

## Investigating the morphology/rheology interrelationships in immiscible polymer blends

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### Abstract

Morphological changes in immiscible polymer blends have been studied in shear flow using an original method based on quenching following deformation of molten samples. Relaxation effects were expected to be negligible during cooling and, hence, the real shear-induced blend microstructure could be analyzed. The method has been successfully applied to follow morphological changes of immiscible blends composed of polystyrene and relatively high amounts of high-density polyethylene during creep experiments. The final steady-state morphology appeared to be intimately related to the applied shear stress and total deformation. Coalescence as well as large deformation and orientation of the dispersed phase particles have been observed depending on the flow conditions. The variations with time of the blend rheological properties and morphological observations are in qualitative agreement.

### 1. Introduction

Blending polymers provides a very attractive technique to generate new materials. First, it represents an economic alternative to synthesizing new polymers and, moreover, a large range of properties can be obtained by an adequate choice of the initial components. Polymer blends can be miscible or not, depending on the specific interactions existing between the polymer chains. Generally, however, polymers are immiscible leading to multiphase blends. These systems combine characteristics of both constituent polymers in a manner that is intimately related to the morphology of the blend, i.e., the shape and the size of the dispersed phase particles. This microstructure develops during the melt processing in a very complex way. Phenomena like deformation, break-up or/ and coalescence of the dispersed phase particles can indeed occur when a multiphase system is submitted to an external solicitation. These processes have been extensively studied during the last decades [Taylor (1934), Cox (1969), Gauthier *et al.* (1971), Flumerfelt (1972), Grace (1982), Elmendorp and Maalcke (1985)]. The influence of viscosity ratio, phase viscoelasticity, normal stresses, interfacial tension, blend composition, and flow type have been largely discussed and useful relationships have been proposed as described in recent reviews by Favis (1991) and Utracki and Shi (1992). However, the influence of all these variables is far from being understood and controlling the microstructure of immiscible polymer blends remains a difficult task.

Morphology development in classical processing equipment such as internal mixers or extruders has received particular attention [Favis and Chalifoux (1987), Favis and Therrien (1991), Scott and Macosko (1991), and Sundararaj *et al.* (1995)]. However, due to the lack of control of the flow conditions and the inability to make a direct observation of the blending process, only qualitative relations between morphology and processing conditions have up to now been proposed. Moreover, several aspects of the dispersion process and the coalescence phenomena remain to be elucidated. In recent years, rheometry has proved to be a very powerful method to analyze morphological changes of multiphase polymer systems during processing [Carreau *et al.* (1994), Vinckier *et al.* (1996, 1997), and Lacroix *et al.* (1998, 1999)]. In most studies, blends have been deformed at constant shear rate until a new stationary microstructure was reached and the resulting morphological changes have been correlated with the rheological properties of the blend components and the flow conditions. Different techniques have been developed to follow the morphology evolution. Direct observations via optical microscopy have been used with success [Levitt *et al.* (1996), Chin and Han (1980), Tsakalos *et al.* (1998), and Mighri *et al.* (1998a)]. However, such observations are not possible for most commercial blends since, at high concentrations of the dispersed phase, multiphase systems are not transparent.

Multidrop systems can be investigated by light scattering methods as proposed by Lyngaae-Jorgensen and Utracki (1991). However, such a technique is limited to very low concentrations of the dispersed phase (typically about 1%). Works have therefore generally focused on isolated drops and have been restricted to the study of deformation and breakup phenomena. Particle-particle interactions and coalescence have not then been considered. In an attempt to analyze concentrated systems and account for possible competition between coalescence and breakup, some authors have proposed using indirect techniques [Grizzutti and Bifulco (1997) and Lacroix *et al.* (1998, 1999)]. In such cases, evolution of the blend morphology was not studied *in situ* in real time. Generally, the flow was stopped when a steady-state microstructure was reached (corresponding to steady-state rheological properties) and the samples were then allowed to relax. Then, the blends were analyzed via optical devices [Grizzutti and Bifulco (1997)] or cooled down rapidly to freeze the microstructure and examined by electron microscopy [Lacroix *et al.* (1998, 1999)]. This method worked quite well and important information about the variation of the size of the dispersed phase particles with the deformation could be obtained. Unfortunately, the real morphology of the blend generated by the applied flow was not accessible. Due to the interfacial tension, the deformed particles should indeed recover their equilibrium shape during the relaxation process and breakup of highly deformed particles could also occur for the same reason. In this work, a new method for determining the shear-induced morphology of concentrated polymer blends is presented. The morphology of the sample is frozen at constant stress within the parallel plates of a rheometer. It is a promising technique that should help us understand the morphology/rheology/processing interrelationship in multiphase systems.

Table 1. Characteristics of the homopolymers

	PS	HDPE
Supplier	Dow Chemical	Dow Chemical
$M_w$ (g/mol)	215 000	79 000
$M_n$ (g/mol)	100 000	24 000
Density (200 °C)	0.974	0.754
Zero-shear viscosity		
Pa s at 200 °C	5422 <sup>a</sup>	1886 <sup>a</sup>

<sup>a</sup>Calculated using the four-parameter Cateau-Yasuda model

## II. Experiment

Blends of commercial polystyrene and high-density polyethylene were used in this study. The two polymers were manufactured by Dow Chemical Co Canada: a polystyrene (PS), and a high density polyethylene. The main characteristics of these polymers are reported in Table 1. A small amount (0.25 wt %) of Irganox B225 (antioxidant from Ciba-Geigy) was added to avoid thermal degradation of the components during blending and subsequent experiments.

