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Crystallization of Polyolefins from Rheological Measurements—Relation between the Transformed Fraction and the Dynamic Moduli

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ABSTRACT: Experimental results from the literature and from this work show the reliability of the dynamic mechanical spectroscopy as a complementary tool to follow the crystallization of polymers from the melt. However the problem of the interrelation between the transformed fraction and the mechanical data is not simple and remains a topic open to discussion. To get a better understanding of these relations, the method was applied to the study of two polyolefins which show very different morphologies during their crystallization from the melt. Their morphological study has shown that, though they both crystallize in a well-defined spherulitic structure, because of the differences of size of the crystalline entities, one can be considered as a suspension of spherical particles in a liquid matrix whereas the other behaves as a colloid of small particles. The study of the rheological behavior of the suspension-like material shows the existence of two critical values of the volume fraction. In agreement with the percolation theory, the first value is related to the appearance of a yield effect and the second indicates the maximum packing. Moreover, in this case, throughout the crystallization, the relaxation times depend on the filler content and the zero-shear viscosity varies upon the $-^3/_2$ exponent of the volume fraction. The colloid-like material behaves in a completely different way since a yield effect appears in the earliest stage of the crystallization. For both materials, the use of an equilibrium modulus is able to characterize the yield effect, and in both cases, it is described by the same type of expression with a universal exponent equal to 3 in agreement with theories for physical gels. Unfortunately, these results show that a unique expression can hardly be used to relate the transformed fraction to the rheological data and that such a derivation always requires an additional investigation of the morphology.

Introduction

The dependence of the viscoelastic properties on the structure of polymers has been pointed out in the case of amorphous and semicrystalline materials. However, this dependence has not been well established for the intermediate states, for example during the crystallization where the structure is complex and biphasic linking together amorphous and crystalline phases. Trying to correlate the structure to viscoelastic properties in such conditions may present a major interest especially since the rheometry may provide a complementary tool to study the crystallization kinetics. This approach has been, at several times, mentioned in the literature but the determination of the crystallized fraction is generally realized without a theoretical support that can justify it. For example Teh et al.[1] have tried to determine the onset and the density of nucleation during the crystallization of polypropylene, polyethylene, and their blends using dynamic mechanical methods. They have shown that results of such an analysis are close to those of DSC and optical microscopy though the isotherms during the crystallization remain rather imperfect in their experiments. Indeed, crystallization has generally already begun before the isotherm is reached. Khanna[2] has used this technique to study the crystallization kinetics of different materials with and without nucleating agent and has shown that the rheological technique is more sensitive than the conventional ones, and in addition he proposes a relation to deduce the crystallization fraction $\alpha(t)$, generally obtained from calorimetric data or dilatometry, from the rheological measurements

$$\alpha(t) = \frac{G'_t - G'_0}{G'_\infty - G'_0} \tag{1}$$

where G'_0, G'_t, and G'_∞ are the storage moduli at time 0, t, and infinity. The dynamic viscoelastic analysis was also used by Gauthier et al.[3] to follow the crystallization of poly(ethylene terephthalate)/glass fiber samples. They have shown that the evolution of the storage modulus not only allows one to evaluate the crystallization kinetics but also allows one to determine the nucleation and growth characteristics. They have proposed the same type of relation than that of Khanna[2] for the determination of the crystallized fraction $\alpha(t)$ from rheological measurements. Lin et al.[4] have used the dynamic mechanical measurements to study physical gels during the crystallization of thermoplastic elastomeric polypropylene. They show the reliability of this technique to study physical gels during crystallization in order to verify that this material follows a power law behavior at the gel point. Te Nijenhuis et al.[5] have also studied the mechanical properties at the gel point of a crystallizing poly(vinyl chloride) by this technique and concluded from the analogy between the physical and chemical gelation that the PVC plastisol is at its gel point when it exhibits a power law relaxation. This makes possible to measure the gel point directly by using a simple rheological test.

To understand the physical phenomena involved and to precisely obtain a possible relationship between the morphology, the crystallized fraction, and the viscoelastic properties, this experimental work, focusing on the viscoelastic behavior at small strains in relation with

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the calorimetric data and the morphology, has been carried out on two polyolefins showing very different trends during isothermal crystallization from the melt. The use of small strains is an obliged step to avoid any disturbance of the structure and of the crystallization kinetics by shear. For a better understanding, an analogy is made between these systems and the structure of filled polymers assuming that the crystalline and the amorphous phases are analogous to a solid phase dispersed in a liquid matrix. This approach is also interesting since the complexity of the study of the rheological behavior of filled polymers in the melt state, related to the great number of parameters involved, is reduced in the present case. Indeed, the system satisfies some fundamental assumptions governing the existing theories in this area: solid phase in a liquid matrix, homogeneity in the distribution of size and geometry, and perfect adhesion between the filler and the matrix due to the presence of a common amorphous phase. Furthermore, the system presents a continuous variation of the volume fraction of the solid.

The goal of this study is on one hand to check the possibility to use the dynamic rheological measurements as a tool to follow the crystallization kinetics which might be interesting if the crystallized fraction can be deduced from rheological measurements. On the other hand, it is also useful to try to build constitutive equations describing the changes of the rheological behavior of polymers during crystallization.

In a recent work,[6] the rheological behavior of an isotactic polypropylene during isothermal crystallization has been partially studied. The results have revealed the existence of a yield effect at high filler content. In the absence of this yield effect, a model was proposed to predict the variation of the rheological parameters with the volume fraction of filler.

In the present paper, we will, on one hand, complete the study of the polypropylene sample, which is a suitable model for a suspension, and on the other hand, we will present that of a nucleated high-density polyethylene which looks much like a colloid. In addition, we will investigate the origin of the yield and of the different exponents found in the model equations in relation to gelation and the percolation theory.

