

The influence of coalescence on the morphology of the minor phase in melt-drawn polyamide-6/HDPE blends

R. González-Núñez and D. De Kee

Department of Chemical Engineering, University of Sherbrooke, Sherbrooke, Quebec J1K 2R1, Canada

and B. D. Favis*

Centre de Recherche Appliquée sur les Polymères (CRASP), Department of Chemical Engineering, Ecole Polytechnique de Montréal, Montréal, Quebec H3C 3A7, Canada

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The influence of coalescence on the final state of elongation of the dispersed phase in polyamide-6/HDPE blends was studied. The blends were prepared by ribbon extrusion and melt drawn at different draw ratios in order to obtain a high variation in the state of fibrillation of the minor phase. In order to separate out the relative role of single particle deformation and coalescence in determining the final morphology, coalescence was suppressed by two techniques. Firstly, coalescence was diminished to a small effect by studying the behaviour of the blend containing only 1 vol% polyamide-6 (PA-6). In the other case coalescence was suppressed in a blend containing 20 vol% PA-6 by adding an interfacial modifier. The results indicate that the form factors for 1% PA-6/HDPE and 20% PA-6/HDPE (compatibilized) are identical over a wide range of hot stretch ratios and the final state of elongation is dominated entirely by single particle deformation phenomena. The 20% PA-6/HDPE (uncompatibilized) system displays an added strong contribution of coalescence to the final morphology. The relative contribution of coalescence and single particle deformation in influencing the final morphology in this latter system can be inferred quantitatively from these results. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

It is well known that both the size and the shape of the minor phase significantly affect the physical properties of immiscible polymer blends¹. During melt processing, due to the deformable nature of the minor phase, a wide range of morphologies can be generated. Fibrillar, lamellar and ellipsoidal forms have been reported in the scientific literature and several basic parameters such as viscosity ratio, composition and interfacial modification have been found to be important in the control of the morphology². It is generally believed that the drop size of the minor phase obtained after melt blending is a result of a balance of two principal forces: normal forces and surface tension forces, which are associated with drop breakup and coalescence³. Little quantitative data, however, have been published on the relative contribution of each of these phenomena in obtaining given dispersed phase morphologies in melt processing environments.

Recently, Tsouris and Tavlarides⁴ published a review article on breakage and coalescence models for drops. They proposed a model based on a phenomenological

approach to describe breakage and coalescence processes in turbulent dispersions. They explain that the coalescence efficiency increases with lower continuous and dispersed phase viscosities, larger drop size and higher energy input. Similar findings have been reported by other researchers. For example, Willis *et al.*⁵ have demonstrated that during the mixing process of immiscible polymer blends the minor phase experiences a combination of both particle breakup and coalescence. They analysed the particle size increase with composition quantitatively. This effect is due to the greater probability of phase contacts and particle–particle interactions. Similar results were found by Tobin *et al.*⁶ and Fortelný and Kovář⁷.

A series of papers from this laboratory has investigated the composition/particle size dependence for a variety of systems both in the presence or absence of interfacial modifiers^{8,9}. These studies indicate that coalescence can be significantly suppressed in the presence of an interfacial modifier. It has also been shown that coalescence can be reduced substantially by reducing the concentration and that at 1% dispersed phase, coalescence effects were found to be negligible¹⁰. Elmendorp and Van der Vegt¹¹ have reported that coalescence is negligible during the single screw extrusion

* To whom correspondence should be addressed

of blends of PP/PS when the concentration of the minor phase was 0.5%.

Relatively little quantitative information has been reported on the role of coalescence in producing fibre-like morphologies. In this study highly elongated minor phase particles were obtained by carrying out ribbon extrusion at different draw ratios. The object of this study is to attempt to separate the relative contribution of coalescence and single particle deformation in the formation of highly elongated morphologies under melt processing conditions.

EXPERIMENTAL

Materials

The high density polyethylene (HDPE) used in this study was 07055C, obtained from Dow in pellet form. The polyamide-6 (PA-6) Zytel 211 from DuPont (in granular form) was used as the minor phase. Surlyn 9020 obtained from DuPont was used as a compatibilizer. This ionomeric resin is a random terpolymer consisting of approximately 80% PE and 20% of a mixture of methacrylic acid and isobutyl acrylate. The methacrylic acid was approximately 70% neutralized with zinc. Previous work¹² has shown that this ionomer is an excellent compatibilizing agent for PA-6/HDPE systems. Covalent bonding was shown to take place between the carbonyl of the ionomer and the terminal amine of the polyamide. Some properties of these resins are shown in Table 1.