### A. Blend preparation

Blends containing 80 wt % PS and 20 wt % high-density polyethylene (HDPE) were prepared using a corotating leistriz twin-screw extruder (screw length of 960 and 34 mm in diameter). The screw geometry used by Bourry and Favis (1998) was chosen for optimum mixing, equipped with a capillary die 3 mm in diameter, 13 mm in length, with a 40° angular entry. The same blending procedure was followed for all the blends. Appropriate amounts of PS and HDPE were first dry mixed with 0.25 wt % of Irganox B225 before feeding into the hopper. Irganox B225 from Ciba-Geigy was found to be very efficient in stabilizing both polymer components. All these components were next blended at a temperature of 200 °C and a constant volumetric feed rate of 140 mL/min. The screw speed was maintained at 100 rpm. The extrudate was rapidly quenched with cold water, pelletized, and dried. The homopolymers were also extruded under the same conditions to ensure that all materials had the same thermal history.

Pellets of both homopolymers and blends were then molded by compression at 200 °C for 14 min in small 25 mm diam disks for rheological experiments. Preliminary tests showed that bubbles or liquid droplets were formed in the polystyrene sample when heating at high temperature. In order to avoid this, a four-step molding was developed. The pellets were first melted for 8 min at 200 °C. During this stage, the press load was progressively increased to 1 ton. The blend was then subjected to a pressure

of 3 tons for 2 min, and then the load was released. This latter procedure was repeated three times. Following molding, the samples for rheological measurements were dried at 90 °C under vacuum for at least 12 h before each test.

### B. Rheological measurements

Experiments were carried out using a Bohlin CSM controlled stress (melt) rheometer equipped with 25 mm parallel plates. A parallel-plate geometry is not expected to be a judicious choice in comparison with a cone-plate geometry since the shear rate is not constant across the sample; it increases from zero in the center to a maximum value at the edge of the disk. However, we will see later that this problem can be turned into an advantage. Moreover, parallel plates present clear advantages. First, the gap setting is not so crucial as that for cone and plate. Second, the gap is relatively large compared to the size of dispersed phase domains, reducing wall interactions and possible morphology modification during sample loading.

All tests were performed in a temperature range of 180-230 °C under nitrogen atmosphere. The gap was set at approximately 1.5 mm. Different tests were carried out. First, the linear viscoelastic properties of the polymers and the blend were measured as a function of the frequency. Depending on frequency and temperature, care was taken to keep the experiment within the linear viscoelastic domain, and the strain response was maintained below 0.05. Annealing tests were performed by holding samples at 200 °C between the plates of the rheometer in the absence of applied shear stress. Finally, the materials were subjected to creep experiments at three different constant stresses: 25, 100, and 200 Pa. Then the samples were cooled down rapidly by blowing air on the sample kept within the parallel plates under constant stress, to freeze the morphology of the blend. It is the application of the constant stress while cooling rapidly that maintains the *in situ* generated morphology. All tests in the linear as well as in the nonlinear viscoelastic domain have been repeated several times using different batches of the blend. The data were reproducible within approximately 5%.

### C. Morphology analysis

The microstructure of the different samples was examined using a JEOL JSM-840 scanning electron microscope. After cooling down under constant stress within the rheometer, the samples were removed and fractured in liquid nitrogen. In order to follow the morphological changes with time, each sample was examined in the direction of the flow, i.e., in a plane perpendicular to the radial direction. As the shear rate linearly increases from the center to the edge of the sample, the morphology of the blend is expected to differ with the radial position of the fracture. Moreover, end effects, secondary flows, and resulting migration may generate a microstructure that is not representative of the real blend behavior expected from the effect of the applied shear flow. This will especially be the case near sample edges or near the plate center, where streamlines present a high curvature. In order to avoid such effects, all samples were fractured at 3/4 of the disk radius. Electron microscopy analysis has been performed in the central region of the fractured surface. This protocol allows us to neglect possible errors in morphological measurements due to end effects or shear rate variations with radial position. The shear rate for the rheological properties, presented below, has also been determined at this radial distance. After fracture in liquid nitrogen, the different blend samples were then coated with a gold palladium alloy prior to examination to avoid charging. The different morphologies were quantified by image analysis using a semiautomatic technique developed in-house. Both volume and number average diameters ( $d_v$  and  $d_n$ , respectively) of the dispersed phase were determined using sigma scan software connected to a digitalization table. For elongated dispersed phase particles  $d_v$  and  $d_n$  refer to the volume and number average diameter, respectively, of an equivalent volume sphere. In this latter case, the length and the width of the deformed HDPE particles were also measured in the same way. For each blend; several micrographs were used to analyze an average of 400 particles.

