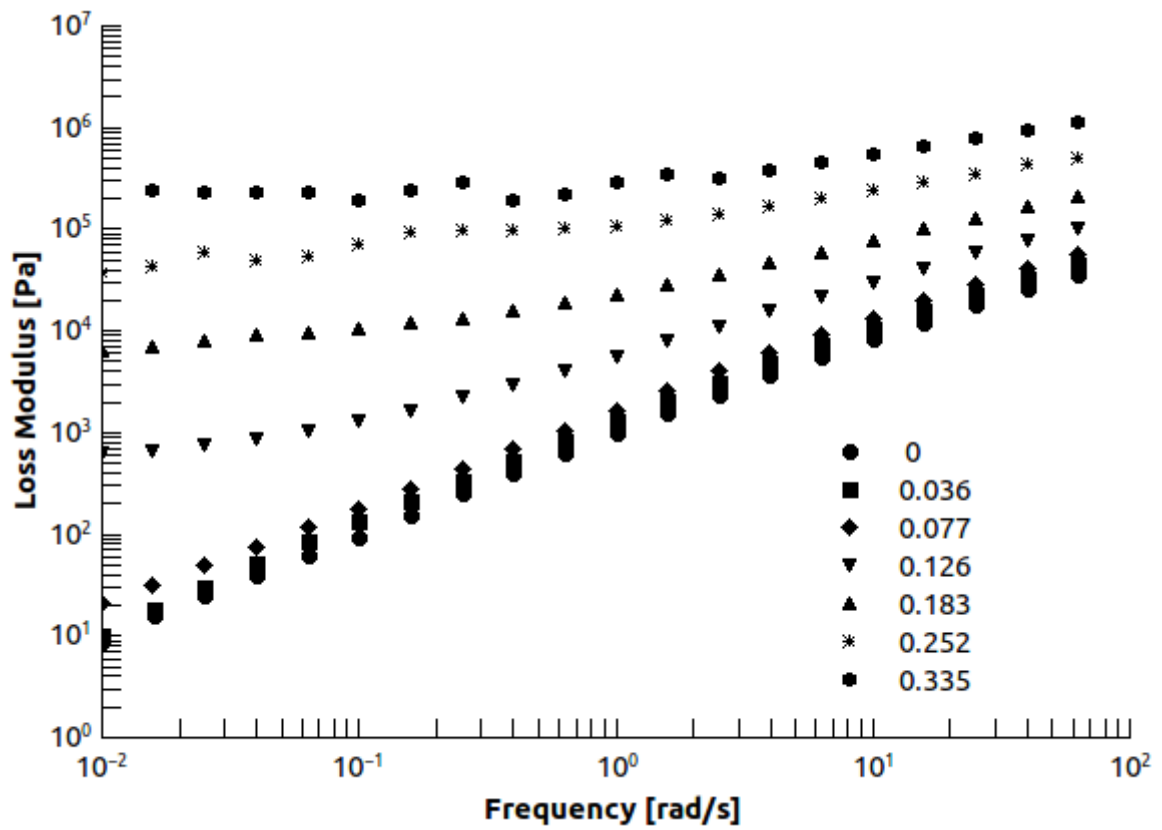
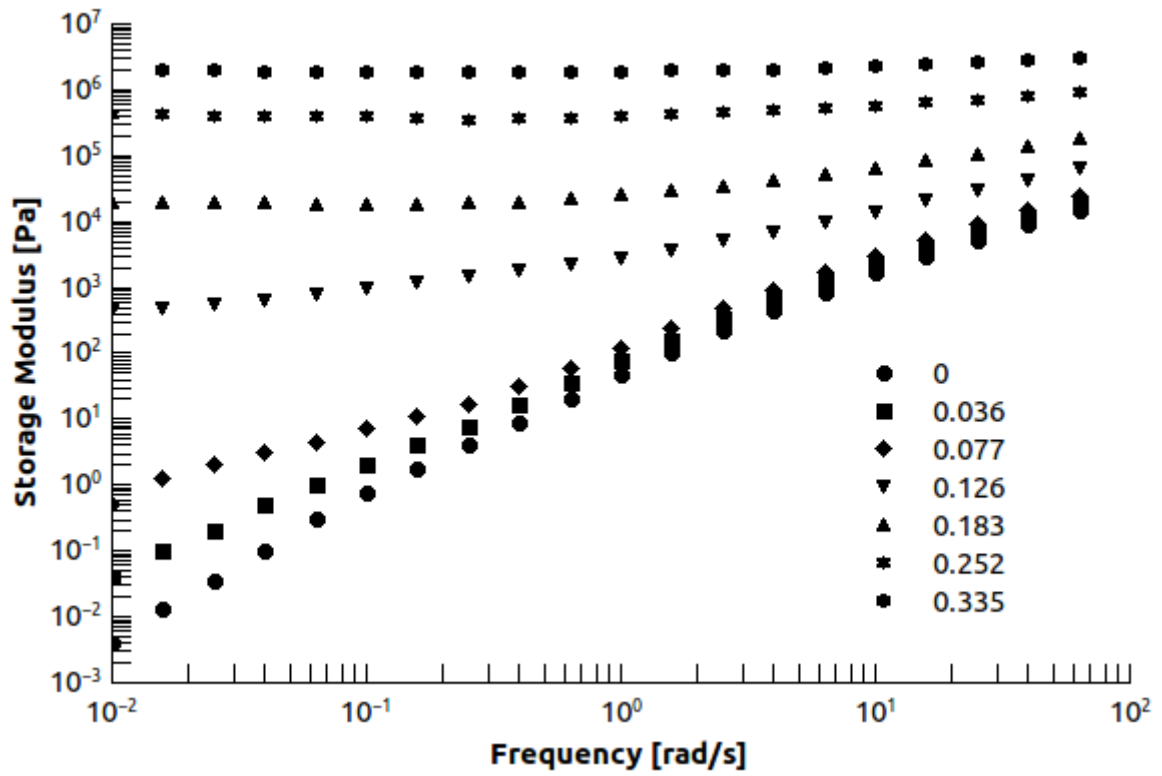


