

# Development and Control of a Blend Morphology by *In Situ* Cross-Linking of the Dispersed Phase

A. DE LOOR,<sup>1</sup> P. CASSAGNAU,<sup>1,\*</sup> A. MICHEL,<sup>1</sup> and B. VERGNES<sup>2</sup>

<sup>1</sup>Laboratoire des Matériaux Organiques à Propriétés Spécifiques, CNRS BP 24, 69390 Vernaison, France;

<sup>2</sup>CEMEF, Ecole des Mines de Paris, BP 207, 06904 Sophia-Antipolis Cedex, France

## SYNOPSIS

The development of the morphology of a reactive blend along a twin-screw extruder has been experimentally studied. A transesterification reaction activated by a catalyst allowed a cross-linking of the dispersed phase during the flow in the extruder. In comparison with the nonreactive system (without catalyst), the resulting morphologies were characterized by larger dimensions. Influence of screw speed and feed rate were similar for both systems, whereas the changes along the screws were more pronounced for the reactive blend. It appeared that the local morphology was strongly dependent on the extent of the reaction. At low extent, the equilibrium between breakup and coalescence was shifted toward coalescence, whereas at high extent, the classical mechanisms were largely modified and replaced by a "coagulation" mechanism. It was shown that, for the fully cross-linked dispersed phase, the final morphology remained remarkably stable during successive extrusion steps. For such products, the observation of a low-frequency plateau of the elastic modulus suggested the formation of a copolymer at the interface with the matrix. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Thermomechanical properties of immiscible polymer blends have been shown to be closely dependent on the morphology of the dispersed phase.<sup>1,2</sup> Therefore, it is important to clearly understand the basic mechanisms of morphology development and the way it takes place in the complex flow fields of industrial processing equipment. On the other hand, control and stabilization of the desired morphology is of utmost importance for industrial applications. For example, spherical droplets with micron or sub-micron diameters will improve impact properties, whereas a minor phase dispersed in relatively large and thin lamellas will be used in solvent barrier applications. Some recent studies have shown the interest in a better knowledge of the morphology development of an immiscible blend along a twin-screw extruder, both theoretically<sup>3,4</sup> and experimentally.<sup>5-9</sup>

However, these studies were carried out on non-reactive polymer blends.

The present article was aimed to discuss more deeply the effect of the *in situ* chemical reaction of cross-linking of the dispersed phase on the blend morphology development along the twin-screw extruder, characterized after the cooling process. Polypropylene (PP)/thermoplastic elastomer blends have generated considerable interest for achieving properties suited to particular applications.<sup>10-16</sup> In the present study, a phase constituted by a miscible blend of ethylene vinyl acetate (EVA) and ethylene methyl acrylate (EMA) copolymers was dispersed in a PP matrix. The chemical reaction was an exchange reaction of ester groups in the presence of dibutyltin oxide as the catalyst. The same system, but without a catalyst, was studied in detail in a previous publication.<sup>9</sup> It was expected that the cross-linking of the elastomeric phase during the extrusion should permit stabilization of the particle size in the melt and prevent demixion phenomena during the cooling process. Therefore, the influence on the morphology of processing param-

\* To whom correspondence should be addressed.

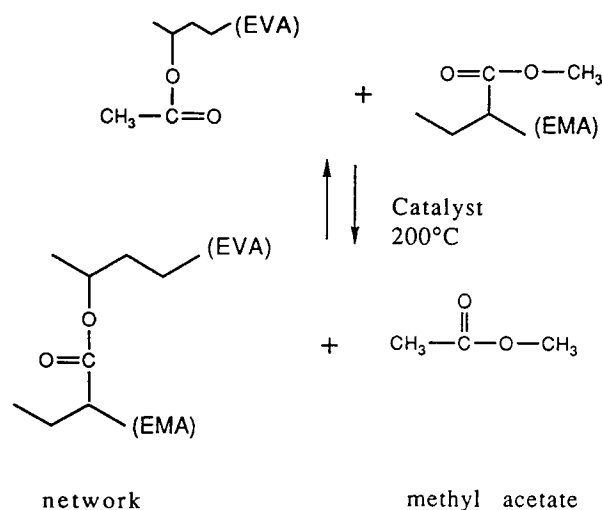
eters such as screw speed, feed rate, and barrel temperatures was quantified and the stability of the blend was tested through a series of successive extrusions.

## EXPERIMENTAL

### Materials

The PP used was an Appryl 3120 MN1 (melt index 12). EVA and EMA commercial copolymers, containing, respectively, in weight, 28% of vinyl acetate (Evatane 2803) and 29% of methyl acrylate (Lotryl 29MA03) were supplied by the Elf-Atochem Co. The blend ratio (in weight) was constant in all the experiments and equal to 80% PP/10% EVA/10% EMA.

As mentioned in the Introduction, the cross-linking reaction of the dispersed phase in the molten state was a transesterification reaction of ester groups of EVA and EMA, in the presence of dibutyltin oxide ( $\text{Bu}_2\text{SnO}$ ) as the catalyst. It is important to underline that the eventual presence of radical scavenging phenol as a thermostabilizer of commercial PP cannot influence the cross-linking reaction of the EVA/EMA phase due to the different chemical natures of the reaction of scavenging and the reaction of transesterification. The transesterification reaction, of which a reactional scheme is given in Figure 1, was well characterized by chemical and rheological experiments.<sup>17</sup> Furthermore, it has been shown that the gel fraction of the EVA/EMA



**Figure 1** Chemical network formation by exchange reaction of ester groups of EVA and EMA copolymers catalyzed by dibutyltin oxide ( $\text{Bu}_2\text{SnO}$ ).

network can be connected to the extent of the reaction.<sup>18</sup> For example, when the temperature was increased from 170 to  $230^\circ\text{C}$ , the gel time reduced from 12 to 2 min and cross-linking became compatible with the residence time in an extruder. Therefore, the necessary time to reach the gel point at a given temperature was known and the determination of the gel fraction  $g$  of the EVA/EMA phase was used to quantify the extent of the chemical reaction.

EVA and EMA copolymers with the addition of catalyst were preblended in a twin-screw extruder (Leistritz LSM 30-34) at a temperature of  $170^\circ\text{C}$  and granulated at the die. As explained before, at these temperatures and residence times ( $t \approx 200$  s), no cross-linking was able to occur inside the extruder barrel.<sup>17</sup> These products were then added with PP in different twin-screw extruders.