## III. Results and discussion

### A. Morphological stability

The rheological as well as other physical properties of polymer blends are closely related to the state of dispersion and the distribution of the droplets of the minor phase. The main objective of this work is to study changes in morphology and in rheological properties of a (80/20) PS/HDPE blend under shear. It is, therefore, of prime importance to determine the initial microstructure of the blend and to verify its stability as a function of time. Indeed, several authors mentioned that the morphology can change

drastically during a, sufficiently long residence time at high temperature, even in the absence of flow. Lacroix *et al.* (1996) have shown that the size of the dispersed particles in polyethylene terephthalate glycol/polyester-ethylene vinylacetate (PETG/EVA) blends increased rapidly under static conditions and reached equilibrium after approximately 5 min of annealing. The effect was more pronounced with increasing temperature. The authors mentioned that there exists a critical annealing time depending on temperature and blend composition, beyond which no change of structure occurred. Important effects of annealing on morphology were also reported by Mekhilef *et al.* (1997) for PS/HDPE blends. In order to verify the morphological stability of the blend in the absence of flow, various samples were submitted to annealing at 200 °C. Different PS/HDPE (80/20) blends were held between the parallel plates of the rheometer for up to 2 h. After annealing, the different samples were removed from the rheometer and analyzed by scanning electron microscopy (SEM). Within experimental error, no significant changes in  $d_v$  and  $d_n$  with time was observed even for long annealing time, indicating that the morphology of the 80/20 PS/HDPE blend was stable with time. This result is crucial with respect to creep experiments. It ensures us that the observed changes in the blend micro-structure will be induced only by shear. Before starting any rheological experiment, each sample was kept at 200 °C for at 10 min. Then, the number and the volume average diameters of the particles of HDPE were determined to be 4.26 and 7.82 µm, respectively. The initial blend morphology will be shown in Sec. III B.

### B. Rheological characterization of the blend components.

Although commercial polymers often contain stabilizers, thermal degradation of the blend components can take place during long rheological experiments, even under a nitrogen atmosphere. Hence, it is of prime importance to check the thermal stability of the blend and its components before any experiment. For this purpose, time sweep tests were carried out for the individual components and the blend at a frequency of 0.01 Hz and temperature of 200 °C. Figure 1 shows the complex viscosity of the PS, HDPE, and (80/20) PS/HDPE blend as a function of time. The "as received" components were clearly unstable after a few minutes at 200 °C under nitrogen atmosphere. The HDPE shows an important increase in viscosity due to probable partial cross linking while a large viscosity decrease was observed for the PS. The blend as well as the components, containing 0.25 wt % additional stabilizer, seemed to be stable for at least 3 h 30 min. The same observations can also be made for the variation of the storage modulus with time. These results show the necessity of adding more stabilizer in order to obtain reproducible and significant rheological properties. However, it is worth noting that the addition of stabilizer B225 modifies the rheological properties of the blend components. The PS viscosity is indeed increased by 10% while a 40% viscosity decrease is observed for the HDPE. These significant effects were probably due to prior degradation in the twin-screw extruder for the nonstabilized samples. The storage modulus and the complex viscosity ( $G'$  and  $\eta^*$ , respectively) of the PS and the high density polyethylene versus frequency are shown in Fig 2. The rheological properties were measured at three different temperatures: 180, 200, and 230 °C and the time-temperature principle was used to generate the master curves of the figure, using 200°C as the reference temperature. The values of the shift factor for the three temperatures are reported in Table II for the two polymers. Both the storage modulus and complex viscosity of the components exhibit a classical viscoelastic behavior. At low frequencies, a terminal zone, where  $G'$  is proportional to  $\omega^2$  is observed (slope of 2 in a log-log plot as shown in Fig 2). In the same range,  $\eta^*$  exhibits a typically Newtonian plateau. It should be noted that, in the case of the HDPE, the terminal zone is not reached at the lowest frequency. The PS is more viscous and more elastic than the HDPE, except at very high frequencies where the opposite behavior is observed. The viscosity curves were fitted with the four-parameter Carreau-Yasuda model to obtain the zero shear viscosity values reported in Table I. The zero shear viscosity ratio between the dispersed phase and the matrix was found to be 0.35 at 200°C.

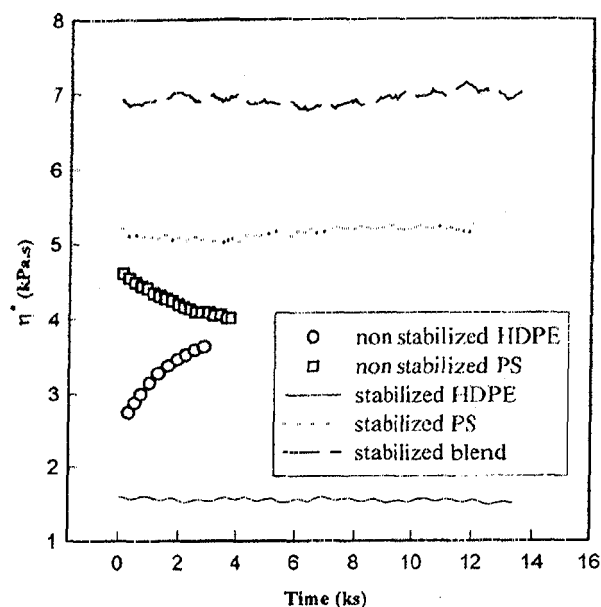


FIG. 1. Variations of the complex viscosity with time for the (80/20) PS/HDPE blend and the homopolymers and 200 °C and 0.0628 rad/s.

