

# Determination of a limiting dispersed phase concentration for coalescence in PA6/HDPE blends under extensional flow

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## Abstract

Blends of PA6/HDPE at different compositions and melt-draw ratio were prepared using a twin-screw extruder with a rectangular slit at 250°C. The morphology results show that at low take up velocity, the final state of deformation is independent of the dispersed phase composition. However, at high take up velocity the drop deformation increases with the composition. To determine a lower limiting concentration, at which coalescence occurs, the average particle volume of the dispersed phase was evaluated. In the concentration range of 1–4 vol% of PA6, the average volume of the particles remains constant (no coalescence) during the stretching process. However, at higher concentrations (>5 vol% of PA6) coalescence takes place and the volume increases with stretching. These results clearly indicate the limiting dispersed phase concentration for coalescence in this system under extensional flow. The approach used here represents a possible technique to separate out the relative contribution of single particle deformation and particle–particle coalescence in dispersed phase fiber formation in an extensional flow field. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Coalescence; Polymer blends; Morphology

## 1. Introduction

The study of polymer blends has had a large impact on commercial applications during the last two decades. From a rheological point of view, polymer blends can be considered to be a dispersion of deformable polymeric drops in polymer melts. The final physical properties of the blends depend on the state of the dispersion, that is, on the shape, size, and orientation of the dispersed phase. During the mixing process of immiscible polymer blends, the dispersed phase experiences a combination of both particle breakup and coalescence.

The earliest study in this area was made by Taylor [1,2]. He studied the deformation and disintegration of a Newtonian-liquid droplet immersed in a Newtonian-matrix. It was found that the droplet shape depends on the viscosity ratio and the capillary number ( $C_a = \eta_m \dot{\gamma} d / \nu$ , where  $\eta_m$  is the matrix viscosity,  $\dot{\gamma}$  the shear rate,  $d$  the droplet diameter and  $\nu$  the interfacial tension). This study has been extended to non-Newtonian systems and different results have been observed. Tsebrenko et al. [3] have summarized experimental results of the deformation and breakup of polymeric

particles in mixtures of immiscible polymers in various flow situations. Rallison [4] and more recently Stone [5] have reviewed the major contributions in this area. Tokita [6] developed a relationship for the equilibrium particle size, which results when particle deformation and coalescence phenomena are balanced. The applicability of Tokita's theory is limited because the probability of particle–particle collision resulting in coalescence is unknown. Moreover, there are other parameters used in this theory, which are difficult to evaluate for immiscible polymer blends [7]. Elmendorp and Van der Vegt [8] have shown that interparticle collisions have a greater probability of resulting in coalescence if the dispersed phase is small and if the interface is highly mobile. However, this mobility is reduced for compatibilized blends, where the interfacial modification results in fewer particle–particle contacts and hence less coalescence is observed with increasing composition. Lepers et al. [9] indicate that the reduction in size of the dispersed phase upon addition of interfacial modifier is mainly caused by two different phenomena; a reduction of interfacial tension and a reduction of the coalescence of the dispersed phase particles. They quantitatively demonstrate the relative contribution of each to size reduction.

Recently, there have been a number of published theoretical

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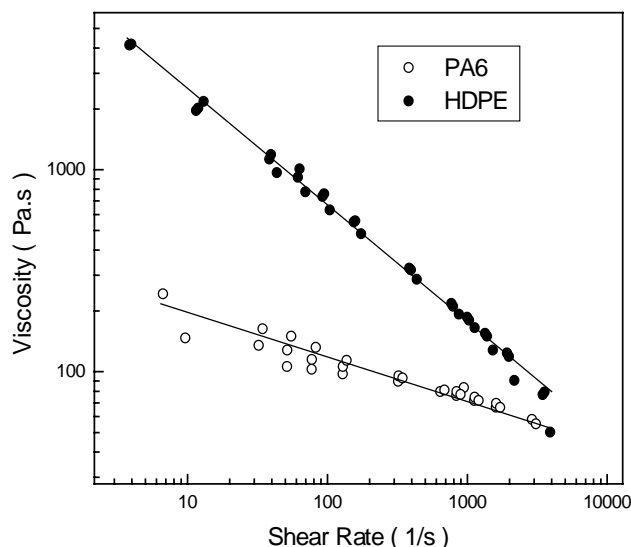


Fig. 1. Apparent viscosity vs. shear rate for the pure materials at 250°C.

studies [10,11] concerning the coalescence in polymer blend melts. Fortelny et al. [12] explain that the coalescence process can be divided into four steps: (I) approach of droplets; (II) removal of the continuous phase between the droplets; (III) rupture of the remainder of the continuous phase; (IV) evolution of the 'neck' to form a coalesced droplet.