Dynamic Oscillatory Experiments of the Samples

Experiments were carried out on a polypropylene (M_w = 300 000 and I_p = 7, unnucleated and referenced HY6100 from Shell) and on a high-density polyethylene (M_w = 90 000, I_p = 4.6, nucleated and referenced 2040MN55 from Atochem). These two specific commercial materials were found to have very different morphologies in the solid state after isothermal crystallization so that they are very useful for the purpose of understanding the connection between the morphology and the rheological behavior during crystallization. However, they should not be considered as representative of all the polypropylenes or polyethylenes but rather as representative of two types of structural arrangements. Therefore, they will be referenced throughout the paper as SL (suspension-like material) and CL (colloid-like material). Rheological oscillatory experiments were performed during isothermal crystallization at 126.2 °C for hdPE and 135 °C for PP in a Rheometrics RDA 700 rheometer with parallel plates geometry (plate diameter = 25 mm; gap = 2 mm). As mentioned previously in the Introduction, different authors[1,5] have used the dynamic rheological measurements to study the crystallization. In this type of experiment, they have generally taken into consideration disturbance of the crystallization that may be induced by shear and small values of the strain have been used. However, the dimensional variation of the sample during the crystallization is often neglected though it may induce large errors on the measurements due to additional stress on the sample and uncertainties in the calculation. In a previous work,[7] we proposed an improved controlled methodology to follow the rheological behavior during isothermal crystallization from the melt: the use of small strains ensures that the rheological parameters are only time and temperature dependent and are not strain dependent and avoids the crystallization kinetics to be modified by shearing. Furthermore, the gap adjustment throughout the test, according to the tensile force transducer of the rheometer, allows the elimination of any longitudinal effort induced by the dimensional variation of the sample and also enables corrections in the calculation of the moduli.

Following the proposed methodology,[7] six frequencies were used (0.3162, 1, 3.162, 10, 31.62, and 100 rad/s), and the measurements were performed at equal intervals during the crystallization. To ensure complete melting of the crystallites, the samples were preheated over 5 min at a temperature well above their thermodynamical melting point (160 °C for PE and 210 °C for PP). The temperature is then lowered to the chosen crystallization temperature T_c in a time interval much shorter than the crystallization time. The sample temperature fluctuations never exceed ±0.1 °C during the isotherm.

Evolution of the Storage and the Loss Moduli G' and G'' during Crystallization

The variations with time of the storage and loss moduli during the crystallization at 126.2 °C for the six frequencies in use are respectively shown in parts a and b of Figure 1 for material CL as an example. The dynamic moduli are sensitive to structural changes inside the material and increase with increasing time until they reach a plateau at the end of the crystallization. This plateau is well distinguished in the case of the storage modulus, but dispersed values are obtained for the loss modulus, which can be attributed to a slippage between the sample and the rheometer plate or to a bad resolution of the phase angle once approaching a highly elastic material. Besides, because of the great sensitivity of the dynamic moduli to the structural changes in the material, the constant value of the moduli at the starting of the experiment is an additional proof of the homogeneity of the melt that is achieved after the thermal treatment.

Differential Scanning Calorimetry

The isothermal crystallizations of the samples were performed in a Perkin-Elmer DSC System 7 under the same conditions as those used for the rheological measurements and at the same crystallization temperature, and satisfactory reproducibility of the results has been obtained. The transformed fraction $\alpha(t)$ is calculated from the thermogram of crystallization by subsequent integration and normalization (Figure 2).

Morphological Studies of the Samples

The morphological investigation of the two types of samples under polarized light optical microscopy during

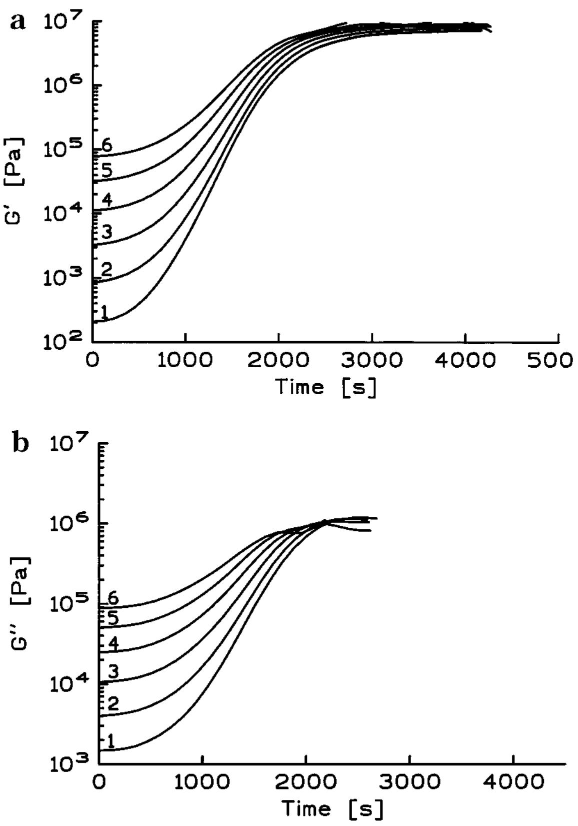

Figure 1. (a) Evolution of the storage modulus during the isothermal crystallization of polyethylene at 126.2 °C. Frequency (rad/s): (1) $\omega = 0.3162$; (2) $\omega = 1$; (3) $\omega = 3.162$; (4) $\omega = 10$; (5) $\omega = 31.62$; (6) $\omega = 100$. (b) Evolution of the loss modulus during the isothermal crystallization of polyethylene at 126.2 °C. Frequency (rad/s): (1) $\omega = 0.3162$; (2) $\omega = 1$; (3) $\omega = 3.162$; (4) $\omega = 10$; (5) $\omega = 31.62$; (6) $\omega = 100$.