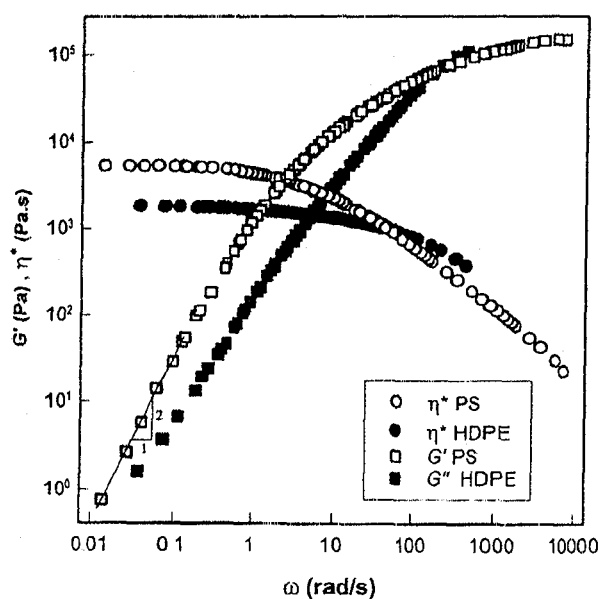


FIG. 2. Complex viscosity  $\eta^*$  and storage modulus  $G'$  vs frequency of unblended PS and HDPE at 200 °C

TABLE II. Thermal shift factor for PS and HDPE with respect to the 200 °C reference temperature

$T$ (°C)/log <sub>10</sub>	PS	HDPE
180	4.45	0.25
200	0	0
230	-0.66	-0.22

### C. Efficiency of the cooling process

As previously mentioned, direct and indirect methods have been developed to study how the morphology of polymer blends changes in a shear flow. Indirect techniques are the simplest ones but, as previously described, do not allow monitoring the deformation process in real time. It is generally the morphology after relaxation that is observed and this may be different from that really induced by the flow field. Many phenomena can occur during the relaxation process that can potentially modify the

morphology induced by the applied flow. The new technique presented here eliminates this disadvantage, even though it is an indirect method. The main innovation is that the applied shear stress to the blend remained constant during the cooling process without interruption. The sample was placed between the parallel plates and a creep test was carried out at 200 °C. After a predefined time of shearing, the heating element was switched off and the sample was then rapidly cooled under constant stress by blowing cold dry air on the plates and on the sample. When the temperature was low enough (around 60 °C attained within less than 2 min), the applied stress was stopped. The sample was then recovered and analyzed by SEM following the method previously described. Figure 3 shows the microstructure of the 80/20 PS/HDPE blend before and after creep experiments carried out at applied stresses of 25 and 200 Pa. The initial spherical particles [Fig 3(a)] of the HDPE are deformed into ellipsoids and fibers, which are oriented in the flow direction [Figs. 3(b)-3(e)]. The quenching method appears then to be efficient and we assume that the morphology shown is that of the samples prior to cooling.

The deformation of isolated droplets in flow is controlled by the well known capillary number defined by

$$Ca = \frac{\eta_m \dot{\gamma} d_p}{2\alpha} \quad (1)$$

where  $\eta_m$  is the matrix viscosity,  $\dot{\gamma}$  is the shear rate,  $d_p$  is the droplet diameter, and  $\alpha$  is the interfacial tension. The capillary number expresses the ratio between the viscous force, which attempts to break the drop and the interfacial force, which seeks to keep it spherical.