Despite the significant effort related to the study of drop deformation in polymer blends, very few attempts have been made to quantify the extent of deformation and the coalescence during melt processing. In previous studies [13,14] a form factor was introduced to measure the shape of the minor phase deformation obtained by extrusion. For example, fiber formation is shown to be very sensitive to draw ratio and in general it has been observed that the final state of deformation is significantly diminished in interfacially compatibilized systems. Also, the influence of coalescence on the final state of elongation of the dispersed phase was studied [14]. In that study, it was reported that coalescence has been suppressed due to either the addition of an interfacial modifier or lowering the concentration of dispersed phase. However, the concentration at which the coalescence effect begins to be observed was not reported in the past. The physical meaning of this concentration can be understood as the limit at which an immiscible blend is considered to be dilute. The importance of this limit is based on the fact that for concentrated solutions, morphological changes are linked to coalescence effects. Thus, further processing does not guarantee a stable morphology.

The goal of this study is to detect a limiting particle concentration for coalescence in extensional flow and to separate out the contribution of single particle deformation and coalescence in fiber formation.

## 2. Experimental

### 2.1. Materials

The materials used in this work were high density polyethylene (HDPE) PX-60003 from PEMEX and polyamide (PA6) 3100 from Celanese.

### 2.2. Mixing

Prior to a typical mixing experiment, the PA6 was dried under vacuum at 90°C overnight. Blends at different compositions from 1 to 15% (volume fraction) of PA6 in HDPE were prepared. The material was blended in a Leistritz intermeshing co-rotating twin-screw extruder having a screw length to screw diameter ratio,  $L/D$ , equal to 40. Feeding was done under nitrogen and vacuum was applied at the decompression zone. A rectangular slit die of 6.2 cm and adjustable gap (fixed at 2.5 mm) was used. Cooling of the extrudates after die exit was performed in water. Typical temperature settings along the barrel were 230, 235, 240, 245, 250°C from feed hopper to exit. The melt temperature was measured at the die by a thermocouple in direct contact with the melt and it remained constant at 250°C. The screw speed was maintained at 100 rpm. The linear velocity of the extrudate ( $V_e$ ) was 100 cm/min calculated from the melt densities, 0.74 and 0.96 g/ml (at 250°C) for HDPE and PA6, respectively, and the flow rate. The speed of the take-up device was varied and the linear velocity ( $V_r$ ) was measured for each run. The draw-down ratio is then defined as  $DR = V_r/V_e$ .

### 2.3. Rheological analysis

The rheological characterization of the resins was performed with an Instron capillary rheometer model 2404, using a set of capillary dies of 0.127 mm diameter and length to diameter ( $L/D$ ) ratios of 40, 60 and 80. The Bagley and Rabinowitsch corrections were applied to the capillary rheometry data. The viscosity curves for the neat materials at 250°C are presented in Fig. 1.

### 2.4. Morphological analysis

For the morphological study, small samples were taken after twin-screw extrusion parallel to the machine direction. The samples were immersed in liquid nitrogen and then fractured. The fracture surfaces were analyzed by scanning electronic microscopy (JEOL JSM 5400 LV).

### 2.5. Image analysis

An image-Pro Express analyzer was used to measure the diameters ( $d_n$ ,  $d_v$ ), the major ( $L$ ) and minor radius ( $B$ ) of the deformed particles. For each sample, approximately 300 diameter measurements were obtained from the digitalized SEM micrographs. A correction was applied to the distribution of diameters for each sample according to the Saltikov