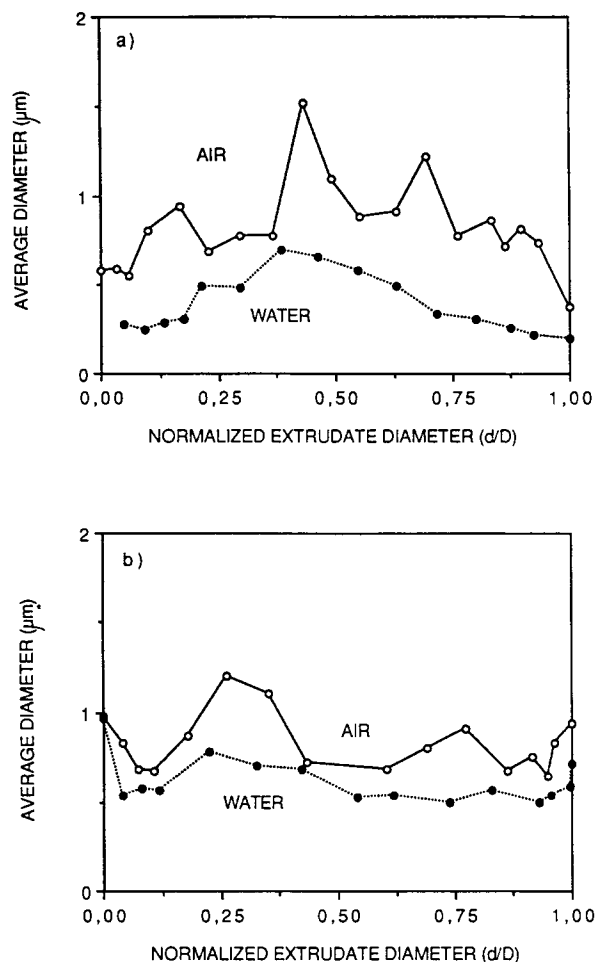
### Processing Equipments

Extrusion experiments were carried out on three different intermeshing self-wiping corotating twin-screw extruders:

- A Clextral BC 45 extruder (centerline distance:  $C_1 = 45$  mm; screw diameter:  $D_s = 50$  mm) with a short barrel ( $L/D = 12$ ) was used for dead-stop experiments. Starting from steady-state extrusion conditions (stable die pressure and temperature), feed rate, screw rotation, and barrel heating were suddenly and simultaneously stopped. The sliding barrel was then removed to collect samples all along the screws.
- A Clextral BC 45 extruder with a long barrel ( $L/D = 35$ ) was used for testing long residence times (greater than 3 min) and obtaining a high extent of the cross-linking reaction.
- A Leistritz LSM 30-34 extruder (centerline distance:  $C_1 = 30$  mm; screw diameter:  $D_s = 34$  mm;  $L/D = 35.5$ ) was used for successive extrusions with the same blend.

Samples were collected at the die exit and along the screws, during the dead-stop experiments. The whole procedure, as well as the screw profile used for these experiments, has been described in detail elsewhere.<sup>9</sup>

The samples were fractured in liquid nitrogen, and after dissolution of the dispersed EVA/EMA phase in tetrahydrofuran (48 h at  $50^\circ\text{C}$ ), the morphology of the blend was examined by scanning electron microscopy (JEOL JSM 35) and characterized by image analysis on 1000–1500 particles, in



**Figure 2** Variations in average diameter of the dispersed phase across the extrudate section, for two different cooling conditions: (a) nonreactive blend (without catalyst); (b) reactive blend (with catalyst).  $N = 100$  rpm;  $Q = 10$  kg/h; die temperature:  $248^{\circ}\text{C}$ .

order to obtain the particle-size distribution and its main parameters (average diameter in number  $d_n$ ; variance  $\sigma$ ).<sup>9</sup>

## RESULTS AND DISCUSSION

### Influence of Cooling Conditions

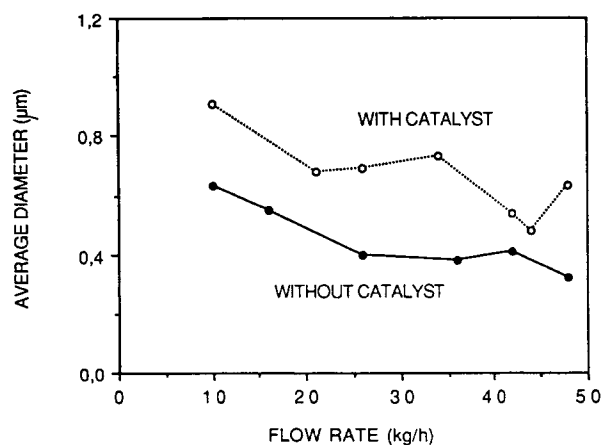
It was shown in a previous study<sup>9</sup> that sample cooling was an important parameter, mainly in the case of semicrystalline polymers such as PP. For these products, the influence of the cooling rate on the droplet-size distribution may effectively be important. The morphologies observed at the die exit for the same extrusion conditions ( $Q = 10$  kg/h;  $N = 100$  rpm), but different cooling conditions (slow

cooling in air at ambient temperature or rapid quenching in cold water), with and without chemical cross-linking of the dispersed phase, are shown in Figure 2. As previously observed for the experiments without a catalyst, the particle size was higher for slow cooling conditions, because droplet coalescence was induced by the growing of the spherulites, whereas the EVA/EMA phase was still in the molten state.<sup>9</sup> However, Figure 2(b) shows that for a partially cross-linked dispersed phase the morphology was quite independent on the cooling rate and more homogeneous across the extrudate section. These first results seemed to prove that the morphology development during the cooling process may be modified by the cross-linking of the dispersed phase. We can assume that the coalescence process induced by crystallization of the matrix was slowed down by the viscosity increase due to the cross-linking reaction and led to the stabilization of the morphology, whatever the cooling conditions.

### Morphology at the Die Exit

The influence of the processing conditions (feed rate  $Q$  and screw speed  $N$ ) on the final morphology at the die exit was investigated on the short-barrel extruder Clextral BC 45 without<sup>9</sup> and with the development of the chemical reaction.