Figure 3: Storage and loss modulus of ethylene-octene copolymer filled with 0 to 33.5 vol-% of magnesium hydroxide.

The figures show that for the compounds, a secondary plateau on the storage modulus appears for volume fraction above 13 vol-%. A secondary plateau also exists on the loss modulus. For high concentration, such an effect is related to gel effect for well dispersed particles but also to internal reorganizations within the agglomerates [20-21]. Whatever their nature, these inter-particle interactions are generally observed at low frequencies and only a slight effect is expected at high frequency, especially regarding the loss modulus. This is evidenced in Figure 4 giving the ratio of the loss modulus at 100 rad/s for a given filler content to that of the pure matrix as a function of the volume fraction of filler. Figure 4 also shows the variation of the function ψ from the experimental data and the fit by Equation 1 considering a dispersed phase with uniform size and the random packing fraction $C_M=0.62$ [19]. These two extreme cases show that, even after long mixing times, the apparent volume of the dispersed phase is always larger than the magnesium hydroxide content indicating agglomerates swollen by the molten polymer. The concentration of filler within the agglomerates is $1/K = 0.84$ if it is calculated from the assumption of uniform size. The corresponding fitted value of the intrinsic viscosity is 5 with this assumption.

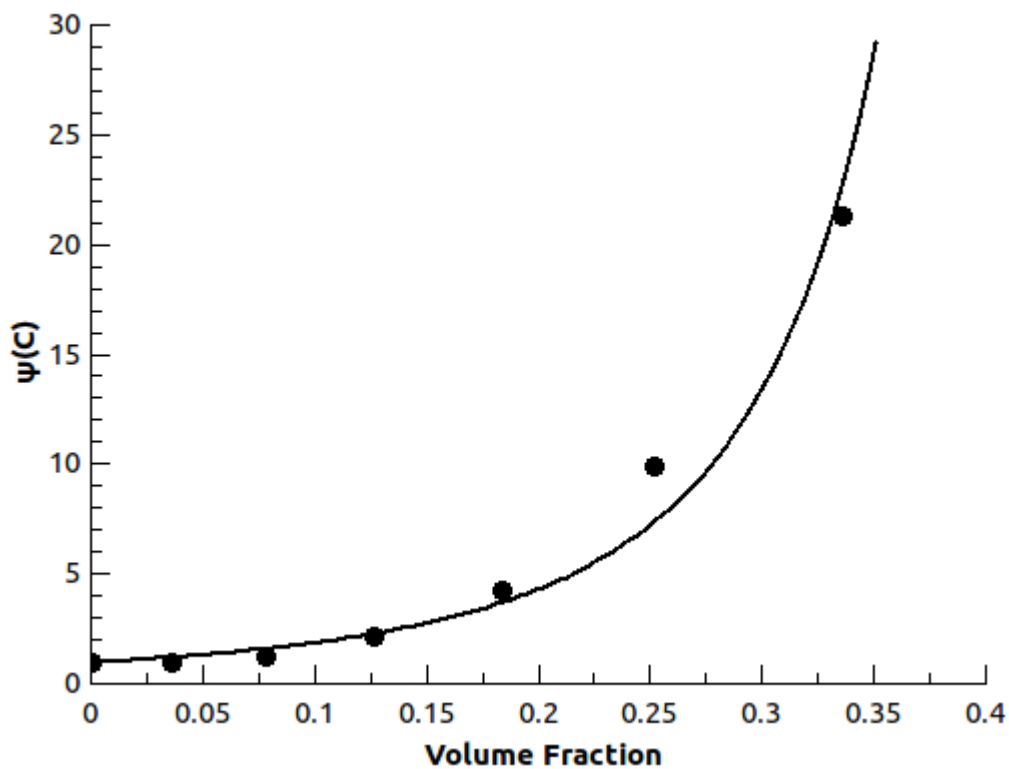


Figure 4: Hydrodynamic function $\psi(C)$, symbols: experimental data from loss modulus, lines: fit with Equation 1 with $C_M=0.62$.

