A Study of Dynamic Vulcanization for Polyamide-12 and Chlorobutyl Rubber

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ABSTRACT: Polyamide-12 and chlorobutyl rubber were blended by dynamic vulcanization in a high shear environment using curing systems based on sulfur, dithiocarbamate/ZnO, and 4,4-methylenebiscyclohexylamine/MgO. As expected, all blends with curing agents show increased tensile strength and elongation at break in comparison to blends without curing agents. Maximum mechanical properties are obtained at relatively low levels of curing agent in all systems. Hexane extraction of the mixtures and measurement of percentage of insolubles along with the swelling index of the rubber phase confirm that a high level of cure is achieved at low levels of curing agent. Although the curatives are designed for the rubber phase, differential scanning calorimetry results indicate that both phases are affected during the dynamic vulcanization process, with polyamide-12 showing a reduced melting temperature that is indicative of molecular weight reduction, structure changes, or reaction with the rubber phase. Scanning electron microscopy results indicate that phase size is reduced with increased blending time and level of curing agent. Rheological studies indicate that blends containing curing agents exhibit non-Newtonian behavior to a greater extent than polyamide or nonvulcanized polyamide/chlorobutyl rubber blends. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 871–880, 2003

Key words: blends; vulcanization; mechanical properties; differential scanning calorimetry; electron microscopy; rhealogy

INTRODUCTION

Polyamides and butyl rubbers have been identified as two useful sets of homopolymers for thermoplastic barrier compositions. Each of these polymers alone is known for its barrier characteristics, and blends of these polymers have been described for use in refrigeration hoses.[1–3] Although polyamide and butyl rubber would normally be incompatible in a mixture, there is evidence that blends of these systems can be successfully made with and without curing agents added to the blend. In a recent study undertaken in our laboratories,[4] we demonstrated that polyamide-12 appears to interact with butyl and bromobutyl rubbers during the blending process to form compatibilizing agents. These agents likely consist of graft and block polymers that persist at the interface of the two phases and stabilize the morphologic structure. No curing agents to promote dynamic vulcanization of the rubber phase during blending were used in that study.

Dynamic vulcanization is a process often used to produce blends of thermoplastics and vulcanizable elastomers, resulting in thermoplastic elastomer materials. Materials made by this method consist of a discontinuous phase of the crosslinked elastomeric component in a continuous matrix of the nonvulcanized thermoplastic component. In the polyamide/butyl rubber system, the continuous phase is expected to be polyamide and the discontinuous phase is expected to be crosslinked butyl rubber. Often these materials have properties that exceed block copolymer-type thermoplastic elastomers or other blends containing uncured mixtures.[5,6] Substantial work has been undertaken to determine the optimum choices for rubber, plastic, and curing systems in blends made by dynamic vulcanization.[7,8] Several publications have appeared over the years on the dynamic vulcanization of polyamide and butyl rubber systems.[1,2,9,10] In some of these blends, the butyl rubber component is modified with carboxyl, anhydride, or epoxy groups.[3] Halogenated copolymers of isobutylene and *para*-methyl styrene mixed with polyamides have also produced materials with useful properties.[11]