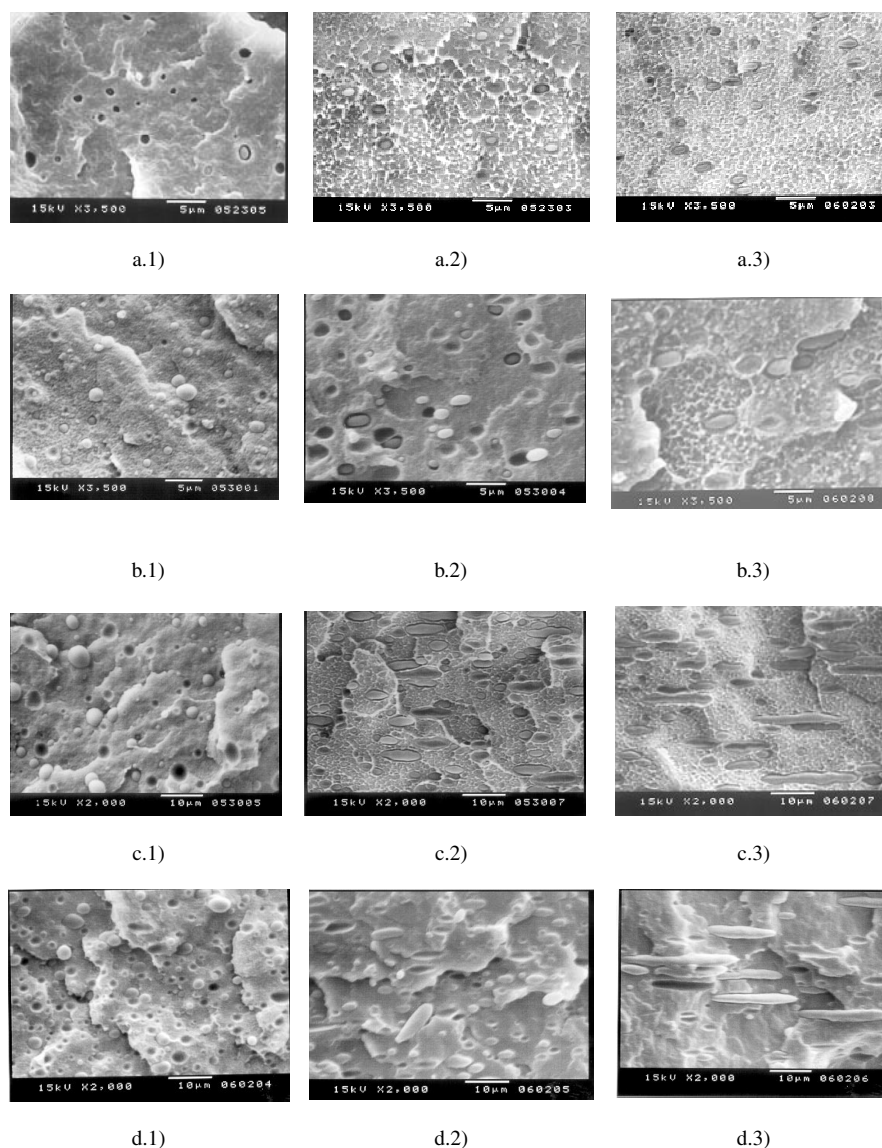


Fig. 2. Deformation of the minor phase as a function of the melt-draw ratio ( $DR = V_f/V_c$ ) and the composition of PA6. (a.1) 1 vol% PA6, DR = 1.1; (a.2) 1 vol% PA6, DR = 2.9; (a.3) 1 vol% PA6, DR = 3.8; (b.1) 4 vol% PA6, DR = 1.1; (b.2) 4 vol% PA6, DR = 2.9; (b.3) 4 vol% PA6, DR = 3.8; (c.1) 5 vol% PA6, DR = 1.1; (c.2) 5 vol% PA6, DR = 2.9; (c.3) 5 vol% PA6, DR = 3.8; (d.1) 15 vol% PA6, DR = 1.1; (d.2) 15 vol% PA6, DR = 2.9; (d.3) 15 vol% PA6, DR = 3.8.

method [7,15]. In the case of deformed particles, using  $L$  and  $B$  values, the average volume particles was calculated with  $V_j = (4/3)\pi(B)^2L$ .

### 3. Results and discussion

In Fig. 2, the deformation of the dispersed phase (PA6) as a function of the composition and the melt-draw ratio (DR) is presented. It is observed that when the melt-draw ratio increases the particles are more elongated. This morphology has also been observed by other authors [16] during melt spinning. The melt spinning operation leads to the development of significant molecular orientation. It is important to note that for DR = 1.0 (same linear velocity

of extrusion and stretching) a spherical morphology is obtained.