Mixing

Prior to a typical mixing experiment the sample mixture was dried under vacuum at 90°C overnight. The materials were blended in a ZSK-30 (Werner-Pfleiderer) intermeshing, co-rotating, twin-screw extruder with a screw length to screw diameter ratio, L/D , of 40. Feeding was performed under dry nitrogen. Vacuum was applied in the decompression zone. The die used was a capillary die with an L/D of 2.2 and a 40° angular entry. The extrudates were cooled in water and pelletized. 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. The temperature remained constant at 250°C and the screw speed was maintained at 250 rpm.

Blends containing 20 vol% (M1PA20) and 1 vol% (M1PA01) of PA-6 were prepared. Another blend of 20 vol% of PA-6 with 10 mass% of ionomer (M1PA20s), based on the minor phase (or 3 mass% of ionomer in HDPE) was prepared. The ionomer was initially mixed with the HDPE and this was then mixed in a second step with the PA-6. In a recent morphological study Willis *et al.*¹² observed a high affinity of the ionomer for the polyamide. They found that the migration of modifier to the interface is facilitated when it is initially mixed with the component with which it has the least affinity (HDPE) and then compounded with the other phase (PA-6).

Rheological analysis

The rheological characterization of the resins was performed using two instruments. For shear rates lower than 10^2 s^{-1} , a Weissenberg rheometer was used. Tests

were carried out with a plate-plate geometry of 40 mm diameter with a 2 mm gap. The measurements were performed under dry nitrogen. For high shear rates, the viscosity data were obtained 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. Bagley and Rabinowitsch corrections were applied to the capillary rheometry data.

Figure 1 shows the viscosity and first normal stress coefficient of the polyethylene (Figure 1a) and polyamide-6 (Figure 1b) resins at 250°C. The solid curves were calculated with the De Kee and Chan Man Fong model¹³.

Ribbon extrusion

Ribbons of the blends previously compounded in the twin-screw extruder were extruded through a 7.6 cm slit die with an adjustable gap at 250°C using a Brabender single screw extruder. The screw has a 1.905 cm (0.75 in) diameter and a 3/1 compression ratio with an L/D of 25. The extrudate was taken up between two water-cooled steel rolls (12.7 cm diameter) having a polished chrome surface. The take up device also had two pinching pull

Table 1 Characterization of the polyethylene, polyamide-6 and Surlyn 9020 ionomer resins

Resins	MI (g per 10 min) ^a	Torque at 250°C after 5 min (N m^{-1})	M_n^a	Density at 250°C ^a
PE/HDPE	7	5.9	16 600	0.74
PA-6	—	8.6	25 000	0.96
Ionomer	1	14.3	25 000	0.74

^a Obtained from supplier

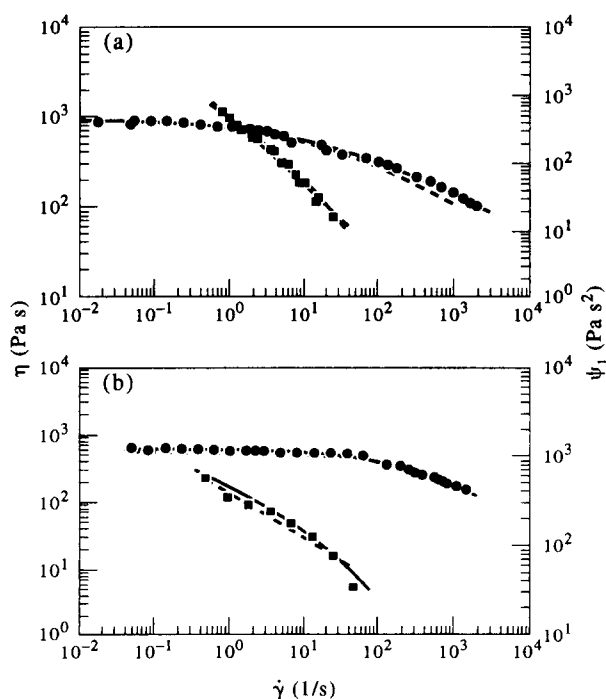


Figure 1 Viscosity and primary normal stress coefficient as a function of shear rate for: (a) high density polyethylene and (b) nylon-6 at 250°C. ●, Viscosity data; ■, primary normal stress coefficient data; —, prediction of De Kee–Chan Man Fong (1994) model; - - -, Cox–Merz empirical relation between η and the complex viscosity η^* ; ····, Laun relation between χ and η^*

Table 2 The influence on particle size (d_v) of the twin-screw and of the reprocessing on the single-screw (0 HSR)