Evidence of agglomerates in semi-concentrated suspensions during mixing

Figure 5 shows the trace of the agglomerates of magnesium hydroxide obtained from the SEM

pictures after X-ray mapping of the magnesium in the case of samples containing 3.6 vol-% of filler at various mixing times. After threshold, despeckling and binarization, the images show an apparent area connected to magnesium that is larger than the actual amount of filler. This evidences that the agglomerates are infiltrated and swollen by the molten polymer and that they are not compact objects.

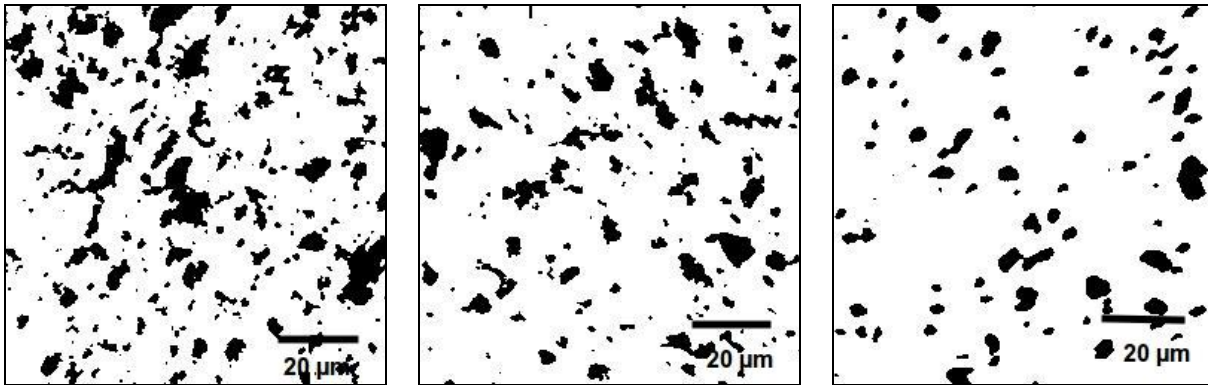


Figure 5: Apparent area of agglomerates at mixing times: 2, 6, 10 min (image size is 100x100µm).

The volume fraction of the agglomerates was calculated from the pictures. It is indicated in Figure 6 and it decreases with the mixing time. Simultaneously, the mean diameter of the observed particles also decreases. These results provide confirmation that, in the present case, the main mechanism for dispersion is erosion. Erosion leads to small elementary particles that are progressively detached from the parent agglomerates. The reduction of the number of particles inside the agglomerates decreases their size and the elementary particles are transferred into the melt. The agglomerates with the smallest size are eliminated and their overall volume fraction is also reduced upon shearing.