The shear stress in the die may affect the drop deformation, particularly at low melt-draw ratio [13]. However, in this study the shear stress effect was not analyzed, because spherical particles were always observed at the exit of the die (Fig. 2a.1,b.1,c.1,d.1). The die gap was large enough to prevent particle deformation when they pass through the die. Therefore, the deformation of the particles takes place after the polymer blend exits the die. As the draw ratio increases, the extruded ribbons becomes thinner and the PA6 dispersed phase is consequently more elongated. The particle size of the dispersed phase at DR = 1.0 is a function of the composition (Table 1). It is observed that the particle size increases three-fold (from 1 to 15 vol% in PA6).

Table 1

Particle size of the dispersed phase after twin-screw extrusion at DR = 1.0 as a function of the composition

Blend composition (vol% PA6)	$d_n^a$ ( $\mu\text{m}$ )	$d_v^b$ ( $\mu\text{m}$ )	Polydispersity ( $d_v/d_n$ )
1	0.7	0.8	1.17
2	0.9	1.1	1.22
3	1.4	1.6	1.12
4	1.6	1.9	1.19
5	1.6	2.1	1.31
7	1.8	2.0	1.11
10	2.0	2.5	1.25
15	2.4	2.7	1.13

<sup>a</sup> Number-average diameter.

<sup>b</sup> Volume-average diameter.

In Fig. 3, the evolution of the deformation ( $L/B$ ) of the particles as a function of the draw rate is presented. At low draw rates, the deformation is independent of the dispersed phase concentration. However, as the draw rate increases the final state of particle deformation depends on composition. It is observed that at DR > 3.0 there are several deformation levels. This difference is clearer at higher draw rates. This phenomenon can be attributed to the fact that at higher concentrations coalescence effects become important. Recently, Chapleau and Favis [16] studied the modification of the morphology of immiscible binary blends in a co-rotating twin-screw extruder equipped with capillary dies of various lengths. They explained that the coalescence leads to a fiber formation for all blends at higher concentration of the minor phase. However, at low dispersed phase

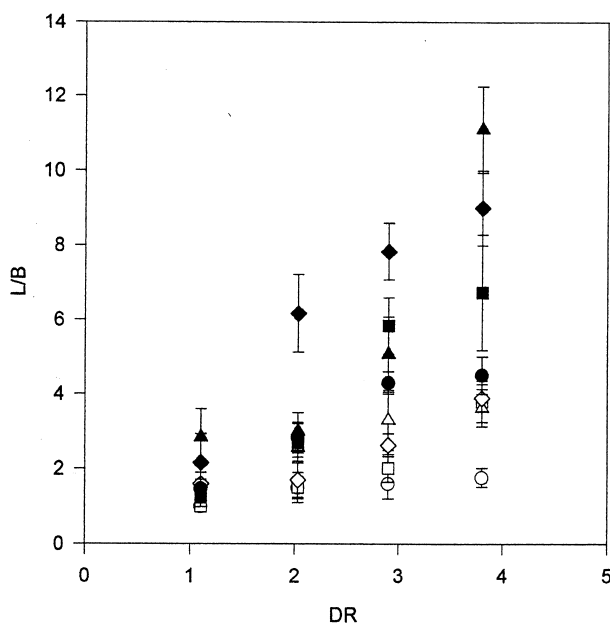


Fig. 3. Drop deformation ( $D = L/B$ ) of the minor phase (PA6) as a function of the melt-draw ratio ( $DR = V_1/V_0$ ) for different compositions of PA6 in HDPE. vol% PA6: 1% ( $\circ$ ), 2% ( $\square$ ), 3% ( $\nabla$ ), 4% ( $\diamond$ ), 5% ( $\bullet$ ), 7% ( $\blacksquare$ ), 10% ( $\blacktriangle$ ) and 15% ( $\blacklozenge$ ).