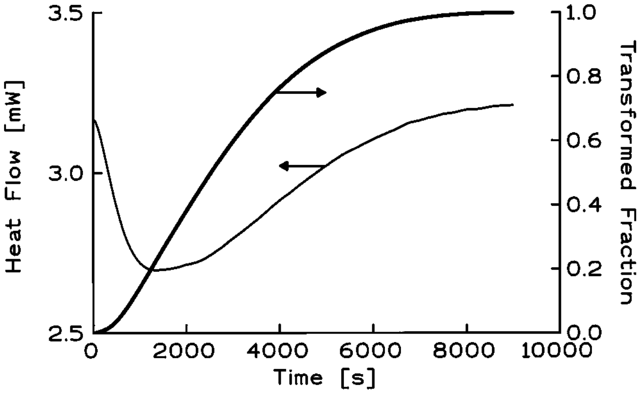

Figure 2. Example of the crystallization thermogram of a polypropylene sample at 135 °C and the corresponding transformed fraction.

their crystallization in the same conditions as those of the rheological and calorimetric experiments has shown that they display very different morphologies. Indeed for the polypropylene sample,[6] all the nucleation sites appear randomly and the crystallization proceeds in a well-distinguished spherulitic structure (Figure 3a). Because it is nucleated, the high-density polyethylene sample shows a very different morphology since a high number of nucleation sites appear instantaneously throughout the space offered for the crystallization (Figure 3b). Furthermore, the aspect remains the same from the beginning until the end of the crystallization, and a large number of spherulites are obtained which restricts their size. However, the crystallization continues to take place as shown by the calorimetric measurements, and it can be considered that the major part of the crystallization process takes place inside the spherulites. Therefore, for this material, the crystallization is characterized by an increase in the crystallite size during time, leading to a further perfection inside the spherulites though their overall size remains unchanged. The interesting point is that, although they crystallize into a three-dimensional structure, the crystallization kinetics and the morphologies of the two samples are very different. From a morphological point of view and in view of the understanding of their rheological behavior, the polypropylene sample is similar to a suspension of spherical particles in a liquid matrix whereas on the opposite, the polyethylene sample appears like a colloid of small particles in a liquid matrix. In such conditions and by analogy to filled polymers, the notion of volume fraction of filler was assigned to spherulites for sample SL and to crystallites for sample CL.

Relation between the Transformed Fraction $\alpha(t)$ and the Filler Content $\phi(t)$

The correlation between the results obtained by DSC and those obtained by polarized light microscopy shows that, in the case of sample SL,[6] the transformed fraction $\alpha(t)$ is a direct indication of the volume fraction of spherulites $\phi_s(t)$:

$$\phi_s(t) = \alpha(t) = \phi(t) \qquad (2)$$

In the case of sample CL and at a given time, the degree of crystallinity inside the spherulite is supposed to be identical to the global degree of crystallinity since the whole material is instantaneously occupied by small spherulites and it is therefore equal to $\phi_c(t)$, the volume fraction of crystallites inside the spherulites, since a crystallite is a totally crystalline entity. Therefore, at a given time, the transformed fraction is

$$\alpha(t) = \frac{\chi(t)}{\chi_\infty} = \frac{\phi_c(t)}{\phi_{c\infty}} = \frac{\phi(t)}{\phi_{c\infty}} \qquad (3)$$

$\chi_\infty = \phi_{c\infty}$ is the final degree of crystallinity. It was determined by density measurements and estimated to 84%.

Rheological Behavior of the Samples

Using results of DSC and rheometry, at the same time of measurement, the evolution of the storage modulus and of the real part of the dynamic viscosity (η') vs frequency with the crystallites content $\phi_c(t) = \phi(t)$ for sample CL and with the spherulites content $\phi_s(t) = \phi(t)$ for sample SL are plotted in Figures 4 and 5. The influence of the frequency on the modulus is clearly displayed in the low-frequency range, and for the viscosity, it changes during the crystallization process. It is clear that the relative rheological quantities, defined as the ratio of these quantities to those for the molten polymer at the same frequency ($G'(\omega,\phi)/G'(\omega,0)$ and $\eta'(\omega,\phi)/\eta'(\omega,0)$) are frequency dependent. As shown in Figures 4b and 5b, the presence of the filler drastically increases the low-frequency viscosity. This increase is sharp for CL from the early stages of the crystallization whereas it is smoother for SL. This is confirmed by the evolution of the storage modulus G'