System	Particle size (d_v) after twin-screw extrusion (μm)	Particle size (d_v) after single-screw at 0 HSR (μm)
1% PA-6/HDPE (non-compatibilized) M1PA01	1.8	1.8
20% PA-6/HDPE (compatibilized) M1PA20s	1.1	1.1
20% PA-6/HDPE (non-compatibilized) M1PA20	3.2	7.2

rolls. Stretching was varied by adjusting the speed of the take-up device. The screw speed was varied between 20 and 60 rpm. In each case the linear velocity of the extrudate (V_E) was calculated taking into account the melt densities. The linear velocity of the rolls (V_R) was also measured for each run. The hot stretch ratio (HSR) is then defined as $\text{HSR} = (V_R - V_E)/V_E$.

Morphological analysis

A scanning electron microscope (type Jeol 35 CF) was used to examine the size and the shape of the dispersed phase (PA-6). In order to study the shape of the minor phase after deformation by ribbon extrusion, samples cut parallel to the machine direction were used. In the case of M1PA20, blend samples were microtomed to create a plane face using a Reichert Jung Supercut 2050 equipped with a glass knife. The microtomed samples were then treated for 1 h in formic acid to extract the minor phase.

Image analysis

A Jandel digitizing table controlled by the Jandel Sigma-Scan system was used to measure the size and the shape of the dispersed phase. In the case of the size study, 200 droplet diameters were measured and a correction was applied to the distribution of diameters for each sample according to the Saltikov method¹⁴. This technique corrects for both polydispersity effects as well as for the fact that the knife does not necessarily cut at the true diameter. Both the volume-average (d_v) and number-average (d_n) diameters were estimated. A form factor, $F = 4\pi A/P^2$ (where A is the area and P the perimeter of the particle), was used to measure the deformation of the minor phase. Between 100 and 200 measurements are performed to obtain an average value of F . The standard deviation for F is 0.07. For the undeformed particle, $F = 1$ (sphere) and for the maximum deformation, $F = 0$ (ultra thin fibre of vanishing diameter).

RESULTS AND DISCUSSION

In order to examine the relative roles of coalescence and single particle deformation in determining the final state of elongation of the dispersed particle, samples containing 1 and 20% of dispersed PA-6 were considered. Both compatibilized and non-compatibilized blends were studied. It is well known that coalescence can be highly suppressed by controlling either the

concentration of the minor phase^{10,11} or the level of interfacial interactions^{8,9}.

Influence of the processing environment on morphology

In this study the various blends of PA-6/HDPE were compounded initially by twin-screw extrusion and then processed on a single screw extruder. Table 2 shows the minor component particle size of the various blends after twin-screw extrusion and after single screw extrusion (0 HSR). The smallest particle size is observed for a compatibilized blend (M1PA20s). It is important to note that for samples M1PA01 and M1PA20s the particle size remains constant after changing the processing environment. In contrast the M1PA20 sample (high concentration and no interfacial modifier) displayed a significant increase in particle size after being reprocessed on the single-screw. In other words despite the fact that the twin-screw and the single-screw are significantly different processing environments, once coalescence is suppressed, the sensitivity of the dispersed phase to further processing changes is minimal. It should be recognized that the apparent insensitivity of M1PA01 and M1PA20s is for the case where the particles were compounded on a more efficient mixer initially and then reprocessed on the less efficient one. It has not yet been verified if the opposite case also yields similar results. The M1PA20 sample on the other hand displayed a significant increase in dispersed phase size after single-screw extrusion. The size increase can be related to the fact that the single-screw extruder is less effective than the twin-screw in breaking down the dispersed particles. These results illustrate that at high concentrations, an unmodified blend rapidly responds to the applied forces, associated with disintegration and coalescence.

Factors affecting the final state of elongation of the dispersed phase

In order to dramatically alter the final state of elongation of these blends, melt drawing was carried out after single-screw extrusion. The deformation in this case is essentially due to an elongational flow field. A significant potential exists for particle-particle interactions and coalescence since the width and thickness of the ribbon is continuously reduced during the drawing process. The extruded materials were studied at different draw ratios and Figure 2 shows the evolution of the final state of elongation with draw ratio for the various blends. It is important to note that little dispersed phase elongation is observed at zero hot stretch ratio.

Figure 3 shows, quantitatively, the results for the final deformation of the dispersed phase. The form factors (F) of the dispersed phase (parallel to the machine direction) are given as a function of the hot stretch ratio (HSR). The final state of deformation of the uncompatibilized M1PA20 blend is greater than that for the M1PA20s (compatibilized, 20% PA) and M1PA01 (uncompatibilized, 1% PA) blends. This difference in deformation is even more pronounced at high draw ratios. A previous study¹⁵ from this laboratory has reported that the final state of deformation of the minor phase is significantly diminished in interfacially compatibilized systems. The addition of an interfacial modifier results in a decrease in the interfacial tension¹⁶. This produces a significant decrease in the particle size and it is generally held that it is more difficult to deform a small droplet than a larger one¹⁷.