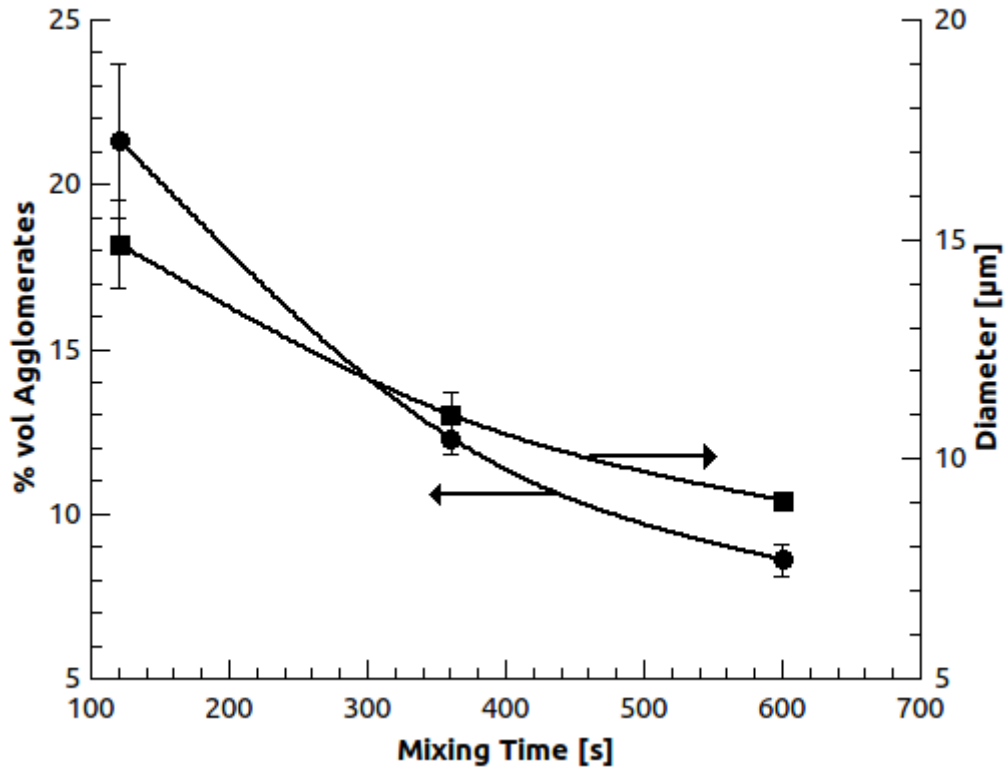


Figure 6: Variation of the apparent volume fraction and diameter of the agglomerates with mixing time.

Direct visualization of the agglomerates was also obtained in the counter-rotating rheometer as shown on Figure 7 for a large agglomerate with a diameter of 100 μm subjected to a shear rate of 9 s^{-1} . These images show, that under this low shear rate, the main dispersion mechanism is rupture in agreement with our previous work [1]. However, the most interesting feature in the frame of the present work is the viscoelastic behaviour of the agglomerate that shows large deformation upon shearing. This is consistent with a large amount of polymer infiltrating the loose space between particles.



Figure 7: Shearing of an individual agglomerate at 9 s^{-1} and times 0 s, 4.8 s, 8.72 s (Image width is $500 \mu\text{m}$).

For such particles and diluted systems, the relation between the critical shear stress for rupture and

the particle diameter obtained in our previous work follows Equation 2 in the form proposed in [1]:

$$\sigma_R > 3300R^{-1.32} \quad (2)$$

with σ_R is the shear stress in kPa,

R is the radius of the agglomerates in μm .

The exponent of Equation 2 is also characteristic for porous agglomerates since for high porosity, the number of bonds between the particles becomes independent of the size and the critical shear stress is inversely proportional to the square of the agglomerate radius.

Relaxation of loose agglomerates in semi-concentrated suspension in oscillatory shear

Figure 8 shows that in oscillatory shear flow, the loose and deformable agglomerates behave as a distinct phase and that the relaxation of shape under oscillation is similar to that reported in blends of molten polymers. The effect of this long relaxation time is visible on the storage modulus as a shoulder at low frequency without great influence on the loss modulus. The results in Figure 8 also show that the amplitude of the phenomena is connected to the amount and size of agglomerates. Increasing the mixing time improves the dispersion and conversely reduces the amplitude of the low frequency relaxation.