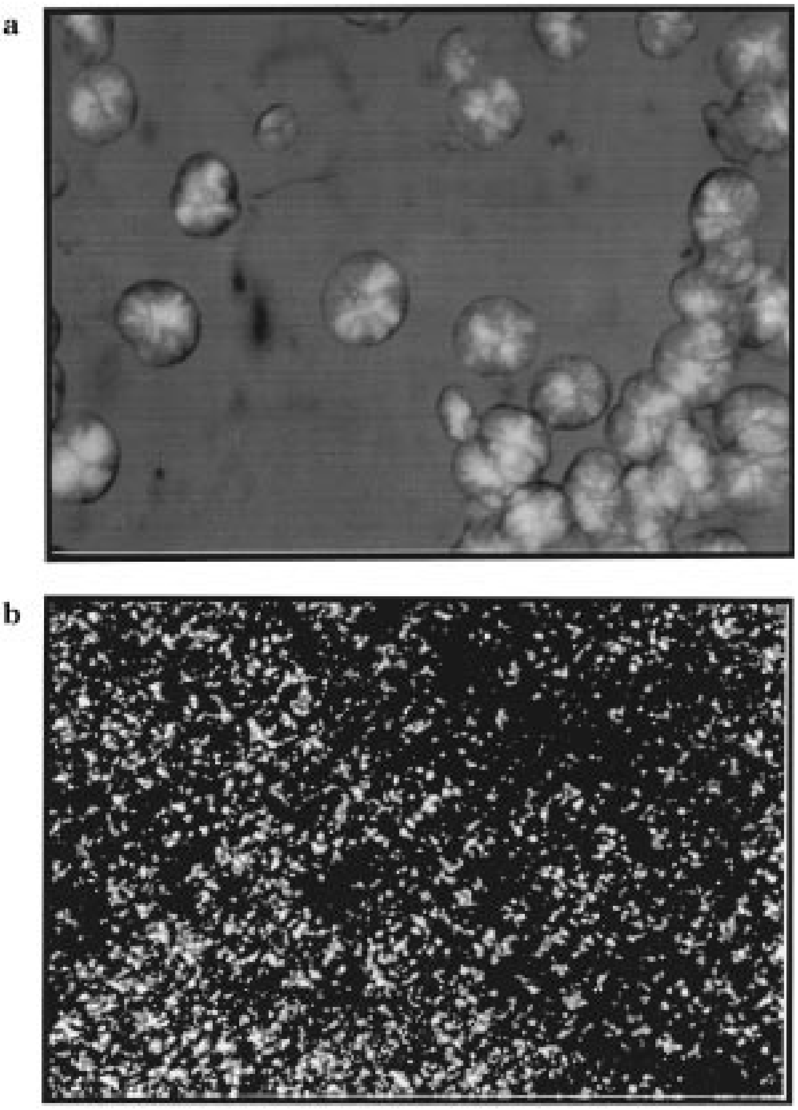

Figure 3. (a) Polarized light microscopy photographs of a polypropylene sample crystallized from the melt at 135 °C taken at $t = 18.1$ min. (width of the figure = 320 μm). (b) Polarized light microscopy photographs of a polyethylene sample crystallized from the melt at 126.2 °C taken at the beginning of the crystallization (width of the figure = 280 μm).

with frequency (Figures 4a and 5a) which displays an inflection point at low frequency from the beginning of the crystallization for CL which indicates a strong yield stress effect where this phenomenon is delayed with in the case of SL.

Determination of the Yield Values of G'

The existence of such a yield effect is still controversial in the literature. However, in the experiments under consideration, it can be reasonably thought as a consequence of the long-term structure generated by the crystalline morphology of the sample and by the interaction between the spherulites or crystallites throughout the remaining molten polymer. Anyway, whatever its nature is, this yield value provides a reasonable way to describe the low-frequency behavior of the material under investigation. These values of G', at the different filler contents, were determined for the storage modulus using the modified Casson[8] relation rewritten by Utracki,[9] from the intercept of the plots $G'^{1/2}(\phi)$ vs $G'^{1/2}(0)$. These plots allow a rough estimation of the yield values and indicate an important yield effect from the beginning of the crystallization for sample CL. Indeed, for $\phi(t) = 0.084$ ($\alpha(t) = 0.1$), the yield value of the storage modulus represents almost 50% of the storage modulus at the lowest frequency. These observations agree with the morphological studies of sample CL where all the material is instantaneously occupied by solids. On the other hand, sample SL shows a delayed yield stress behavior at $\phi(t) = 0.4$.

Modeling of the Experimental Data by a Cole and Cole Equation

To obtain more reliable information concerning the value of the yield stress and the variation of the viscosity, moduli and relaxation times, the experimental data of both SL and CL were fitted using two types of phenomenological models for liquids and solids. The first type of models (Cole and Cole[10] or Tschoegl[11]) requires the knowledge of the matrix parameters only and was found to be suitable when the behavior is that of a liquid, i.e., in the absence of the yield effect. However, if necessary, to take into consideration the yield effect, an equilibrium modulus G_e is added to the equation of G^*. The equation of the complex modulus is given as:

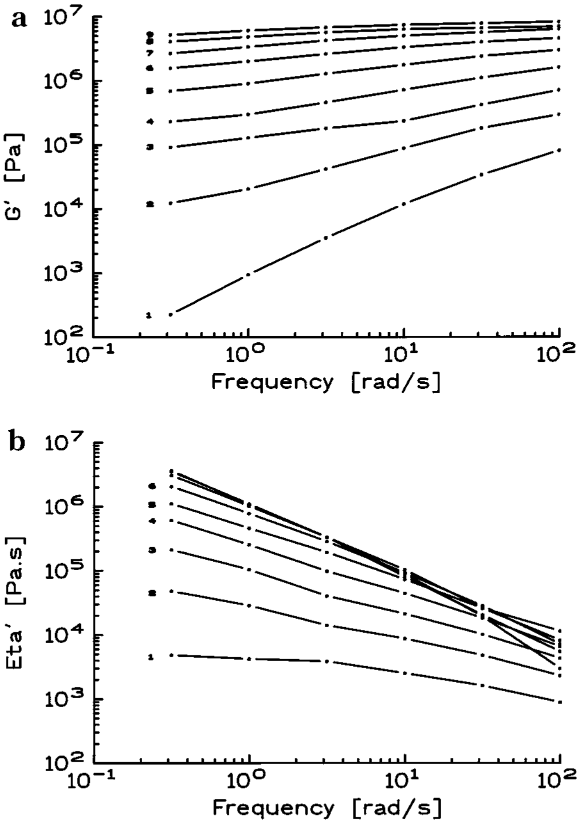

Figure 4. (a) Evolution of the storage modulus of sample CL with the frequency. Filler content: (1) $\phi = 0$; (2) $\phi = 0.084$; (3) $\phi = 0.168$; (4) $\phi = 0.252$; (5) $\phi = 0.336$; (6) $\phi = 0.420$; (7) $\phi = 0.504$; (8) $\phi = 0.588$; (9) $\phi = 0.672$. (b) Evolution of the real part of the dynamic viscosity of sample CL with the frequency. Filler content: (1) $\phi = 0$; (2) $\phi = 0.084$; (3) $\phi = 0.168$; (4) $\phi = 0.252$; (5) $\phi = 0.336$; (6) $\phi = 0.420$; (7) $\phi = 0.504$; (8) $\phi = 0.588$; (9) $\phi = 0.672$.

$$G^*(\omega) = \frac{\omega\eta_0}{1 + (i\omega\lambda_0)^{1-h}} \tag{4}$$

where η_0 is the zero-shear viscosity, λ_0 a characteristic time of the model, and h the distribution parameter of the relaxation times.