At a constant screw speed of 175 rpm, it was observed (Fig. 3) that the average particle diameter decreased when increasing feed rate. Similar trends were followed by reactive and nonreactive blends. However, droplet size was higher when the catalyst was added. Between 10 and 48 kg/h, the average diameter decreased from 0.63 to 0.32  $\mu\text{m}$  without



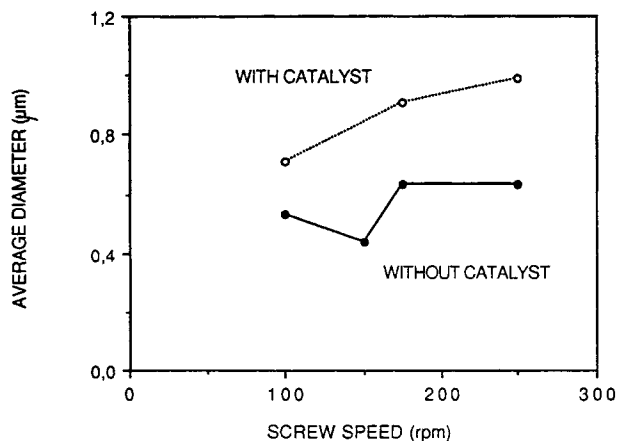
**Figure 3** Influence of feed rate on average diameter at the die exit, with and without catalyst ( $N = 175$  rpm).

**Table I** Influence of Processing Conditions on Final Particle Size at the Die Exit, With and Without Catalyst

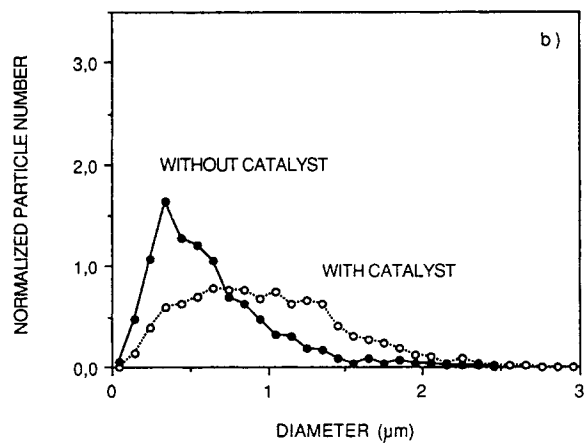
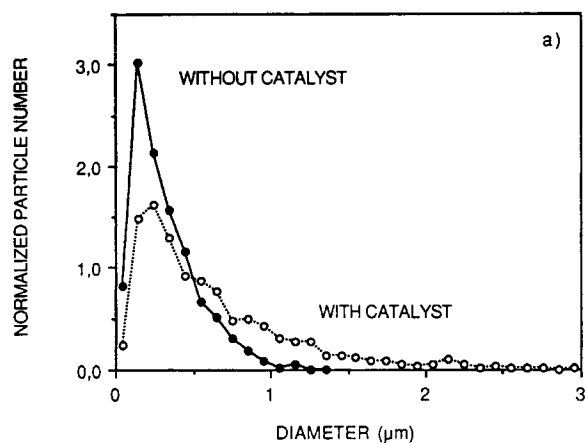
Feed Rate (kg/h)	Screw Speed (rpm)	Without Catalyst		With Catalyst	
		Average Diameter ( $\mu\text{m}$ )	Variance ( $\mu\text{m}$ )	Average Diameter ( $\mu\text{m}$ )	Variance ( $\mu\text{m}$ )
10	175	0.63	0.40	0.91	0.47
16	175	0.55	0.32	—	—
21	175	—	—	0.68	0.41
26	175	0.40	0.27	0.69	0.30
34	175	—	—	0.73	0.46
36	175	0.38	0.25	—	—
42	175	0.41	0.29	0.54	0.29
44	175	—	—	0.48	0.25
48	175	0.32	0.21	0.63	0.54
10	60	0.63	0.34	0.47	0.31
10	100	0.49	0.33	0.71	0.43
10	150	0.44	0.26	—	—
10	250	0.63	0.40	0.99	0.49

the catalyst and from 0.91 to 0.63  $\mu\text{m}$  with the catalyst. At the same time, the variance of the distribution was also reduced (Table I).

At a constant feed rate of 10 kg/h, the average diameter tends to increase with the screw speed for the reactive blend, whereas the nonreactive system exhibited a more irregular evolution (Fig. 4). Once again, particles were bigger for the reactive blend, varying from 0.47 to 0.99  $\mu\text{m}$  when the screw speed increased from 60 to 250 rpm (Table I). This observation was confirmed by the comparison of droplet-size distributions (Fig. 5). Whatever the processing conditions, a broadening of the distribution was observed with the development of the cross-



**Figure 4** Influence of screw speed on average diameter at the die, with and without catalyst ( $Q = 10$  kg/h).



**Figure 5** Example of droplet-size distributions: (a)  $Q = 48$  kg/h,  $N = 175$  rpm; (b)  $Q = 10$  kg/h,  $N = 250$  rpm.

**Table II** Experimental Processing Parameters (Reactive Blend)

Feed Rate (kg/h)	Screw Speed (rpm)	Final Product Temperature (°C)	Mean Residence Time (s)	EVA/EMA Gel Fraction
10	175	255	85	0.20
21	175	246	45	0.10
26	175	248	40	0.10
34	175	253	30	0.10
42	175	248	28	0.10
44	175	241	30	0.10
48	175	246	25	—
10	60	205	110	0.10
10	100	223	100	0.10
10	250	275	85	0.30

linking reaction, which seemed to favor the coalescence of the EVA/EMA phase and shifted the distribution to higher values of diameters (up to 3  $\mu\text{m}$ ).

It has been shown<sup>5,6,8,9,19-21</sup> that the final morphology observed at the die exit resulted from all the thermal and mechanical history experienced by the blend during the process. In Table II are reported experimental parameters such as final product temperature, average residence time, and gel fraction. At a constant screw speed, an increase in feed rate from 10 to 44 kg/h resulted in a decrease in both the mean residence time (from 85 to 30 s) and the final temperature (from 255 to 241°C). It means that the cross-linking reaction was less developed at the high feed rate, even if, in these conditions, the measured gel fraction (around 10% for all the trials) was too inaccurate to confirm this assumption. On the contrary, at a constant feed rate, an increase in screw speed from 60 to 250 rpm induced a sharp increase of final temperature (from 205 to 275°C) and a low decrease in residence time (from 110 to 85 s), leading thus to a more developed reaction, which was confirmed by the change in gel fraction from 0.10 to 0.30.