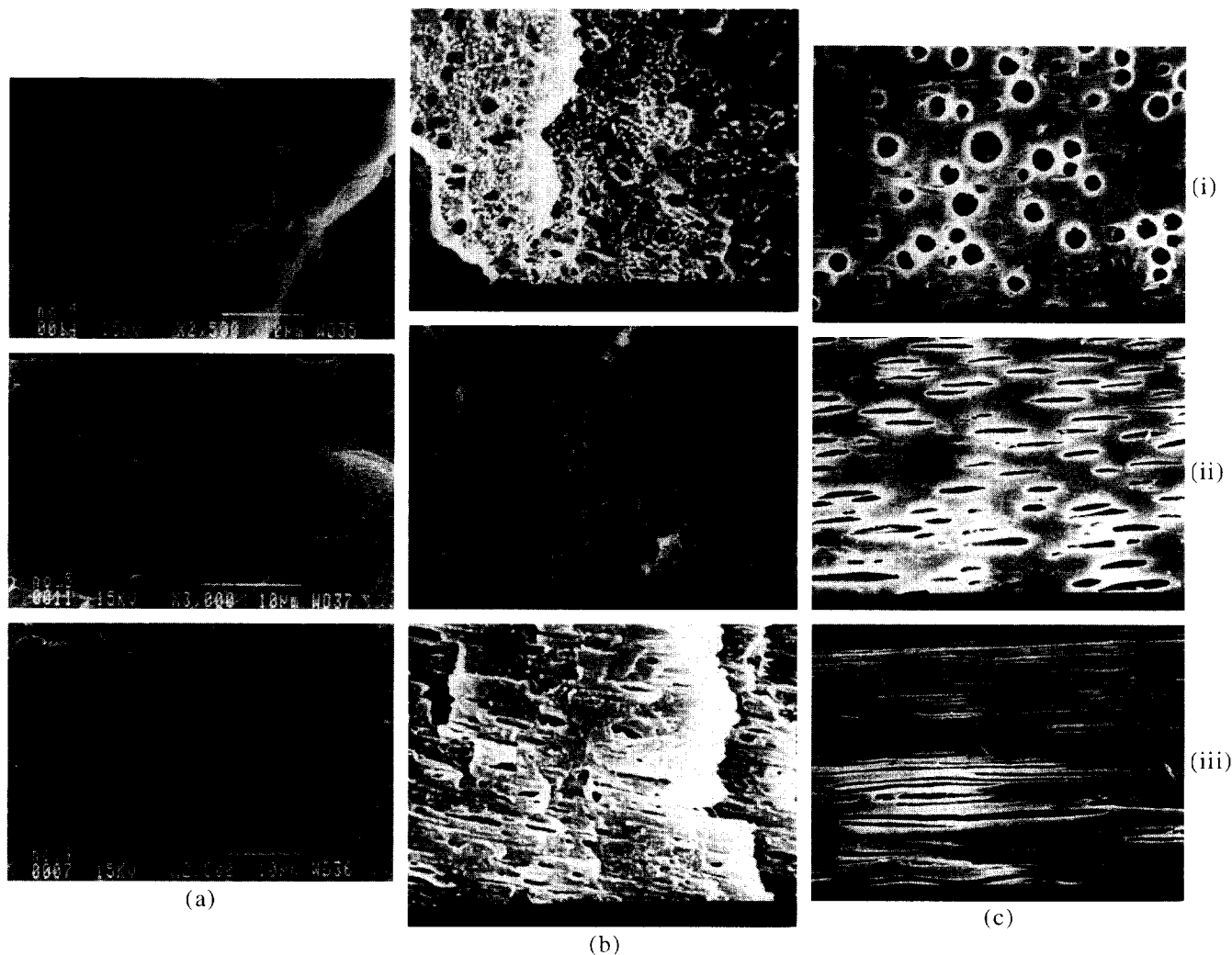


Figure 2 Deformation of the minor phase as a function of hot stretch ratio (HSR): (i) 0.0, (ii) 1.82 and (iii) 2.97. The SEM micrographs show (a) 1% PA-6/99% HDPE (non-compatible); (b) 20% PA-6/80% HDPE (compatible) and (c) 20% PA-6/HDPE (non-compatible). Magnifications: (a,i) and (a,iii) 2500 \times ; (a,ii) 3000 \times ; (b,i) 5000 \times ; (b,ii) and (b,iii) 3500 \times ; (c,i), (c,ii) and (c,iii) 1000 \times