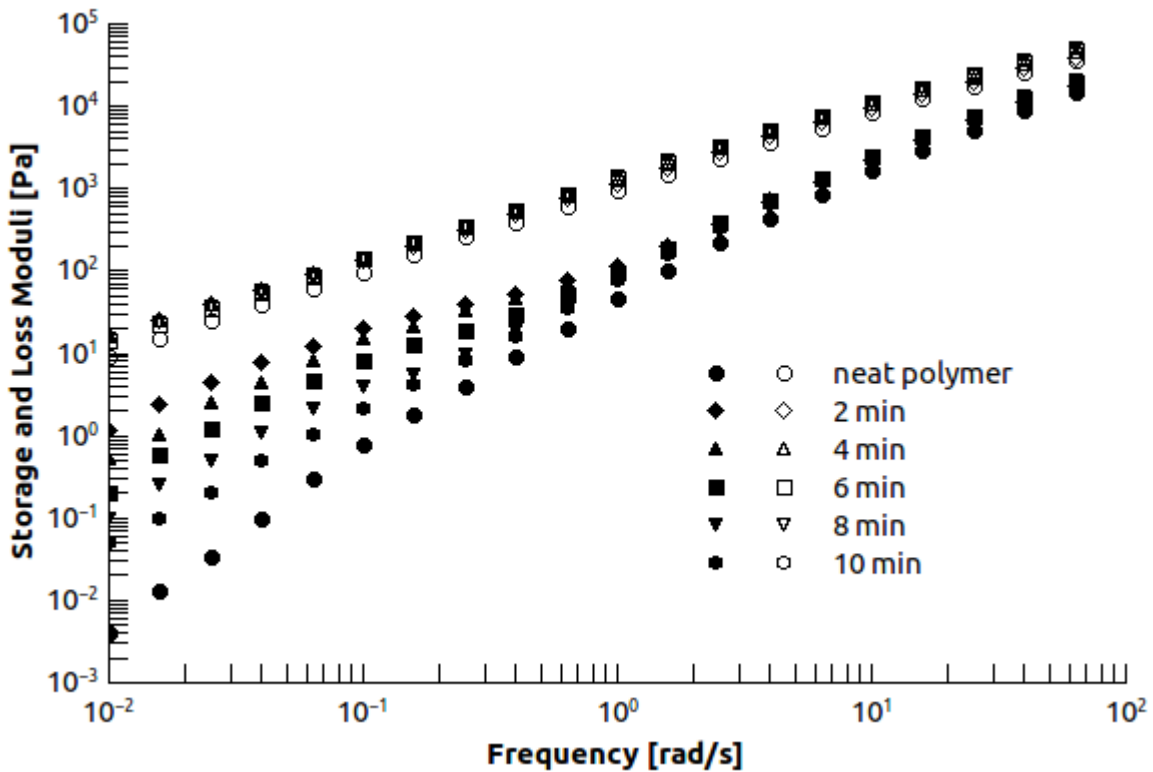


Figure 8: Storage and loss modulus of ethylene-octene copolymer filled with 3.6 vol-% of magnesium hydroxide

The phenomenon is best viewed on the relaxation spectra of Figure 9. These results show that the relaxation time of the agglomerates is quite constant and that only the intensity of the mode attributed to the agglomerate is changing in agreement with the decrease of the volume fraction of agglomerates.

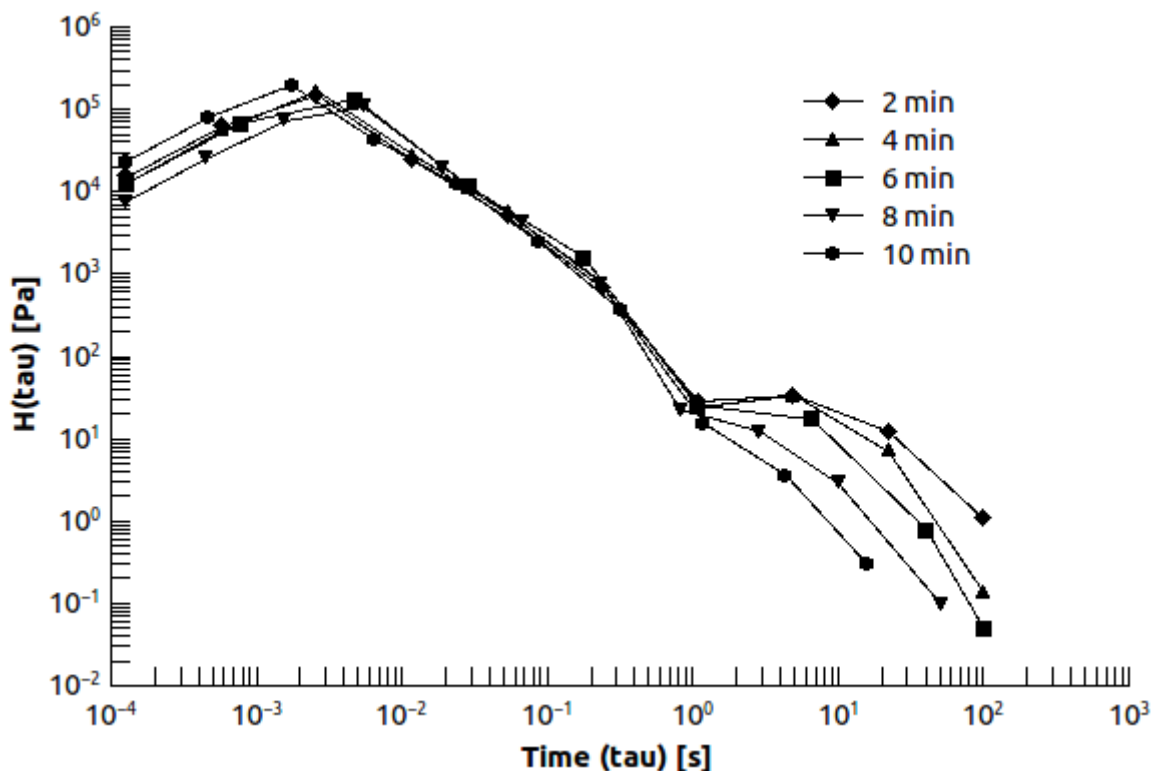


Figure 9: Relaxation spectrum of ethylene-octene copolymer filled with 3.6 vol-% of magnesium hydroxide

DISCUSSION

Use of the Palierne model for the modeling of the relaxation of agglomerates in semi-concentrated suspension in oscillatory shear.