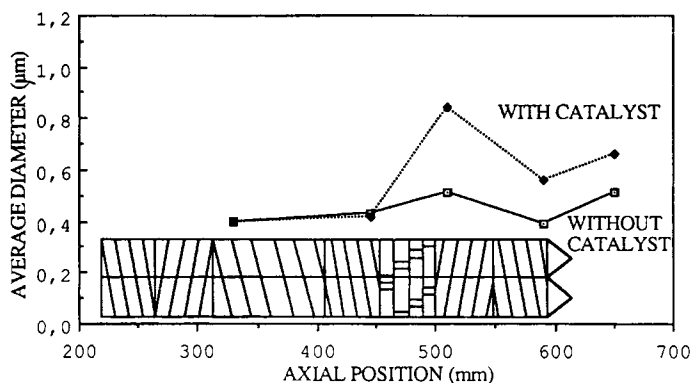
Thus, it appeared that the final size of the particles was affected by the cross-linking reaction, the mean diameter being higher as the reaction was developed. Such an effect was already observed by Bhowmick and Inoue during dynamic vulcanization of hydrogenated nitrile rubber/nylon blends.<sup>22</sup> It could be explained by the change in the rheology of the dispersed phase during the cross-linking reaction. Indeed, the influence of the viscosity ratio on the morphology has been proved by many authors.<sup>23-25</sup> Wu,<sup>23</sup> e.g., proposed the following formulation, predicting an increase of the droplet size with the viscosity ratio:

$$R = \frac{\sigma}{\eta_m \gamma} 4 \left[ \frac{\eta_d}{\eta_m} \right]^{\pm 0.84} \quad (1)$$

with  $R$  as the particle radius;  $\sigma$ , the interfacial tension;  $\eta_m$ , the viscosity of the matrix;  $\eta_d$ , the viscosity of the dispersed phase; and  $\gamma$ , the shear rate.

In fact, this is an empirical relationship obtained by characterizing the blend morphology at the exit of a twin-screw extruder. It considers, thus, the different mechanisms occurring in the system, such as breakup and coalescence, for a blend composition of 85/15, similar to our own experiments. It is clear that we use this formulation only to obtain an order of magnitude and to propose a possible explanation of the observations. More precise computations are presently in progress and will be published later.

In the absence of a chemical reaction, the viscosities of the both phases were very close and the ratio  $\eta_d/\eta_m$  was in the range 1-2, which was favorable for obtaining a fine morphology.<sup>9</sup> For example, at 10 kg/h and 175 rpm, the mean shear rate was around 240 s<sup>-1</sup> and the corresponding viscosity ratio, equal to 0.9, led to a particle diameter of 0.76  $\mu\text{m}$ . When cross-linking developed, the viscosity of the dispersed phase increased rapidly. At the gel point, its value was around 1000 Pa-s at 200°C, leading, in the same conditions, to a viscosity ratio of 9.1 and, thus, to a mean diameter of 4.5  $\mu\text{m}$ . Consequently, a result of the cross-linking reaction of the dispersed phase was to perturb the mechanisms of dispersion and coalescence. Due to the formation of the EVA/EMA network, the breakup process may be assumed to be slowed down by the increase of the viscosity and the development of the elasticity, though the coalescence process was slightly modified, leading to larger particles. Such an assumption



**Figure 6** Evolution of the average droplet size along the screws ( $Q = 10 \text{ kg/h}$ ;  $N = 100 \text{ rpm}$ ) with and without catalyst.

will be discussed below. Direct observations of the morphology development all along the extruder were thus carried out in order to better understand the

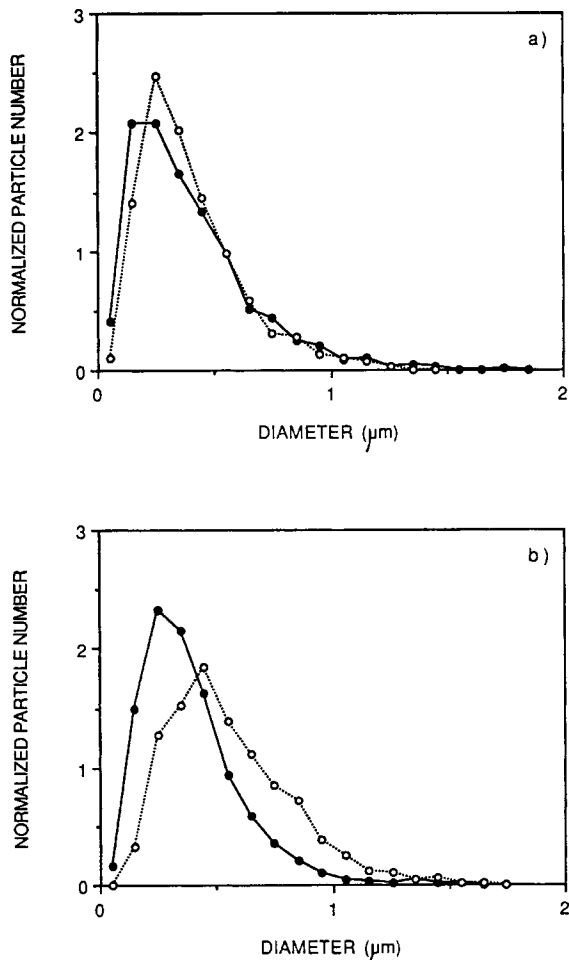
changes in droplet sizes with the extent of the chemical reaction.

### Morphological Changes Along the Screws

#### General Observations

As described in a previous study,<sup>9</sup> the following procedure was chosen as the best procedure of sampling: After the screw rotation was stopped and the sliding barrel removed, samples still in a molten state were directly taken off the screws and quenched in cold water. This method seemed to be the more efficient for assessing the real morphology of the melt blend.

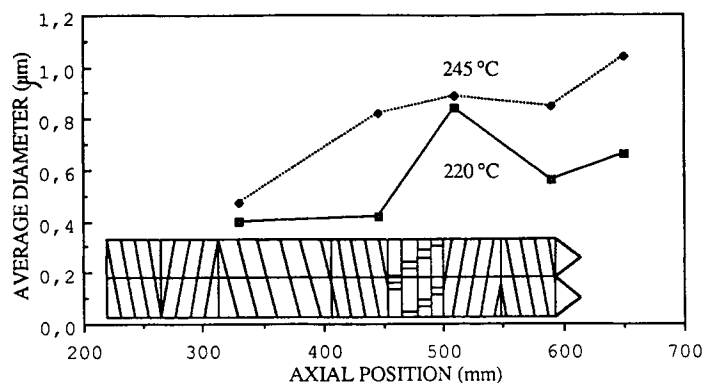
The influence of the progressive development of the cross-linking reaction along the screws is shown in Figure 6. As already observed, a fine dispersion of the EVA/EMA phase was obtained just after the melting section of the extruder, located at the first left-handed screw element. At this location, we can assume that no cross-linking occurred and similar size distributions were observed, whatever the presence of the catalyst, which proved that the initial dispersion mechanism remained unchanged [Fig. 7(a)]. As the blend progressed inside the extruder, the reaction of cross-linking started and developed. Consequently, initially during the flow through the kneading discs, a significant change of behavior in comparison with the nonreactive blend was observed. Similar changes were then followed by the two systems, but, as already mentioned, *in situ* cross-linking of the dispersed phase increased the size of the particles and the broadening of the distribution [Fig. 7(b)].