In the case of SL, Figure 6 shows the evolution of the experimental relative viscosity ($\eta_{0r} = \eta_0(\phi)/\eta_0(0)$) and relative relaxation time ($\lambda_{0r} = \lambda_0(\phi)/\lambda_0(0)$) vs $(1 - \phi)$ obtained from the Cole and Cole parameters at different filler contents (or spherulite contents). The rheological behavior follows two mechanisms below and above the yield appearance ($\phi = 0.4$). In the absence of the yield effect ($\phi \leq 0.4$), the variation of the zero-shear viscosity η_0 and of the relaxation time λ_0 is well described by[6]

$$\eta_0(\phi) = \eta_0(0)(1 - \phi)^{-3/2} \tag{5}$$

$$\lambda_0(\phi) = \lambda_0(0)(1 - \phi)^{-1/2} \tag{6}$$

$$h = \text{constant} \tag{7}$$

$$G_0(\phi) = \frac{\eta_0(\phi)}{\lambda_0(\phi)} = G_0(0)(1 - \phi)^{-1} \tag{8}$$

It should be mentioned that the use of an equilibrium modulus in the Cole–Cole equation does not provide a satisfactory tool for the modeling of the observed behavior since the yield effect above a volume fraction of $\phi = 0.4$ is also noticed on the loss modulus. The nature of the yield effect is thus more complex, and it is not clear whether the presence of a contribution to the loss modulus should mean the existence of some relaxation mechanism at long times.

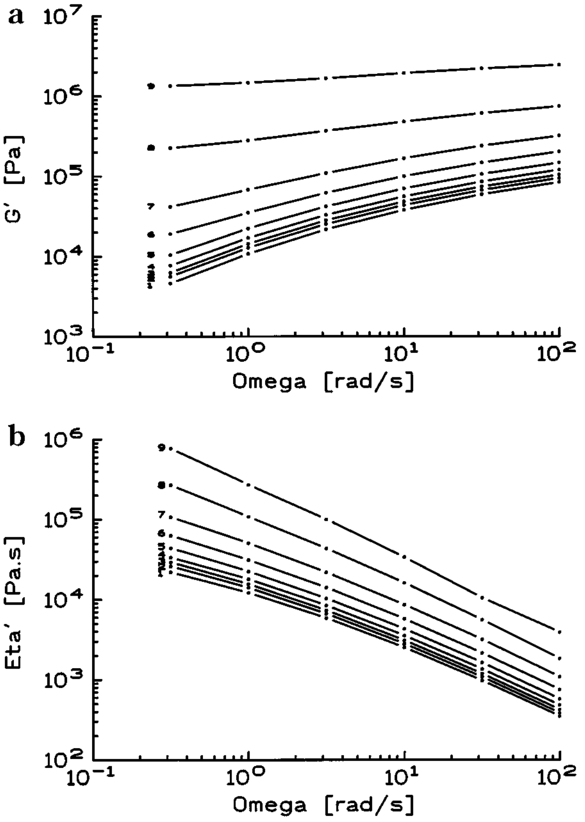

Figure 5. (a) Evolution of the storage modulus of sample SL with the frequency. Filler content: (1) $\phi = 0$; (2) $\phi = 0.1$; (3) $\phi = 0.2$; (4) $\phi = 0.3$; (5) $\phi = 0.4$; (6) $\phi = 0.5$; (7) $\phi = 0.6$; (8) $\phi = 0.7$; (9) $\phi = 0.8$. (b) Evolution of the real part of the dynamic viscosity of sample SL with the frequency. Filler content: (1) $\phi = 0$; (2) $\phi = 0.1$; (3) $\phi = 0.2$; (4) $\phi = 0.3$; (5) $\phi = 0.4$; (6) $\phi = 0.5$; (7) $\phi = 0.6$; (8) $\phi = 0.7$; (9) $\phi = 0.8$.

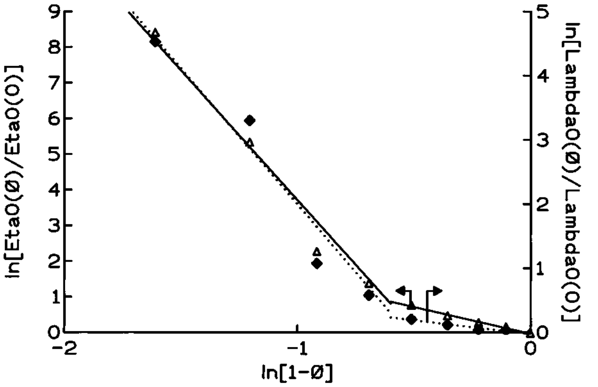

Figure 6. Evolution of the relative viscosity and the relative relaxation time of the sample SL calculated from the Cole and Cole model with the filler content.

In the case of sample CL, the results show that the yield effect rapidly gains great importance, which completely hides the effects of the viscoelastic matrix, and above $\phi = 0.084$, it represents the major contribution to the observed behavior. Though the equilibrium modulus is not able to describe, at the same time, the variations of the loss and the storage moduli, the yield appearance is also displayed in this case in the Cole and

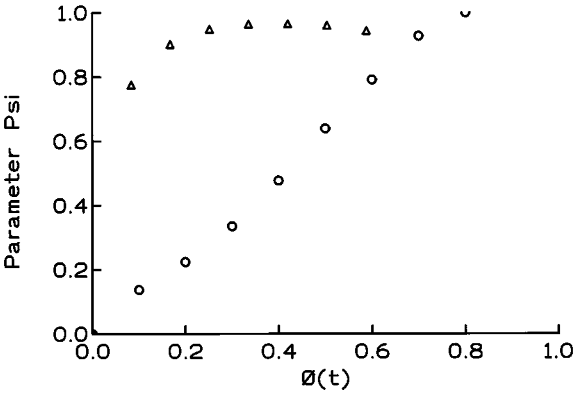

Figure 7. Evolution of the parameter Ψ of the mechanical model of Takayanagi et al. with the filler content in the case of sample SL and sample CL. (○, sample SL; △, sample CL).

Cole model by a drastic modification of the parameters of the relaxation time distribution.