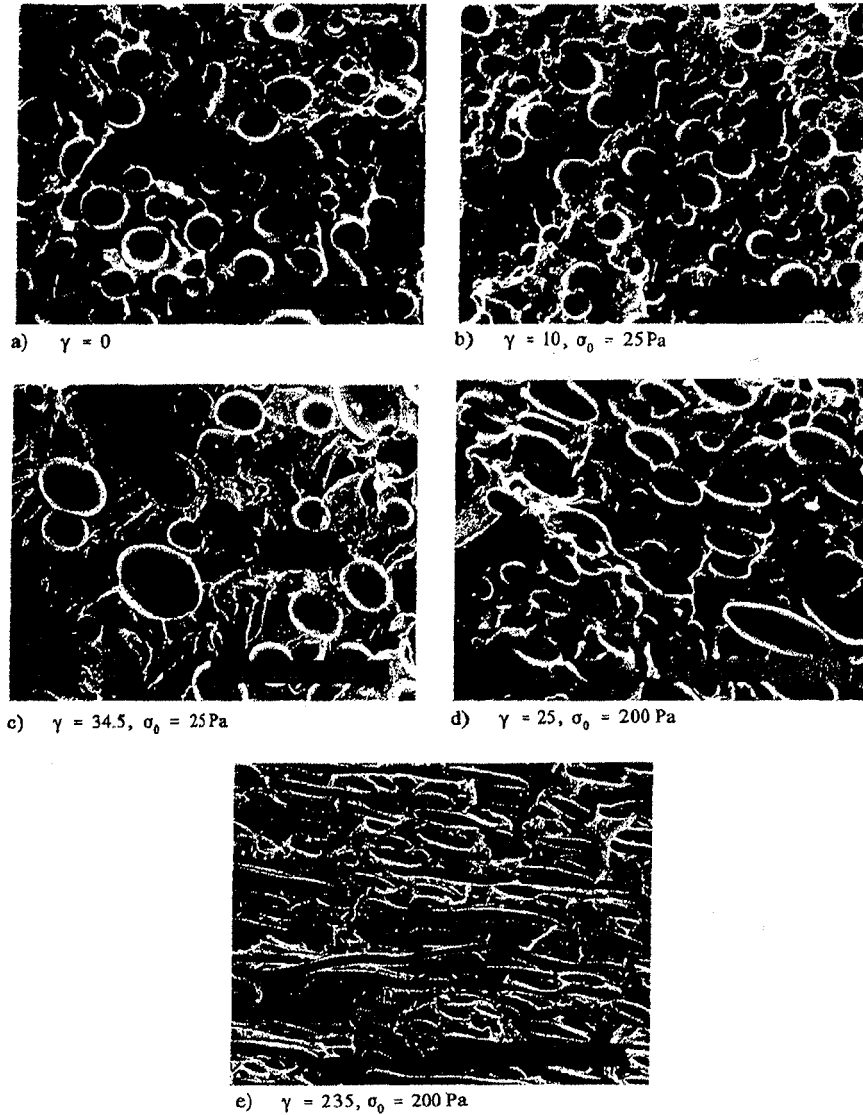


FIG. 3. Evolution of the morphology of the 80/20 PS/HDPE blend vs strain during creep at 200 °C: (a) initial morphology  $\gamma = 0$ ; (b) creep at 25 Pa,  $\gamma = 10$ ; (c) creep at 25 Pa,  $\gamma = 34.5$ ; (d) creep at 200 Pa,

$\gamma = 25$ ; (e) creep at 200 Pa,  $\gamma = 235$

One can define a critical Capillary number  $Ca_C$ , which marks the separation between two extreme conditions. For small values of  $Ca$ , i.e.,  $Ca < Ca_C$ , the two forces balance each other and droplets attain an equilibrium shape, which may be spherical or not [see for example Mighri *et al.* (1998a)] For  $Ca \gg Ca_C$ , the interfacial force can no longer compensate for viscous effects and the droplets deform initially in filaments which soon break up into smaller domains. For Newtonian phases, several studies [see for examples Taylor (1934) and Grace (1982)] have shown that in steady shear flow  $Ca$  is a strong function of the viscosity ratio,  $p = \eta_d / \eta_m$  in (where  $\eta_d$  is the viscosity of the drop).

TABLE III. Effect of the cooling rate on the recovered morphology for PS/HDPE (80/20) blend

Cooling rate (°C/s)	$d_v$ (μm)	$B$ (μm)
1.51	13.25	8.77
1.34	14.67	9.91
1.24	14.67	10.07
0.78	15.61	9.39

When cooling under a constant stress, the capillary number  $Ca$  remains constant or possibly decreases due to the expected increase of the interfacial tension with temperature decrease. The viscosity of the blend components increases rapidly, possibly affecting both  $Ca$  and the critical capillary number,  $Ca_C$ . However, breakup of filaments and coalescence of deformed droplets should be rapidly inhibited due to the high viscosity of both polymer components. In contrast, disturbing effects due to the HDPE crystallization or to the thermal expansion of the two polymers cannot be dismissed out of hand. All the phenomena discussed above are temperature and time dependent and their extent is intimately related to the cooling rate. To verify the efficiency of the proposed quenching method different samples were subjected to a creep experiment at an imposed shear stress of 200 Pa for 20 min. As suggested in Fig. 3(d), these conditions are sufficient to deform the particles of HDPE from their initial spherical shape to ellipsoids. Four different cooling rates ranging between 0.8 and 1.5 °C/s were investigated and the results for the volume average diameter  $d_v$  and the minor axis  $B$  of the ellipsoids of the HDPE component are presented in Table III. No significant variations in the size  $d_u$  and the shape  $B$  of the dispersed phase were observed in the range of cooling rates considered. Hence, break up or shape recovery are believed to play no significant role during cooling. Also the possible disturbing effects due to HDPE crystallization and thermal expansion can be excluded for the same reasons. In conclusion, it appears clearly that, in the range of cooling rates investigated, the structure obtained from SEM is quite representative of the shear-induced structure at high temperature.