**Figure 7** Droplet size distribution (○) with and (●) without catalyst: (a) after the melting zone; (b) before the die.

#### Influence of the Temperature

Considering a nonreactive blend, results concerning the influence of the temperature on the particle size



**Figure 8** Evolution of the average droplet size along the screws ( $Q = 10$  kg/h;  $N = 100$  rpm). Influence of the barrel temperature in the presence of the catalyst.

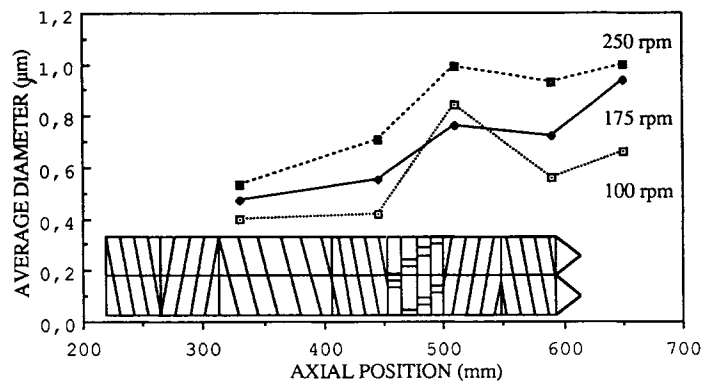
are often contradictory. In the case of ethylene-propylene rubber (EP)/polyamide (PA) blends, Luciani<sup>26</sup> observed an increase of the droplet size with mixing temperature, explained by the relative variation of the viscosities. Oppositely, Tokita<sup>27</sup> observed, for natural rubber (NR)/ethylene propylene diene copolymers (EPDM) systems, a decrease in the particle size with increase of temperature. A probable explanation may be found in the decrease of the interfacial tension with temperature.

For the reactive blend studied, experiments were carried out at two different regulation temperatures of the barrel. These temperatures were fixed (from hopper to die) at, respectively, 140–180–200°C and 230–230–230°C. For the same processing conditions ( $Q = 10$  kg/h;  $N = 100$  rpm), similar residence times (around 100 s) but different exit temperatures (respectively, 221 and 253°C) were measured. As shown in Figure 8, starting from identical morphologies after the melting zone, the mean diameter increased more rapidly at higher temperature, because the

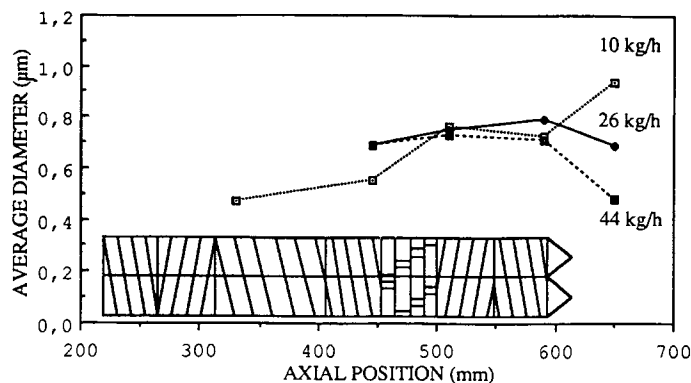
cross-linking reaction was more rapid. These results confirmed the assumption that the particle-size variations were controlled by the chemical reaction, through the variations of the viscosity of the dispersed phase, and were in agreement with the work of Bhowmick and Inoue.<sup>22</sup> Moreover, it appeared that a more cross-linked dispersed phase was less conducive to particle breakup. Effectively, at higher temperature, the mean diameter increased more monotonously along the screws.

#### *Influence of Processing Parameters*

Influence of screw speed at a constant feed rate is indicated in Figure 9. At 100 rpm, the morphology changes were very similar to those observed for the nonreactive system (see Fig. 6), because the cross-linking reaction was poorly developed in these processing conditions (low product temperature). When the screw speed was increased, the melt temperature increased also (to 255 and 275°C) and,



**Figure 9** Evolution of the average droplet size along the screws in the presence of the catalyst. Influence of screw speed ( $Q = 10$  kg/h).



**Figure 10** Evolution of the average droplet size along the screws in the presence of the catalyst. Influence of feed rate ( $N = 175$  rpm).

thus, the extent of the reaction, although the mean residence time decreased from 110 to 85 s, leading to particles of larger diameter and less subject to breakup.

In the same way, the influence of feed rate at a constant screw speed is shown in Figure 10. In this case, the effect of feed rate was less important. In the tested flow conditions, temperature profiles were similar (see Table II) and, thus, the changes in particle diameters along the screws were very close. The main differences occurred during the flow through the die, where the high shear and elongation rates experienced at a high feed rate led to a decrease in the final morphology.<sup>9,25</sup>

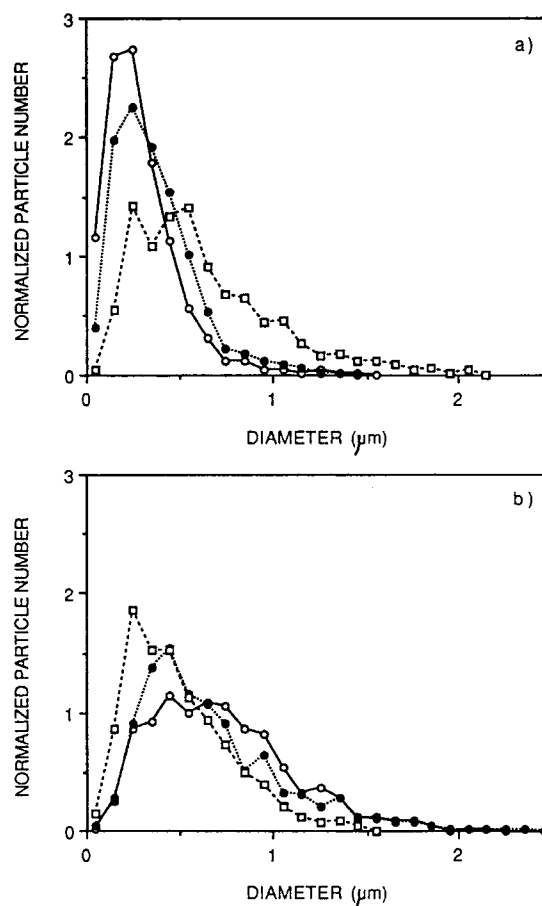
As for nonreactive blends, the morphological changes along the screws were very dependent on local flow conditions and resulted from equilibrium during all the processes between dispersion and coalescence. As previously mentioned, development of *in situ* cross-linking of the EVA/EMA phase led to the development of larger particles.