Modeling of the Experimental Data Using the Models of Takayanagi et al.[12]

These models require the knowledge of the dynamic moduli of both the matrix and the filler particle. The mechanical model of Takayanagi et al.[12] represents the distribution of stresses in each component of the composite assuming that, under stress, some lines of force cross only the matrix phase while some others cross the two phases (matrix and filler). Two models, in series (model I) and in parallel (model II) are generated with two adjustable parameters Ψ and λ, whose product gives the volume fraction of filler $\phi(t)$.

$$\text{model I:}\quad G^* = \left[\frac{\psi_{\mathrm{I}}}{\lambda_{\mathrm{I}}G^*_{\mathrm{i}} + (1-\lambda_{\mathrm{I}})G^*\mathrm{m}} + \frac{1-\psi_{\mathrm{I}}}{G^*_{\mathrm{m}}}\right]^{-1} \tag{9}$$

$$\text{model II:}\quad G^* = \lambda_{\mathrm{II}}\left(\frac{\psi_{\mathrm{II}}}{G^*_{\mathrm{i}}} + \frac{1-\psi_{\mathrm{II}}}{G^*_{\mathrm{m}}}\right)^{-1} + (1-\lambda_{\mathrm{II}})G^*_{\mathrm{m}} \tag{10}$$

where G^*, G^*_{m}, and G^*_{i} are the dynamic moduli of the composite, the matrix, and the filler.

These models are generally more suitable for describing the solid and elastomeric behavior of multiphase composites which might be more appropriate in the case of strong yield effect. For sample SL, the matrix parameters ($\phi = 0$) were taken at the beginning of the isotherm before the appearance of any solid entity. Since, at the end of the crystallization, all the space offered for the crystallization is occupied by spherulites (or filler particles), we estimate that the dynamic moduli measured at the end of the crystallization, when the plateau moduli are reached, correspond to the filler moduli. For model I, with or without an equilibrium modulus, the variation of the adjustable parameter Ψ with the filler content $\phi(t)$ is linear (Figure 7). According to Takayanagi et al.,[12] the parameters Ψ and λ are related to the material composition ($\phi = \Psi\lambda$) and to the mixing state. In the case of SL, parameter Ψ might be related to the growth of the solid entities and their distribution in the matrix. Its linear increase indicates a homogeneous distribution of the spherulites in accordance with observations of the morphology. Above $\phi = 0.8$, Ψ tends to 1 which means that the stress is transmitted by the filler particle with a low strain indicating phase inversion and that crystalline entities now form the matrix. It is worth noticing that this critical value ($\phi = 0.8$) might have the meaning of a maximum packing fraction. In agreement with the Cole and Cole[10] model, a significant yield appears at a spherulites content higher than 0.4. Indeed, in the mechanical models of Takayanagi et al.[12] below $\phi(t) = 0.4$, the yield represents less than 5% of the value of the storage modulus at the lowest frequency.

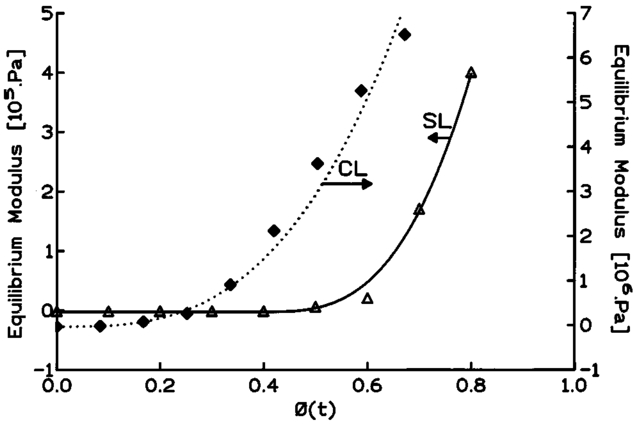

Figure 8. Evolution of the equilibrium modulus with the filler content for sample SL and sample CL.

On the other hand, in the case of CL, the volume fraction of filler represents that of the crystallites. Therefore, the use of the mechanical models of Takayanagi et al.[12] requires the values of the storage and loss moduli of the dispersed phase (crystallites) which were taken to be 10^{10} and 10^5 Pa since a crystallite can be considered as a purely elastic entity ($G' \gg G''$). Fulchiron et al.[13] have already used such an approach with the same type of model. The values of the adjustable parameter Ψ of the model were found to reach the unity instantaneously at the different $\phi(t)$ (Figure 7). Assuming that parameter Ψ represents the dispersion state of the solid phase in the medium, this peculiarity confirms the instantaneous building of a continuous network of the solid phase which can be considered to be formed of interconnected crystallites.

Evolution of the Equilibrium Modulus with the Filler Content

The values of the equilibrium modulus obtained from the modeling of the experimental data with the mechanical models of Takayanagi et al.[12] have been fitted using the following type of relations commonly used in the literature[9]

$$G_{\mathrm{e}} = k(\phi - \phi_0)^f \qquad \text{for } \phi \geq \phi_0 \tag{11a}$$

$$G_{\mathrm{e}} = 0 \qquad \text{for } \phi \leq \phi_0 \tag{11b}$$

where ϕ_0 is the critical value of the filler content for the onset of the yield. The result of the fitting, in the case of samples SL and CL, is shown in Figure 8. In the case of sample CL, the values of the equilibrium modulus provided by the Takayanagi et al. model[12] at different crystallite contents show that the yield appears instantaneously, and therefore, we estimate ϕ_0 to be equal to zero. Table 1 summarizes the values of k, f, and ϕ_0 for the two materials.

If classical notions of the rheology of filled systems allow one to correctly describe the observed behavior

Table 1. Values of the Parameters k, f, and ϕ_0 (Eq 11) for Both SL and CL Samples

sample	k [Pa]	f	ϕ_0
SL	5.10 10^6	3	0.4
CL	2.54 10^7	3	0

in the case of relatively dilute suspensions, the yield notion appears to be necessary for highly concentrated suspensions (the case of sample SL for $\phi \geq 0.4$) or for systems which behave as colloids (the case of sample CL). Unfortunately, this notion still remains empirical, and the use of an equilibrium modulus remains unsatisfactory from the physical point of view. Postulating the existence of an interparticular network at the origin of this effect might be better explained by the introduction of the concept of physical gels. This could allow to complete the understanding of the existing relations between the transformed fraction and the observed behavior.