#### D. Creep experiments

Applied constant shear stresses of 25, 100, and 200 Pa were chosen. The samples were sheared for increasing time periods. The evolution of the blend morphology during creep experiments at 25 and 200 Pa is shown in Fig. 3 and is also compared to the initial microstructure (note the differences in magnification between the different micrographs). The volume average diameter  $d_v$  of the HDPE particles versus the total strain (time multiplied by shear rate) for the three applied stresses is presented in Fig. 4. Two different types of behavior are observed. For low stresses (25 Pa), the particles of HDPE remained approximately spherical even at high deformations [note that small particle deformations were observed at relatively large strain,  $\gamma = 34.5$ , as illustrated in Fig. 3(c)]. Important coalescence was detected, however, and the volume average diameter of the minor phase increased from 7.82 μm for  $\gamma = 0$  to 51.7 μm for  $\gamma = 34.5$ , which corresponded to more than 3 h of creep. For higher applied stresses (100 Pa and especially 200 Pa), the initial matrix-droplet morphology was subjected to important changes. The initial spherical HDPE particles were first transformed into ellipsoids somewhat oriented in the flow direction.

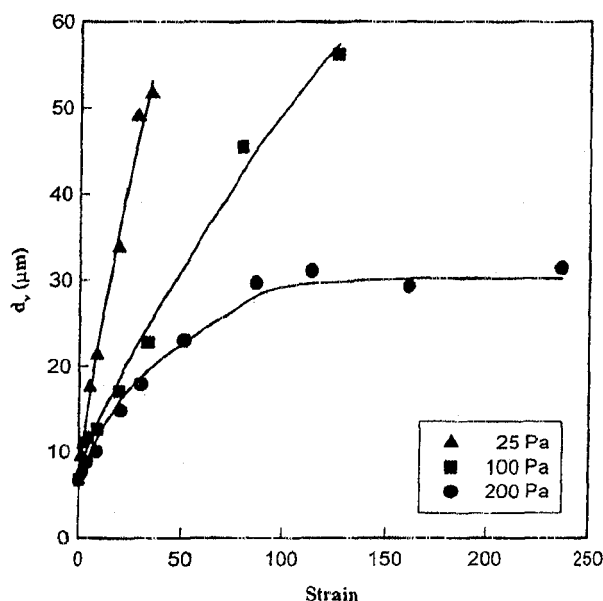


FIG. 4. Volume average equivalent diameter of the minor phase vs strain during creep experiments at different applied shear stresses and 200 °C.

Then, as the deformation of the whole sample increased, the HDPE ellipsoids were more and more stretched and oriented in the flow direction. Finally, a fibrillar structure was obtained at high deformations. These shape variations were expected since the PS was more viscous than the HDPE. Less pronounced morphological changes would have been observed for blends based on the HDPE matrix. SEM observations along the radial direction, i.e., in a plane perpendicular to the flow, revealed that the elongated HDPE particles observed in Fig. 3(e) had a circular cross section. We could not detect any flattening due to normal stresses as observed by Levitt *et al* (1996).

The observation of the fibrillar morphology [Fig. 3(e)] was possible due to the quenching method efficiency. It was verified that the fibrillar structure disappeared if the flow was stopped and the blend allowed to relax before quenching. A matrix-droplet (emulsion) structure was then obtained. The appearance of such a fibrillar structure could be related to the blend composition, which is very close to the phase inversion composition, estimated to be about 30 wt% HDPE for such blends [Bourry and Favis (1998)]. For highly concentrated polymer emulsions, containing between 30 and 50 wt % of the dispersed phase, Elemans *et al* (1997) have demonstrated that disintegration of highly elongated threads was delayed for a certain period of time due to the presence of neighboring threads. The disintegration process can be very long depending on the blend composition and the flow conditions. We assumed that the breakup time for our samples was very long at these very low shear rates and for the blend composition used (for creep at 200 Pa, the maximum shear rate was equal to  $0.0262 \text{ s}^{-1}$ ). It is worth noting that the flow conditions used here were relatively mild compared with those encountered in teal processing. Under more severe conditions, breakup of the dispersed phase is expected to occur to a larger extent.

Figure 4 shows that the volume average diameter of the minor phase versus deformation is closely related to the applied shear stress. In the case of ellipsoids, the volume average diameter represents the diameter of a sphere of equal volume and, therefore, it does not take into account the orientation of the dispersed phase.

TABLE IV. Values of  $Ca$  for each creep test and  $Ca_c$ .

Creep at 25 Pa	Creep at 100 Pa	Creep at 200 Pa	$Ca_c$
0.07	0.36	0.46	0.65

However, it is a very useful parameter since it quantifies the degree of coalescence. We see clearly from the figure that coalescence played a major role in the range of shear stresses investigated and that the size of the domains was closely related to the applied stress. However, for the higher applied stress, the increases in  $d_v$  were much less pronounced. These results can be due to breakup of the HDPE particles with increasing shear rate. As previously mentioned, deformation or breakup of a single



droplet in shear flow is controlled by the capillary number,  $Ca$ . If the capillary number is smaller than the critical number,  $Ca_c$ , the hydrodynamic and interfacial forces balance each other, which results in deformed droplets.