Because of the similarity of the observed behaviour with that of molten incompatible polymer blends, the Palierne model was used as a theoretical frame for a tentative explanation of the low frequency relaxation. The Palierne model [22] considers the behaviour of emulsions of incompressible viscoelastic materials in which the interfacial tension gives rise to an excess of elasticity due to the variation of the interfacial area upon deformation. The average complex shear modulus of the medium accounts for the mechanical interactions between inclusions and may be written as:

$$G^*(\omega) = G_m^*(\omega) \frac{1 + 3 \sum_i \phi_i H_i(\omega)}{1 - 2 \sum_i \phi_i H_i(\omega)} \quad (3)$$

with:

$$H_i(\omega) = \frac{4 \frac{\alpha}{R_i} [2G_m^*(\omega) + 5G_d^*(\omega) + [G_d^*(\omega) - G_m^*(\omega)][16G_m^*(\omega) + 19G_d^*(\omega)]}{40 \frac{\alpha}{R_i} [G_m^*(\omega) + G_d^*(\omega) + [2G_d^*(\omega) + 3G_m^*(\omega)][16G_m^*(\omega) + 19G_d^*(\omega)]}}$$

Where G_d^* , G_m^* are the complex moduli of the dispersed phase and matrix,
 Φ_i are the volume fraction of the inclusions with radius R_i ,
 α is the interfacial tension.

The model was used with the behaviour of the pure polymer as the modulus of the matrix. For sake of simplicity, only average values of the radius and volume fraction were used instead of the distribution. The average radius of the agglomerate was taken from Figure 6 and the volume fraction was assumed to be that of the agglomerates accordingly. The next problem was to choose the viscoelastic behaviour of the agglomerates. For that, we tried various complex moduli of filled polymers such as those given in Figure 3 which were considered to correspond to the most homogeneous systems because the mixing time was longer. This is not absolutely true since even in these conditions of long mixing times, agglomerates were observed. Tests using the behavior of the samples containing various amounts of filler until $C=0.335$ was carried out in the case of the sample with the actual 3.6 vol-% of filler and a short mixing time of 2 minutes. The interfacial tension that enables the reproduction of the experimental results was set at 1.5 mN m^{-1} . A zero interfacial tension does not generate any long relaxation mode. Results are presented in Figure 10 for two selected concentrations C within the agglomerates. The comparison shows that systems containing a large amount of filler lead to non-deformable agglomerates and in this case the shape relaxation does not exist since the agglomerate can never be deformed. Agglomerates containing $C=0.077$ of filler yields the best modeling of the experimental results. In the model the hydrodynamic factor in the form of Equation 1 was also used because part of the filler is already dispersed as elemental particles and not present in the agglomerates. The packing fraction was taken at 0.62, K was set to unity because this refers to elemental dense particles and the exponent was -2.