Determination of the Gel Point from Dynamic Rheological Measurements

In physical gels such as those induced by partial crystallization, the network is built by thermoreversible processes. From a rheological point of view, the polymer is said to be at the gel point if its steady shear viscosity is at the infinity and its equilibrium modulus is zero. Therefore, the first method to localize the gel point would be the determination of the steady shear viscosity. According to Winter,[14] although it is simple, this method presents several disagreements: first, the gel point is determined by extrapolation because the network structure might be destroyed by shear leading to a delay in the gelation; second, the divergence of the viscosity to the infinity might also be related to other phenomena like the glassy transition or phase separation. Furthermore, measuring the equilibrium modulus, at the gel point, is a difficult task since its value may remain under the detection limit for a considerable time. To overcome these disagreements, the dynamic measurements are frequently proposed and used to localize the gel point and to give a more precise definition of the latter. Indeed, it has been shown that, at the gel point, the relaxation modulus follows a power law relationship. Thus, different authors[5,15,16] show that, at the gel point and in the linear viscoelastic domain, $G'(\omega)$ and $G''(\omega)$ follow a power law dependence on the frequency with the same exponents and, consequently, the phase angle δ is frequency independent, which leads to the following rheological definition of the gel point:

$$G'(\omega) \propto G''(\omega) \propto \omega^n \tag{12}$$

$$\tan \delta = \tan\left(n\frac{\pi}{2}\right) = C^{\text{ste}} \tag{13}$$

However, in the case of sample SL and sample CL, the definition of eqs 12 and 13 fails. The examination of the curves of the loss angle for both materials do not show any crossing points.

These disappointing results concerning the determination of the gel point can be explained by the high elasticity of the viscoelastic melt in the frequency and the crystallization temperature window used in the study. Indeed, under these conditions, the storage modulus remain always greater than the loss modulus. Therefore, any crossing point of the moduli can hardly be observed.

The Percolation Model and Gelation

Though the above relations fail, the study of the zero shear rate viscosity η_0 before the gel point ($\eta_0 = \lim_{\omega\to 0} G''/\omega$) and of the shear modulus after the gel point ($G_e = \lim_{\omega\to 0} G'$) remains interesting. Indeed, the percolation and the gelation theories provide relations for the two parameters[17] (eqs 14 and 15). The exponent k is associated with the viscosity and the exponent f to the shear relaxation modulus.

$$\eta \propto (p_c - p)^{-k} \qquad \text{for } p \leq p_c \tag{14}$$

$$G \propto (p - p_c)^{f} \qquad \text{for } p \geq p_c \tag{15}$$

If applied to chemical gelation, p is the extent of the reaction and p_c the critical extent of the reaction or the percolation threshold. In the present work, the extent of the reaction will be represented by the filler content $\phi(t)$, which changes during the crystallization. Sahimi[17] has given a summary of experimental data of k and f. Experimental values of f with chemical gels often lay between 1.9 and 2.2. However, Adam et al.[18] found exponent f as high as 3.2 ± 0.6 for polycondensation. On the other hand, measurements with physical gels gave a value of 3.8. The experimental data of k may also be divided into two sets. The first set of measurements indicates that the value of k varies between 0.6 and 0.9 whereas the second sets gives values between 1.3 and 1.5. According to Arabi et al.,[19] the existence of two sets of values for k might be related to the dynamics of the systems. With hard hydrodynamic interactions, the dynamic of the system corresponds to the Zimm approximation, and in the other case, the system follows the Rouse dynamic characterized by the absence of hydrodynamic interactions. De Gennes[20] also focused on the dynamics of a system of hard spheres dispersed in a viscous fluid under shear and showed that when the volume fraction ϕ of spheres increases, the spheres progressively become associated in clusters and postulated that the onset of an infinite cluster is related to some critical value ϕ_0. Campbell et al.,[21] working on the viscosity of concentrated suspensions of monodisperse hard spheres in a solvent, proposed that, at a critical filler content ϕ_0, an infinite percolating cluster is formed but, above the percolation threshold, this cluster can be rearranged allowing the flow. Only at ϕ_M, the infinite cluster hinders the mobility of the particles. For intermediate values, $\phi \leq \phi_0 \leq \phi_M$, the particles can move, but this motion becomes more and more restricted as ϕ tend to ϕ_M. The determination of the value of the critical filler content ϕ_0 or the percolation threshold has been done by simulation by Pike et al.[22] by studying the conductivity of systems with different geometry. For a three-dimensional network and a random dispersion of spheres, the percolation gave a critical content ϕ_0 of 0.306 for a uniform spheres size and 0.303 for spheres with variable sizes. According to these studies, we assume that, for sample SL, $\phi = 0.4$ is related to the yield appearance and represents the percolation threshold in the same order of magnitude as what was mentioned previously. Thus, according to the percolation theory, the yield effect might be associated with an interparticular network formation where the mobility of the solid entities is difficult but still possible. Furthermore, this is also confirmed by the proposed expressions for the variation of the zero shear rate viscosity η_0 with the spherulites content,

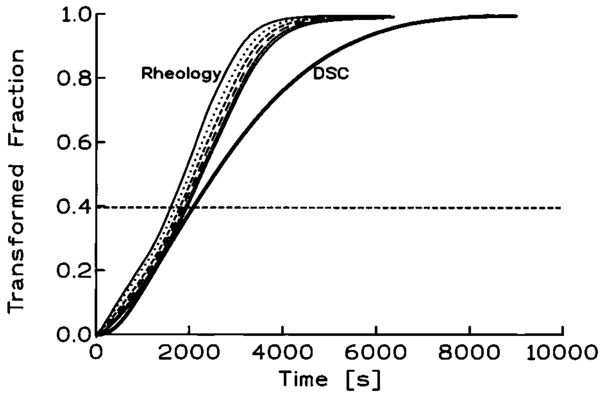

Figure 9. Comparison between the transformed fraction of sample SL determined from rheological measurements (relation 17) and that determined from calorimetric measurements.