For  $Ca \gg Ca_c$ , the interfacial force can no longer compensate for viscous effects and the droplets break up into smaller domains. As already explained,  $Ca_c$  is a strong function of the viscosity ratio  $p$ . It is minimum for  $p$  close to 1, which corresponds to the most favorable conditions for breakup. Gauthier *et al.* (1971), Flumerfelt (1972), and Mighri *et al.* (1998a) have studied the effect of the viscoelasticity and have shown that  $Ca_c$  increased with elasticity of the fluids. Mighri *et al.* have also reported that the time for breakup increases with elasticity. In this study, the values of  $Ca$  were calculated for each creep experiment and compared to the value of the critical capillary number. The maximum shear rates were obtained at the end of each creep experiment and were calculated to be  $2.44 \times 10^{-3}$ ,  $1.11 \times 10^{-2}$ , and  $2.62 \times 10^{-2} \text{ s}^{-1}$  for tests at 25, 100, and 200 Pa, respectively. For this range of shear rates, the PS and the HDPE can be assumed to be Newtonian fluids. Using the zero-shear values of Table I, the viscosity ratio  $p$  is equal to 0.35 and the interfacial tension was estimated using the breaking thread method as  $4.7 \text{ mN/m}$  [Mekhilef *et al.* (2000)]. From Grace (1982), a value of  $Ca_c$  equal to approximately 0.65 is obtained. This is larger than the value reported in Table IV for  $Ca$  calculated at the end of each creep test, when the shear rate is maximum (the most favorable conditions for breakup). Therefore, we can conclude that, in the range of the shear rates studied, the observed morphological changes presented in Figs. 3 and 4 are due to coalescence, and not to breakup. Coalescence during this type of flow study can occur in two ways: (a) collisions between neighboring HDPE droplets, due to differences in the relative velocity, and (b) head-to-tail interactions. The second type appears when the droplets are elongated by the shear flow and the interactions between HDPE particles depend on the deformation of the particles. It is logical to assume that at low shear stresses coalescence will be dominated by collisions between neighboring particles on different flow path lines. As the shear stress is increased, the width of the deformed droplets decreases and this type of collision is no longer possible. Coalescence can only occur by head-to-tail collisions between particles belonging to the same path lines (or at least very close to each other). The relative magnitude of the two steps depends on the applied shear stress. At 25 Pa, the HDPE particles are barely deformed and remain spherical so that the interactions between path lines are large. As the volume fraction of the dispersed phase is relatively high in our case, the interparticle distance is small and coalescence by collisions between neighboring droplets on different path lines is the major phenomenon. Under these conditions, well below  $Ca_c$ , the deformation of isolated particles is not large. However, with increasing shear stress (hence shear rate) the droplet deformation increases [see for example the results of Mighri *et al.* (1998a)] and at 200 Pa, the deformation becomes large enough to result in head-to-tail collisions explaining the fibrillar morphology described in Figs. 3(d) and 3(e). The differences between the domain sizes reported for 25 and 200 Pa in Fig. 4 suggest that coalescence resulting from head-to-tail collisions at low shear rate is significantly less frequent than coalescence between particles on different path lines.

Shear-induced coalescence was recently investigated by Vinckier *et al.* (1998), following the droplet-size evolution in PIB/PDMS blends during step-down experiments at constant shear rate. The final shear rate was chosen to be low enough to avoid any breakup. Coalescence in shear flow could be correlated with the applied strain, the step ratio, and the blend composition. More rapid coalescence was observed for highly concentrated blends and at low applied shear rates. This is in agreement with our results.

In this study, SEM observations (confirmed by image analysis) have shown that the minor axis  $B$  of the deformed particles was relatively constant during the experiments, approximately equal to  $10 \mu\text{m}$ . Monticciolo *et al.* (1998) reported similar observations for HDPE/PBT blends under elongational flow. This result is in agreement with our assumption of head-to-tail coalescence. It is indeed expected that, without coalescence, the width of the HDPE ellipsoids would decrease continuously. For a critical value of  $B$ , breakup of the deformed particles into small spherical droplets should then occur due to interfacial tension effects. Head-to-tail coalescence prevents subsequent decreases of  $B$ . Figure 4 also suggests that a steady-state structure is obtained at high deformations. The size and shape of the HDPE dispersed particles do not change after a critical shearing time (or a critical deformation). This period appears to be inversely proportional to the applied shear stress or shear rate. It is approximately equal to  $1 \text{ h}$  ( $\dot{\gamma} = 86$ ) at 200 Pa and more than  $3 \text{ h}$  ( $\dot{\gamma} = 28$ ) at 25 Pa. These data were obtained for capillary numbers significantly smaller than the critical value (see Table IV).

## E. Rheological considerations

In the last decade, several studies have focused on the development of relationships between morphology and rheology in polymer blends during flow [Takahashi and Noda (1995), Tsakalos *et al* (1998), Lacroix *et al* (1998, 1999), Vinckier *et al.* (1996, 1997), Minale *et al* (1997, 1998b, 1999)]. The relationships between morphology and rheology have also been examined here, but we did not attempt to solve the coupled governing equations for the morphology and the stress tensor. These equations, written in terms of the flow kinematics [see for example Lacroix *et al.* (1998 or 1999)] become quite difficult to solve for creep experiments.