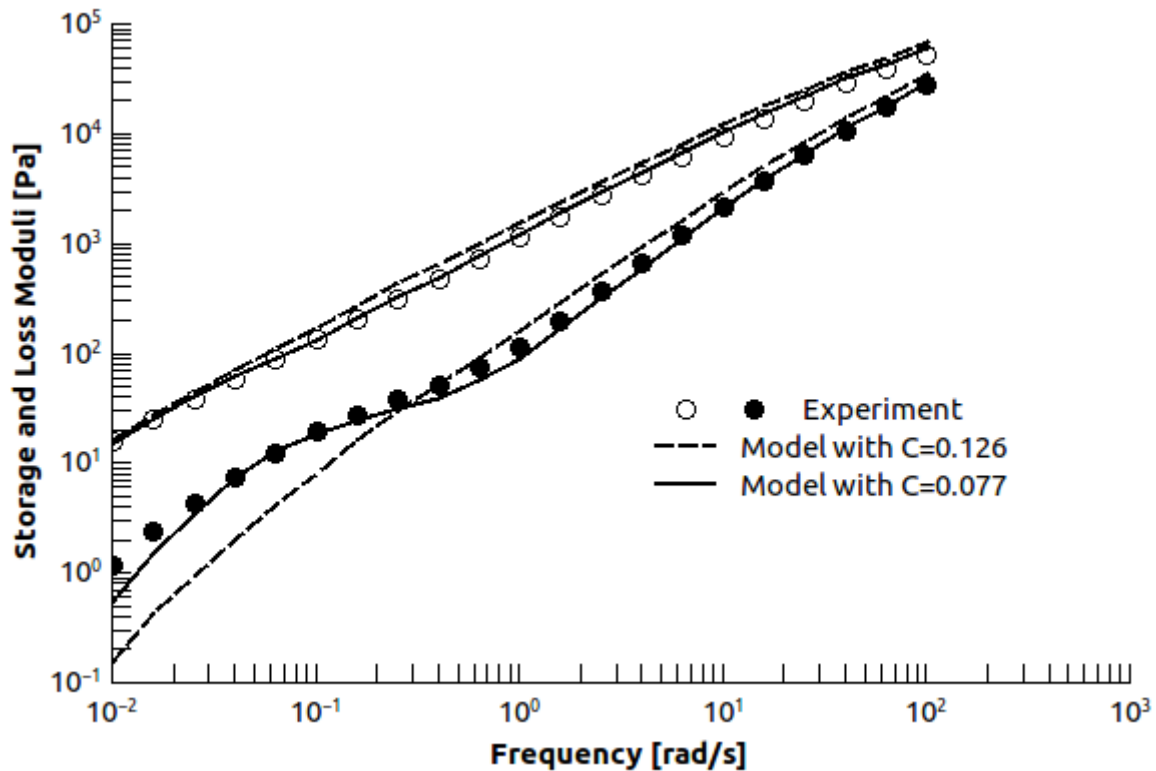


Figure 10: Moduli of ethylene-octene copolymer filled with 3.6 vol-% of magnesium hydroxide at mixing time 2 min. Experiments versus model for two selected concentrations (C) inside the agglomerates.

Figure 11 shows the results in the case of the various mixing times using the same sets of values and data of Figure 6 for the amount and size of agglomerates. For the long mixing time, however the amount of agglomerates measured on the SEM pictures was found to be too high to reproduce the experimental results and 2 vol-% of agglomerates were used in the model. The discrepancy can be explained by the lack of accuracy of the SEM measurements because at very long mixing time the agglomerates have almost disappeared.

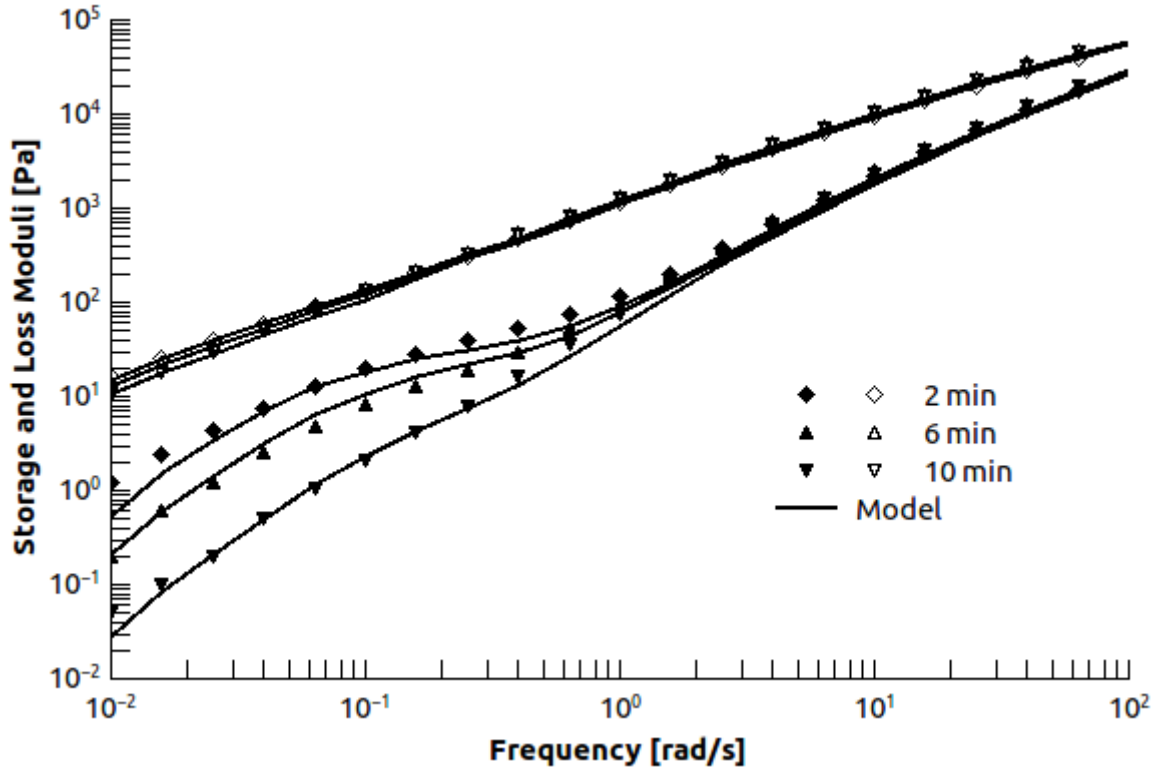


Figure 11: Moduli of ethylene-octene copolymer filled with 3.6 vol-% of magnesium hydroxide at various mixing times. Experiments versus model with concentrations $C=0.077$ inside the agglomerates.

Significance of the interfacial tension between the agglomerates and the pure polymer.