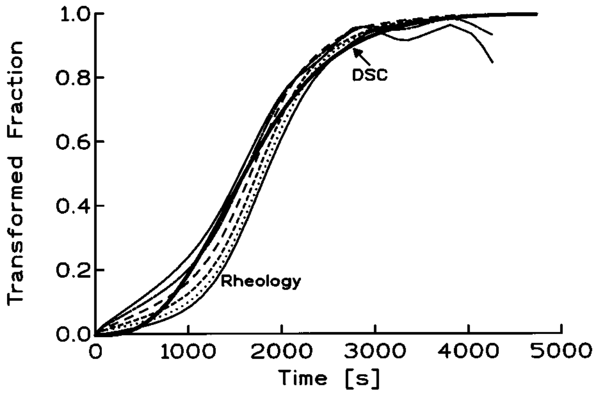

Figure 10. Comparison between the transformed fraction of sample CL determined from rheological measurements (relation 20) and that determined from calorimetric measurements.

where an exponent of 1.5 is found. This value is in accordance with those proposed by the percolation theory below the threshold for systems characterized by the absence of hydrodynamic interactions (Rouse limit). On the other hand, for the sample CL, whose behavior is that of a colloid, the yield effect appears instantaneously and the interparticular network is formed at the earliest stage of the process. The percolation threshold is therefore nearly equal to zero. It is interesting to notice that for both materials, the evolution of the equilibrium modulus is described by the same type of expression with an exponent equal to 3. This value is close to the value proposed for physical gels (3.8) and confirms the universality of this exponent for this type of gels.

Determination of the Transformed Fraction from the Proposed Models

All the previous observations and proposed models for the variation of the dynamic quantities with the filler content lead us to propose some guidelines for the determination of the transformed fraction from the rheological measurements. The situation is obviously different for the two materials. In the case of sample SL, the rheological behavior generated by the appearance of the spherulites in the liquid melt is a typical physical behavior of suspensions at low transformed fractions. Taking into account that $\alpha(t)$ is equal to $\phi(t)$, and assuming that the storage modulus is nearly the plateau modulus at high frequency, eq 8 leads to

$$G'(\phi) \approx G_0(\phi) \tag{16}$$

Thus

$$\alpha(t) \approx 1 - \frac{G'(0)}{G'(\phi)} \qquad \text{for } \alpha(t) \leq 0.4 \tag{17}$$

This relation is effectively verified for $\alpha(t) \leq 0.4$. Figure 9 presents the transformed fraction from DSC data and from rheological measurements at different frequencies, using eq 17. The correspondence between the rheological measurements and the DSC data is only correct within the calculation assumptions for $\alpha(t) \leq 0.4$ and at high frequency. When the frequency decreases, because the behavior of the suspension is viscoelastic, a more complex expression must be considered for better accuracy (Cole and Cole model for example), though the curves at different frequencies remain representative of the transformed fraction $\alpha(t)$. Above $\alpha(t) = 0.4$, the behavior is no more that of a simple suspension since a mechanism of percolating physical gel is taking part (yield effect) which is superimposed to the viscoelastic behavior of the suspension. Then, the observed variation for $G'(\phi)$ is more complex, and a simple and satisfactory expression to describe this behavior has not been found yet.

In the case of sample CL, the rheological behavior is mainly governed by the immediate existence of the yield. Using expressions 3 and 11, it can be written that, in the low-frequency range, the storage modulus is that of the yield added to that of the matrix:

$$G'(\phi) \approx G_e(\phi) + G'(0) \tag{18}$$

On the opposite at $\phi = 0.84$, the crystallization is finished ($\alpha(t) = 1$) and the modulus has reached its maximum value; therefore

$$G'(0.84) \approx G'_\infty \tag{19}$$

Thus

$$\alpha(t) = \left(\frac{G'(\phi) - G'(0)}{G'_\infty}\right)^{1/3} \tag{20}$$

Figure 10 gives an example of the validity of this expression. The correspondence between the DSC data and the rheological measurements at different frequencies is satisfactory at low frequency, whereas a viscosity effect is observed when the frequency increases. This shows that the establishing of relations between the transformed fraction and the rheological behavior during crystallization is not an easy task. The type of relations generally depends on the morphology which is developed during the crystallization even in the case of spherulites. The observed rheological behavior mainly depends on the size of the crystalline entities, in accordance with existing theories for filled systems. For spherulites with high sizes (case of sample SL) and a moderate transformed fraction, the absence of interspherulitic interactions leads to a typical suspension behavior. For low spherulites sizes or a higher transformed fraction, gel mechanisms associated with percolating mechanisms hardly influence the behavior and dominate so that the behavior is that of colloids.

Conclusion

The morphological study of two samples of polyolefins has shown that they crystallize into a spherulitic structure but with very different morphologies. This feature was interesting since, during crystallization from the melt, these two materials display two extreme behaviors for the rheological behavior of filled systems. One system behaves as a suspension of solid spherical particles in a liquid matrix while the other appears like a colloid of small spherical particles in a liquid matrix. By analogy to filled systems, the notion of volume fraction of filler $\phi(t)$ was assigned to spherulites or to crystallites. The comparison between the calorimetric results and the morphological studies leads us to postulate that, for the SL sample, the transformed fraction $\alpha(t)$ is a direct indication of the volume fraction of spherulites. However, for the CL sample, $\alpha(t)$ is related to the volume fraction of crystallites using the maximum crystallinity. The use of the percolation theory associated with gelation in the case of the suspension-like system and the colloidlike system show that the yield effect might be related to an interparticular network formation, inducing a percolation threshold. Furthermore, these theories together with experiments confirm some typical exponents for the variation of the rheological quantities with the volume fraction of spherulites for the suspension like material. Indeed, the value of the exponent k for the variation of the zero shear rate viscosity agrees well with the value that is proposed for systems in the absence of hydrodynamic interactions. On the other hand, for both materials, the variation of the equilibrium modulus shows an exponent equal to 3, pointing out its universality. For both materials, predictive expressions of the transformed fraction from the rheological measurements have been established within the calculations assumptions. However, because of various physical mechanisms, the differences in the relations between the transformed fraction and the moduli indicate that a unique expression relating these quantities can hardly be obtained. In any case, the viscoelastic study could not be well understood either quantitatively or qualitatively within the economy of a deep knowledge of the morphology.

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