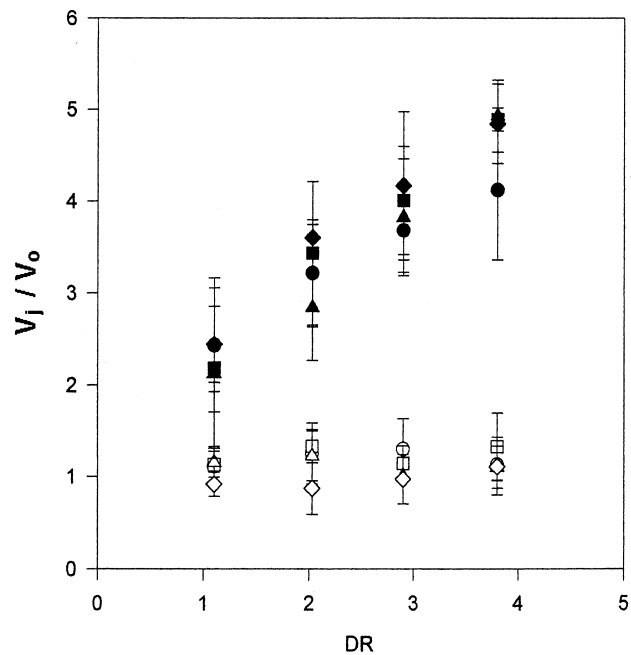


Fig. 4. Normalized average volume of PA6 particles ( $V_j/V_0$ ) as a function of the melt-draw ratio ( $V_1/V_0$ ) for different compositions of PA6 in HDPE. Same symbols as in Fig. 3.

concentration it has been shown that the coalescence effects diminished.

The deformation data of the dispersed phase alone is not sufficient to detect the onset concentration at which coalescence phenomena occur. However, if coalescence does occur the particle volume will increase. The normalized average particle ( $V_j/V_0$ , where  $V_j$  is the volume of deformed particles and  $V_0$  for undeformed particles) is shown in Fig. 4. In the concentration range of 1–4 vol% of PA6, the average volume of the particles remains constant during the stretching process. This indicates that during the stretching process there is a deformation of individual particles and no coalescence takes place. However, at higher concentrations (>5 vol%) it can be observed that the average volume increases. This effect is more pronounced at higher draw rates. For example, the 10 vol% PA6 blend, the normalized volume of a deformed particle at high stretch ratio is 5. This implies that during the deformation, about five particles coalesce to a single particle. These results, in an elongational flow field, demonstrate that below 4% concentration all observed deformation is due to single particle phenomena. Above 4% concentration, coalescence and droplet–droplet interactions also begin to contribute substantially to the overall deformation and eventual fiber formation. These results are valuable since they essentially allow one to factor out, quantitatively, the relative contributions of single particle deformation and coalescence in fiber formation in an elongational flow field. The onset concentration for coalescence is related to the ability and extent to which the particle deforms and the original droplet–droplet particle distance at DR = 1. Coalescence can be

observed at lower concentrations during dynamic mixing since particles are moving randomly in three dimensions. Under such conditions some authors have reported the observation of coalescence at dispersed phase concentrations as low as 1%. In this study, we apply a uniaxial draw (elongational flow) and it is entirely expected that coalescence phenomena under such conditions should occur at higher concentrations than in dynamic mixing. It is furthermore expected that a lower original interparticle distance or a highly deformable dispersed phase would reduce the onset concentration for coalescence in such experiments.

Elmendorp and Van der Vegt [8] have indicated that coalescence phenomena play an important role at concentrations as low as 1%. However, the mixing was carried out in a shear flow-mixing device. In our case, the deformation of PA6 drops in HDPE was examined in uniaxial extensional flow. The observed limiting concentration for coalescence could be modified by parameters such as the viscosity ratio. In this work, this ratio was 0.2 for an apparent shear rate of 100 l/s. This corresponds to particles of low viscosity within a more viscous matrix where deformation is highly favored. However, in the opposite case (highly viscous droplets within a low viscosity matrix) one would reasonably expect that the critical concentration for the onset of coalescence would be shifted to higher values. Work is underway to confirm this expectation.

#### 4. Conclusions

The final state of deformation and coalescence of PA6 drops in HDPE as a function of the composition and the melt-draw ratio was studied. At low draw rates, the deformation is independent of the dispersed phase concentration. As the draw rate increases, the final state of particle deformation depends on the composition. At concentrations between 1 and 4 vol% of PA6, the average volume of the particles remains constant (no coalescence effects) during the stretching process. However, at concentrations higher than 5 vol% of PA6, coalescence begins to play a role.

These results clearly indicate the limiting dispersed phase concentration for coalescence in this system under extensional flow. The approach is valuable since it is a route towards quantitatively demonstrating the relative contributions of single particle deformation and coalescence in fiber formation in an extensional flow field. In conclusion, it was

demonstrated in this paper a possible technique to separate out the relative contribution of single particle deformation and particle–particle coalescence in dispersed phase fiber formation in an elongational flow field.

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