The instantaneous blend viscosity during the creep experiments has been calculated and the results are presented in Fig 5. The viscosity tends, for high strain values, to a constant (steady-state) value, which decreases with the applied stress. These values at the larger strain values are 10 230, 9 020, and 7 640 Pa s at 25, 100, and 200 Pa, respectively, and the corresponding steady shear rates are  $2.44 \times 10^{-3}$ ,  $1.11 \times 10^{-2}$ , and  $2.62 \times 10^{-2} \text{ s}^{-1}$ , respectively. Steady-state conditions were not reached yet. Note that the viscosity values are considerably larger than the zero-shear viscosity of the more viscous matrix component (see Table I). More interesting is the shape of the three curves. At the lower stress, the viscosity increases continuously before reaching approximately a constant value larger than  $10^4 \text{ Pa s}$ . At 100 and 200 Pa, two steps are visible. First,  $\eta$  grows up rapidly, then decreases to eventually reach a plateau. For each applied stress, creep tests carried out on the individual homopolymers did not reveal any significant stress overshoots.

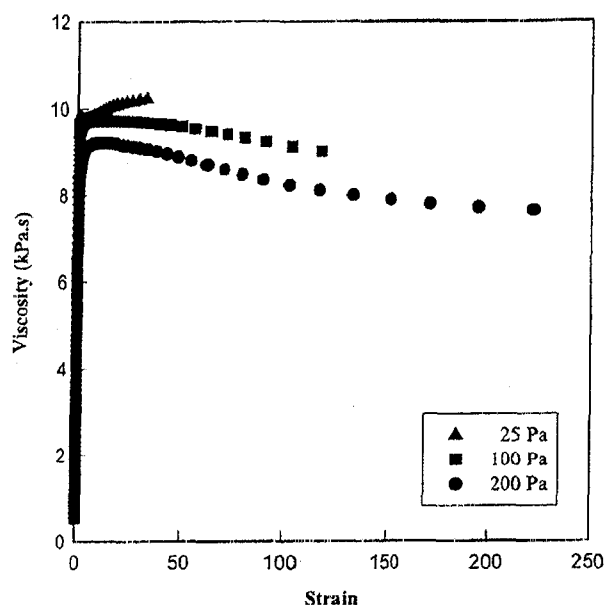


FIG. 5. Variation of the blend viscosity as a function of strain during creep at different applied shear stresses and 200 °C.

The observed overshoots for the experiments conducted at 100 and 200 Pa are therefore due to changes in the blend morphology and droplet deformation, as discussed by Lacroix *et al.* (1998, 1999), and not due to intrinsic properties of the components. Figure 5 reveals no overshoot for creep at 25 Pa. The shear rate is believed to be too small to favor important deformation and the large and increasing viscosity with strain or time is related to droplet deformation and increases in droplet size due to coalescence. It is worth mentioning that the maximum in the creep viscosity is very close to the zero-shear value obtained for the complex viscosity of the same blend ( $H^*$  was found to be equal to 10 800 Pa s at  $6.28 \times 10^{-3} \text{ s}^{-1}$  in the linear viscoelastic regime).

All the observations can be related to the coalescence process discussed in Sec III D. The formation of larger, dispersed, particles results in an important increase in viscosity while fibrillation causes a large decrease of viscosity, probably due to the deformation and the orientation of the dispersed particles in the shear flow. This reasoning is in qualitative agreement with that of the previous studies cited above, mostly carried out for strain controlled experiments. It is also worth noting that the viscosity decrease appears more rapidly at higher applied stress. This is once again in agreement with our morphological observations. For the same deformation, the HDPE particles were less deformed for creep at 25 Pa. The

above results show clearly the relationship between rheological measurements and morphological changes occurring in a flow field. The transient blend rheological behavior is largely governed by the morphology evolution in the applied flow. Conversely, the blend microstructure variations are strongly dependent on the rheological properties of the components.

#### IV. Conclusions

A new strategy has been proposed in order to analyze morphological changes in concentrated immiscible polymer blends, induced by shear in a rheometer. The technique consists of rapidly quenching the blend under constant stress using a dry air jet. The samples are then recovered and analyzed by SEM. In contrast with other existing techniques such as direct optical microscopy observations or indirect analysis, this method appears to be very effective for analyzing the shear-induced morphology of high concentrated blends. The technique has been used to study the behavior of a (80/20) PS/HDPE droplet-in-matrix blend during creep experiments. In this context, particular care has been taken in order to avoid end effects, static coalescence, thermal degradation, and crystallization effects.

The blend morphology was submitted to important changes during creep experiments. Although the morphology evolution appears to be coalescence controlled in the range of shear rate investigated here, the near steady-state microstructure is greatly affected by the applied shear stress and the total deformation. At low shear stresses, a large increase in the diameter of the dispersed HDPE particles was observed, but the droplets kept their spherical shape even at relatively high deformations. At higher shear stresses, the initial emulsion-like structure was transformed into a fibrillar one. The observation of such structures was made possible via the proposed quenching method. Coalescence was less pronounced in this latter case suggesting a two-step process: coalescence by collisions between neighboring droplets when the particles diameter is greater than interparticle distance and a head-to-tail collision process when the dispersed particles are elongated.

Breakup of the dispersed phase particles is expected to occur only to a small extent due to the low shear rates under the experimental conditions used for this blend composition. The transient blend rheological behavior is closely related to the morphology changes under the applied flow.

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