#### Effect of Thermomechanical History

Generally, the extrusion itself represents only one step of the whole process leading to the elaboration of final products. To simulate the effect of different transformation processes that a polymer blend may undergo and to test the stability of the morphology, three successive extrusions were carried out with the Leistritz extruder on both reactive and non-reactive blends ( $Q = 3$  kg/h,  $N = 100$  rpm, exit temperature  $\approx 220^\circ\text{C}$ ). Such experiments allowed confirmation of the role of chemical modification of the dispersed phase on the control of the final morphology.

The evolution of the particle-size distribution with the number of passages in the extruder is shown

in Figure 11(a) for the nonreactive blend. The size of the particles increased regularly from 0.30 to 0.50  $\mu\text{m}$  with the number of extrusions. Between the first



**Figure 11** Effect of successive extrusions on the particle-size distribution: (a) without catalyst; (b) with catalyst. (○) First extrusion; (●) second extrusion; (□) third extrusion.



**Table III** Average Droplet Diameter After Repetitive Passages in the Extruder

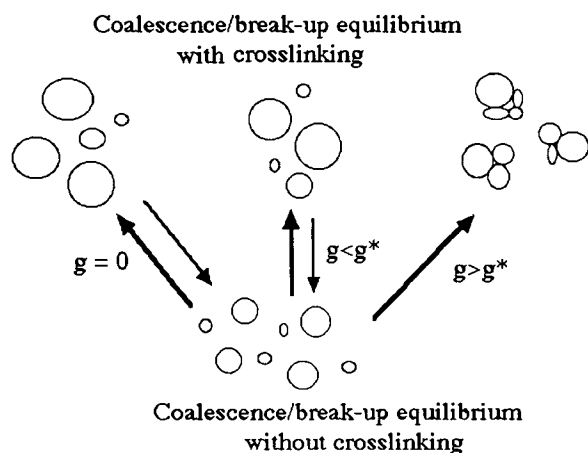
		First Passage	Second Passage	Third Passage
Without catalyst	Average diameter ( $\mu\text{m}$ )	0.30	0.37	0.50
	Variance ( $\mu\text{m}$ )	0.22	0.23	0.29
With catalyst	Average diameter ( $\mu\text{m}$ )	0.72	0.68	0.64
	Variance ( $\mu\text{m}$ )	0.38	0.40	0.40
	Gel fraction	0.40	0.60	0.80

and the last passage, the variation was about 70% for the droplet mean diameter and 30% for the variance (width of the distribution) (Table III). These results were rather unexpected and in apparent contradiction with those of Tokita<sup>27</sup> and Fortelny et al.,<sup>28</sup> who observed a decrease in the droplet size with mixing time, in the case of continuous reactors.

Such evolution in the droplet size may be attributed to a coalescence process, which should be enhanced by the chosen processing conditions. These results may be also attributed to a degradation of the PP matrix with the number of passages in the extruder. Consequently, the viscosity of the matrix could decrease and, according to eq. (1), the droplet size could increase with the number of passages. The limiting viscosity  $\eta_0$  of each blend was measured with a mechanical spectrometer (Rheometrics RMS 800), at 153°C in order to avoid an evolution of the blend during the measurement. The values of  $\eta_0$  varied from  $9.5 \cdot 10^3$  Pa-s, for the first passage in the extruder, to  $9 \cdot 10^3$  Pa-s for the second, and  $6.5 \cdot 10^3$  Pa-s for the third. These results confirmed the degradation of the PP matrix when the blend was extruded.

As expected, the morphology obtained with the reactive blend was more stable and only a low decrease in the mean diameter was observed, whereas the extent of the reaction increased with processing time (Table III). The variation of the dimension of the particles between the different passages remained limited, about 10% only, with a constant value of the variance. The corresponding size distributions are presented in Figure 11(b).

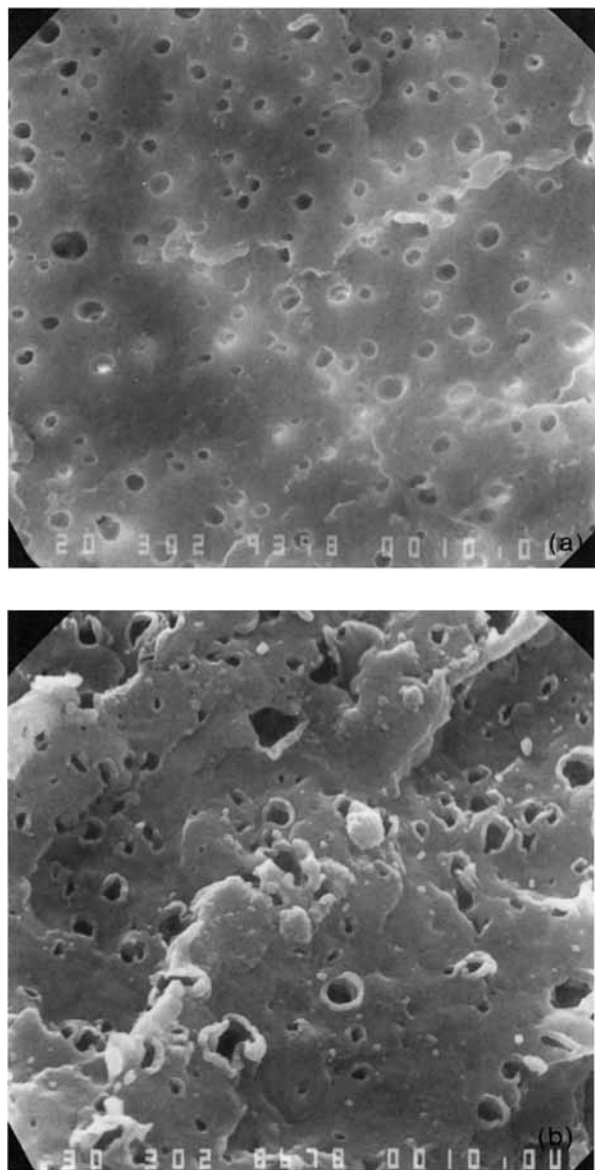
In fact, the introduction of a chemical cross-link into an uncross-linked polymer tends to convert it from a viscoelastic liquid to a viscoelastic solid. Thus, the question to answer is that of the validity of the concepts of coalescence and breakup processes for such partially cross-linked particles. The role of the elasticity in these mechanisms is still not completely understood.<sup>29</sup> However, as illustrated in Figure 12, three different mechanisms can be proposed depending on the extent of the cross-linked network, characterized by the gel fraction  $g$ :



**Figure 12** Schematization of development of coalescence and breakup processes with the gel fraction. Coagulation process at a high gel fraction.