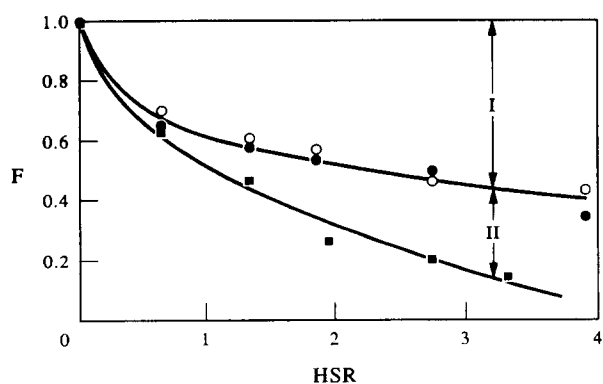


Figure 3 Form factor (F) vs hot stretch ratio (HSR): (○) 1% PA-6/HDPE (non-compatible), (●) 20% PA-6/80% HDPE (compatible) and (■) 20% PA-6/80% HDPE (non-compatible). Region I depicts the contribution of single particle deformation to the final state of elongation (coalescence is suppressed) at a given hot stretch ratio. Region II illustrates the added contribution of coalescence

One of the most interesting features of *Figure 3* is that the curve at reduced composition (1% PA-6, open circles) and the curve for the modified interface (20% PA-6 compatible, filled circles) superimpose. This is

very important since it indicates that these two curves represent the baseline case of deformation in the absence of coalescence (region I). In this elongational flow field, the above systems behave in a similar fashion and the final state of elongation is entirely dominated by single particle deformation phenomena (no coalescence contribution). It should also be noted for these two systems where coalescence has been suppressed, that the presence or absence of strong interfacial interactions has no effect on the final state of elongation. Curve 3 (*Figure 3*, filled squares) on the other hand, illustrates the added significant contribution of coalescence to the fibrillation of the minor phase (region II). Clearly, the 20% PA-6/HDPE (non-compatible) system displays significantly increased levels of anisotropy due to particle-particle impingement (coalescence). A quantitative comparison of the contribution of coalescence can be inferred from *Figure 3* and it can be seen that the influence of coalescence on particle elongation becomes more and more pronounced with hot stretch ratio.

Table 3 confirms the above results and shows the typical volume of a dispersed particle (PA-6) as a function of HSR. In the case of blends containing 1% PA-6 and the compatibilized 20% PA-6, the volume

Table 3 Volume (arbitrary units) of typical dispersed particle as a function of HSR

System	Relative volume at a given HSR				
	0.7	1.3	1.9	2.8	3.3
20% PA-6/HDPE (non-compatible)	110	208	228	278	346
20% PA-6/HDPE (compatibilized)	constant volume				
1% PA-6/HDPE (non-compatible)	constant volume				

remained constant. However, the 20% PA-6/HDPE non-compatible blend shows a volume increase with the hot stretch ratio. These results confirm that the relative effects of single-particle deformation and coalescence were separated in *Figure 3*.

Tsebrenko *et al.*¹⁸ observed that fibre formation in immiscible polymer blends is significantly influenced by coalescence effects. This study quantitatively confirms that work and also indicates that for compatibilized blends, even at the relatively high composition of 20% dispersed phase used in this study, the role of coalescence in determining the final morphology is negligible.

CONCLUSIONS

This study has shown that once coalescence has been suppressed, due to either lowering the concentration of the dispersed phase or through the addition of an interfacial modifier, the sensitivity of the dispersed phase morphology to reprocessing in a less efficient mixer is negligible. On the other hand, an uncompatibilized sample of 20 vol% PA/HDPE which had undergone processing on a twin-screw extruder displayed a significant increase in dispersed phase size after it was reprocessed on a single-screw extruder.

It is shown that during melt drawing: (a) 1 vol% and 20 vol% PA-6/HDPE (compatibilized) blends behave in an identical fashion and the final state of elongation is

dominated by single particle deformation phenomena (no coalescence contribution), (b) for the above two systems where coalescence has been suppressed, the presence or absence of strong interfacial interactions has no effect on the final state of elongation and (c) the 20 vol% PA-6/HDPE (non-compatible) system displays significantly increased levels of anisotropy due in large part to particle-particle impingement (strong coalescence contribution). The relative role of coalescence and single particle deformation in determining the final state of elongation can be readily obtained quantitatively from these results.

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