The results indicate that there must exist an interfacial tension between the pure polymer and the filled polymer constituting the agglomerates. Therefore, an effective surface tension of the filled polymer can theoretically be calculated as suggested by Elias et al. in their work on blends of olefinic polymers containing hydrophobic or hydrophilic silica [4-6]. The value of interfacial tension between pure polymer and polymer containing $C=0.077$ of magnesium hydroxide is 1.5 mN m^{-1} . Assuming that the surface tension of the matrix is that of polyethylene, $\gamma_{PE}=35.3 \text{ mN m}^{-1}$ [23, 24], the surface tension of PE containing $C=0.077$ of homogeneously dispersed magnesium hydroxide can be calculated by the Girifalco-Good Equation [25]:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1\gamma_2} \quad (3)$$

This yields the value of 39.9 mNm^{-1} . If the argument based on free energy developed by Elias et al. is valid, the effective surface tension is an averaged value combining the surface properties of both the polymer and the mineral. The average must be calculated by accounting for the fraction of area occupied by the polymer and the filler on a given area. A calculation using a simple blending law with the volume fraction is therefore possible assuming that the dispersion is homogeneous. For

$C=0.077$, the calculated surface energy of the magnesium hydroxide is 95 mN m^{-1} . Value for comparison can not be found in the literature and can hardly be measured on the powder surface because of the porosity. However, the high value of the surface energy tends to indicate a hydrophilic surface as it is generally recognized for untreated hydroxides and other minerals [26]. In comparison, surface energies range from 32 to 80 mN m^{-1} for hydrophobic and hydrophilic silicas. Of course, in this rough analysis, no separation can be made between dispersive and polar components of the surface energy. Nevertheless, for polyethylene, the polar component is zero. On the opposite, it must also be taken into account that for solid minerals, the prevalent theory used in surface chemistry for the calculation of surface tension is the Van Oss-Good-Chaudhury equation [27]. In this theory, the surface tension is divided into three components (γ^{LW} : Lifshitz Van der Wals component, γ^+ : polar electron acceptor component, γ^- : polar electron donor component) related by:

$$\gamma_s = \gamma^{\text{LW}} + 2\sqrt{\gamma^+\gamma^-} \quad (4)$$

In Table 1, we indicate some values of surface tension components of minerals from the literature especially oxides from magnesium and aluminium, hydrophobic and hydrophilic silica and calcium hydroxide or other minerals commonly used in polymer applications. Other values can be found in the review of Lewin and al. [26].

Table 1: Surface tension components of minerals used in polymer applications for comparison with magnesium hydroxide (values in mN m^{-1}).

Materials	γ_s	γ^d	γ^p	γ^{LW}	γ^+	γ^-	Ref
Al_2O_3	41.3			35.1	0.6	16.1	[28]
Al_2O_3	39.7			31.6	0.6	27.2	[26]
SiO_2	32	30	2				[24] (*)
Hydrophobic							
SiO_2	80	29.4	50.6				[24] (*)
Hydrophilic							
SiO_2	50.7			39.2	0.8	41.4	[26]
MgO	-	95			-		[29] (*)
Ca(OH)_2	70						[26]

(*) Only dispersive component or polar components are given.

The surface energy of the {1000} plane of natural magnesium hydroxide (brucite) was calculated ab

initio by many authors and reported values ranges from 3.3 to 8 meV Å⁻² [30-31] or 53 mN m⁻¹ to 128 mN m⁻¹ in the units used in this paper. The energy is much larger for the other planes but the plane is considered to be the most open and the largest surface. Therefore, the experimental value obtained indirectly in this work by experimental means is consistent with this range.

CONCLUSIONS

Various states of dispersion of magnesium hydroxide in an olefinic polymer were obtained by mixing the mineral with the polymer in the molten state and by varying the mixing time. In particular, agglomerates can be obtained at short mixing times. These agglomerates show a low frequency shape relaxation in oscillatory shear flow in the melt indicating that they behave as a distinct phase. Optical and SEM measurements show that this phase is much more concentrated in minerals than the matrix. Magnesium hydroxide is wetted by the melt and this mix forms loose and deformable agglomerates. The relaxation is all the more pronounced than agglomerates are large and vanishes for well-dispersed materials.

The system looks like a polymer blend and by analogy, the Palierne model for the relaxation of a viscoelastic liquid droplet within a viscoelastic liquid medium was tested. The shape relaxation not only implies a two-phase system with different viscoelastic behaviour but also the existence of an interfacial tension between the phases. This was found to be 1.5 mN m⁻¹. From the experimental conditions and from the knowledge of the surface tension of the liquid olefinic polymer, the surface free energy of magnesium hydroxide was calculated to be 95 mN m⁻¹.

This value is consistent with ab-initio calculations on the {1000} plane of brucite, the natural magnesium hydroxide mineral, reported in the literature. Also it indicates a highly hydrophilic mineral and it is comparable with the value for hydrophilic silica or calcium hydroxide.

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