*Case 1:  $g = 0$ .* Although the chemical reaction of cross-linking develops, the EVA/EMA network is only constituted of a few coupled chains, which do not constitute a real three-dimensional network. The EVA/EMA system may be viewed as a viscoelastic liquid with a higher viscosity. Thus, the mechanisms of coalescence and breakup can be imagined as generally discussed in the literature, on the basis of the model proposed by Wu.<sup>23</sup> Therefore, the equilibrium between coalescence and breakup is shifted to the coalescence process with the increase of the EVA/EMA viscosity and leads to higher particles. The shape of the particles is regular and spherical, as observed in Figure 13(a).

*Case 2:  $0 < g < g^*$ .* At a low gel fraction ( $g^* \approx 0.4$ ), although the gel point has been reached, most of the EVA/EMA chains, mainly those of low molecular weight, are still free in the network. Consequently, the coalescence process can be still developed by interpenetration of droplets, but the mechanisms of dispersion are considerably slowed down by the increase of the elasticity in the EVA/



**Figure 13** SEM pictures of (a) nonreactive and (b) reactive blend, after solvent extraction of the dispersed phase.

EMA network. The shape of the particles of the extruded blend in which the gel fraction of the EVA/EMA phase is low ( $g \approx 0.1$ ) remains spherical. However, the extent of cross-linking reaches a critical value, where the classical theories of coalescence and breakup become no more valid.

*Case 3:  $g^* < g$ .* At a higher gel fraction, the number of free chains in the EVA/EMA network vanishes. Then, interpenetration of EVA/EMA droplets is only partially possible, as illustrated in Figure 12, and it should be more appropriate to discuss a “coagulation” mechanism. SEM observations [Fig.

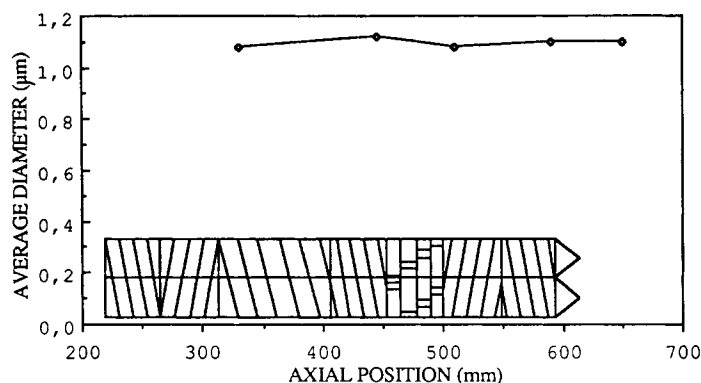
13(b)] show that the shape of the largest particles is no more spherical when the gel fraction of the dispersed phase is about 0.8. We can expect that the morphology of such a blend would be stabilized by the total cross-linking of the dispersed phase.

To verify this last assumption, a complementary experiment was performed for a reactive blend preliminary extruded with the long-barrel extruder, described in the Materials section. This extruder allowed long residence times (about 3 min), which permitted the full development of the cross-linking reaction. The insoluble fraction of the EVA/EMA phase obtained was 0.40 and droplet size was 1.1  $\mu\text{m}$ . This blend was then extruded through the short-barrel extruder, to observe the morphological changes along the screws. It can be verified in Figure 14 that the initial size of 1.1  $\mu\text{m}$  was conserved all along the screws, from the feeder zone to the die. In this case, the dispersed phase can be considered as a “solid elastic” filler, which cannot be subjected any more to deformation and breakup or to coalescence.

Therefore, these results put into evidence that development of *in situ* cross-linking of the EVA/EMA phase was a good way to stabilize the blend morphology for further processing steps.

### ***Rheological Behavior of the Reactive Blends***

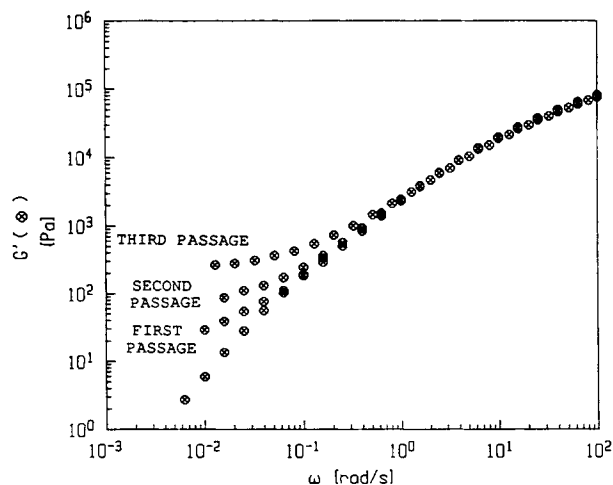
To explain the mechanisms of stabilization of the morphology, some experiments were carried out on a mechanical spectrometer (Rheometrics RMS 800) using a parallel-plate geometry. Extruded samples were melt at a temperature of 180°C during 3 min and experiments were carried out at a temperature of 153°C. At this temperature, a curing time experiment had shown that no modification developed in the sample during the measurements. The variations of the storage modulus  $G'$  for the successive extrusions are shown in Figure 15. At high frequency, the different samples exhibited the same behavior, identical to that of the nonreactive blend. However, at low frequency, a secondary plateau was observed. The value of this plateau increased with the number of extrusions and, thus, with the extent of the reaction, characterized by the gel fraction. This plateau could be attributed to an agglomeration of the particles during the successive extrusions. In fact, SEM observations refuted this assumption, although a “coagulation” process leading to a nonspherical shape of the particles was previously observed for a high value of the gel fraction of the EVA/EMA phase (in the third repetitive extrusion,  $g$  was about 0.8).



**Figure 14** Evolution of the average droplet size along the screws for a preextruded blend with a fully cross-linked dispersed phase ( $Q = 10$  kg/h;  $N = 100$  rpm).

Generally, such a secondary plateau is attributed to the deformability and shape relaxation of the droplets of the dispersed phase.<sup>30</sup> However, in the case of impact PMMA, Bousmina and Muller<sup>31</sup> showed that the corresponding long relaxation time mechanisms were not only due to the deformation of the rubber particles. On the other hand, cross-linked particles remain almost undeformed in a macroscopic strain. Therefore, the origin of this secondary plateau can provide from the presence of an interphase matrix/particle, which could induce a modification of long relaxation time mechanisms by trapping physical entanglements of the matrix chains. This interphase could be due to the presence of polymer structure, such as copolymers PP-(EVA/EMA). It was also proved, in the case of impact polyamide, that the secondary plateau mod-

ulus increased with the concentration of the copolymers at the interphase.<sup>32</sup> Therefore, this interpretation implies that an interphase has been created between EVA/EMA droplets and the PP matrix. Effectively, on SEM pictures, it may be observed that the outline of the droplets was very different between the reactive blend with high [ $g \approx 0.8$ , Fig. 13(b)] and low [ $g \approx 0.1$ , Fig. 13(a)] values of the gel fraction. As previously mentioned, the shapes were more irregular, but the pictures suggested the presence of an interphase PP-(EVA/EMA), which has been swollen by the solvent during the extraction step of the EVA/EMA phase. This interphase might result from thermal degradation of PP, which would induce free radicals in the system. These radicals would then start a reaction of cross-linking between the EVA/EMA chains and the PP chains of the matrix, allowing the formation of a copolymer at the interface. This interphase might also result from the trapping of PP chains at the interface by the EVA/EMA network.



**Figure 15** Variations of storage modulus vs. frequency with the number of passages in the extruder: (●) non-reactive blend.

## CONCLUSIONS

The cross-linking reaction of the dispersed phase largely modified the evolution of the blend morphology along the twin-screw extruder. A fine dispersion was always observed after the melting zone, but the increase of the viscosity of the dispersed phase during the chemical reaction shifted the equilibrium between breakup and coalescence and led to larger particles. As the EVA/EMA chemical network developed, different interpretations of coalescence and breakup processes have been proposed. For the higher values of the gel fraction of the dispersed phase ( $g > 0.4$ ), it seems more realistic to speak about a coagulation than a coalescence pro-

cess. *In situ* cross-linking of the EVA/EMA phase allowed the stabilization of the morphology, whatever the different stages of transformation processes of the polymer blend. No morphological changes were observed along the screws for a reactive blend preliminarily extruded at high temperature, in order to obtain a full extent of the cross-linking reaction.

Rheological studies have put into evidence the existence of a low-frequency plateau of an elastic modulus for the blends with a cross-linked dispersed phase. This permitted us to suspect high interactions at the interface PP-EVA/EMA.

This study has shown that the use of a chemical reaction that permitted us to modify *in situ* the rheology of the dispersed phase was an original way to understand the mechanisms of development and stabilization of the morphology in the incompatible polymer blends.

Financial support from the French Ministère de la Recherche et de l'Espace and from the Multibase Co. are gratefully acknowledged. The authors wish to thank Messrs. Coiffier, Coutier, and Milesi for fruitful discussions concerning this work.

## REFERENCES

1. S. Wu, *Polymer*, **26**, 1855 (1985).
2. L. A. Utracki, *Polymer Alloys and Blends-Thermodynamics and Rheology*, Hanser, Munich, 1989.
3. H. M. Elemans, PhD Dissertation, Eindhoven University of Technology, The Netherlands, 1989.
4. Z. H. Shi and L. A. Utracki, *Polym. Eng. Sci.*, **32**, 1834 (1992).
5. V. Bordereau, Z. H. Shi, L. A. Utracki, and C. M. Sammut, *Polym. Eng. Sci.*, **32**, 1846 (1992).
6. S. Lim and J. L. White, *Int. Polym. Proc.*, **8**, 119 (1993).
7. T. Nishio, Y. Suzuki, K. Kojima, and M. Kakugo, *J. Polym. Eng.*, **10**, 123 (1991).
8. U. Sundararaj, C. W. Macosko, R. J. Rolando, and H. T. Chan, *Polym. Eng. Sci.*, **32**, 1814 (1992).
9. A. De Loor, P. Cassagnau, A. Michel, and B. Vergnes, to appear.
10. A. K. Gupta, B. K. Ratman, and S. R. Srinivasan, *J. Appl. Polym. Sci.*, **45**, 1303 (1992).
11. D. Hoppner and J. H. Wendorff, *Colloid Polym. Sci.*, **268**, 500 (1992).
12. B. Z. Jang, D. R. Uhlmann, and J. B. Van der Sande, *J. Appl. Polym. Sci.*, **30**, 2485 (1985).
13. V. Choudary, H. S. Varma, and I. K. Varma, *Polymer*, **32**, 2534 (1991).
14. S. Thomas and A. George, *Eur. Polym. J.*, **8**, 1451 (1992).
15. S. Thomas, S. K. De, and B. R. Gupta, *Kunststoffe*, **7**, 665 (1987).
16. S. Thomas, *Mater. Lett.*, **5**, 360 (1987).
17. P. Cassagnau, M. Bert, V. Verney, and A. Michel, *Polymer*, **34**, 124 (1993).
18. P. Cassagnau, A. De Loor, R. Fulchiron, and A. Michel, *Polymer*, **34**, 1975 (1993).
19. T. Bartilla, T. Kirch, J. Nordmeier, E. Promper, and Th. Strauch, *Adv. Polym. Technol.*, **6**, 339 (1986).
20. J. M. Willis, B. D. Favis, and J. Lunt, *Polym. Eng. Sci.*, **30**, 1073 (1990).
21. K. Eise, J. Curry, and J. F. Nangeroni, *Polym. Eng. Sci.*, **23**, 642 (1983).
22. A. K. Bhowmick and T. Inoue, *J. Appl. Polym. Sci.*, **49**, 1893 (1993).
23. S. Wu, *Polym. Eng. Sci.*, **27**, 335 (1987).
24. G. Serpe, J. Jarrin, and F. Dawans, *Polym. Eng. Sci.*, **30**, 553 (1990).
25. B. D. Favis and D. Therrien, *Polymer*, **32**, 1474 (1991).
26. A. Luciani, PhD Dissertation, Université P. et M. Curie, Paris, 1993.
27. N. Tokita, *Rubber Chem. Tech.*, **50**, 292 (1977).
28. I. Fortelny, D. Michalkova, J. Koplikova, E. Navratilova, and J. Kovar, *Makromol. Chem.*, **179**, 185 (1990).
29. L. A. Utracki and Z. H. Shi, *Polym. Eng. Sci.*, **32**, 1824 (1992).
30. D. Graebler, R. Muller, and J. F. Palierne, *Macromolecules*, **26**, 320 (1993).
31. M. Bousmina and R. Muller, *J. Rheol.*, **37**(4), 663, (1993).
32. H. Pernin, PhD Dissertation, Université de Pau et des Pays de l'Adour, 1992.

Received December 2, 1993

Accepted April 10, 1994