The majority of the publications on dynamic vulcanization of polyamide/butyl rubber blends focus primarily on the blending procedures and mechanical properties of the blends. There appears to be a lack of comparison data for differently prepared blends that have been molded under similar conditions, particularly samples made by injection molding. Little information also seems to be available on the rheological properties of blends made by different methods, the microstructure of mixtures during blending, and the effect of vulcanization on the polyamide component in
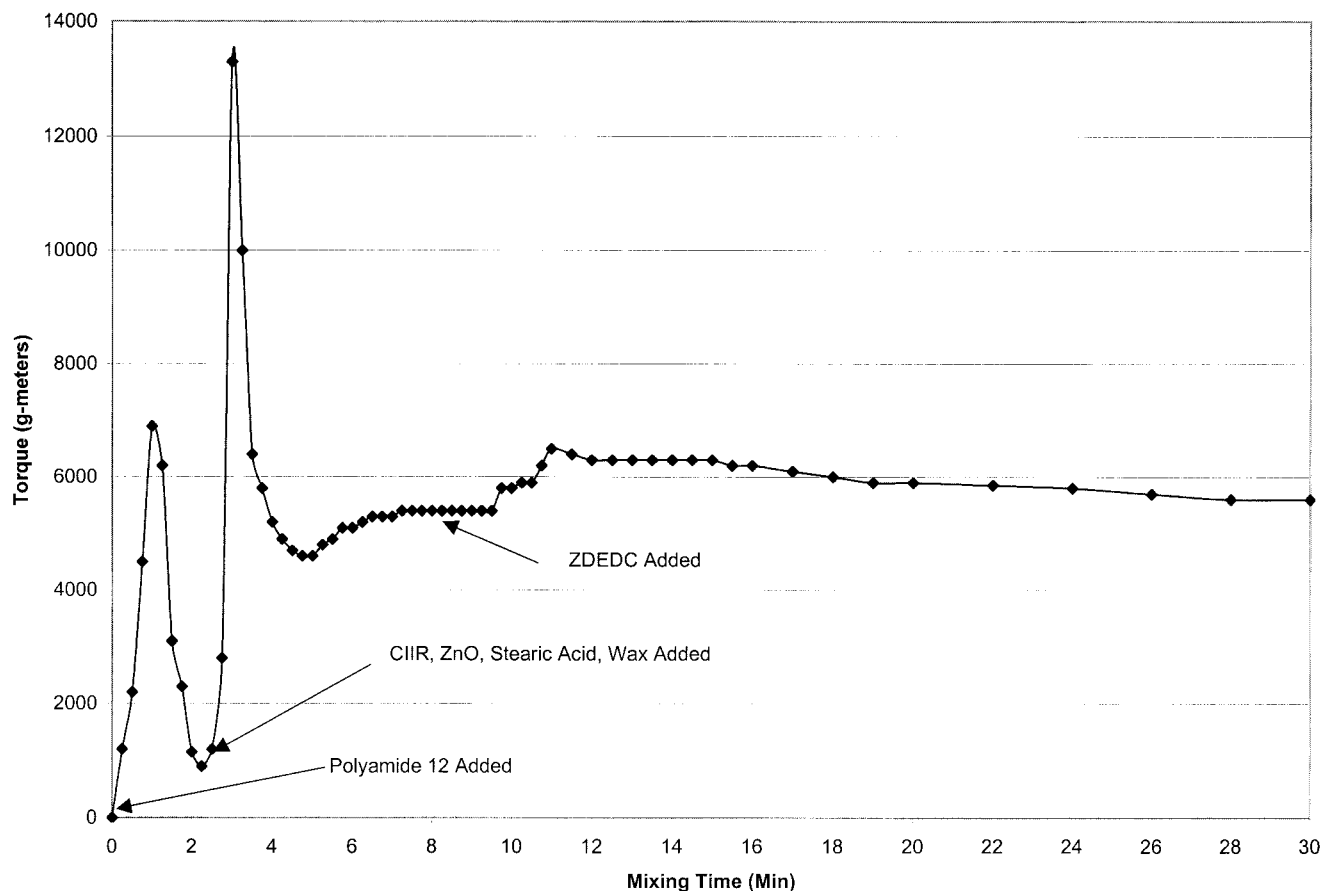
Figure 1 Torque measurement during extended mixing of 40PA/60CIIR blend with ZDEDC/ZnO curing system.

the rubber system. The present study will focus on elastomeric blends (i.e., those that have > 50% rubber) and attempt to address a number of these issues that are not described in detail in the literature.

Some of our preliminary dynamic vulcanization studies using polyamide-12 with both butyl and halobutyl rubber systems have shown that improved mechanical results can be obtained when the rubber chosen for these blends is chlorobutyl rubber. Thus, this paper focuses on a systematic study of dynamic vulcanization for polyamide-12/chlorobutyl (PA/CIIR) rubber. A ratio of 40PA/60CIIR was chosen to achieve a balance between mechanical properties and hardness. Three different vulcanization systems were considered in this study and compared with the case where no vulcanizing agents are added.

EXPERIMENTAL

Materials

Polyamide-12 (PA; Grilamid L25) was obtained from EMS-American Grilon, and chlorobutyl rubber from Exxon Chemical (CIIR; Chlorobutyl 1068; unsaturation, 2 mol%; chlorine level, 1.18–1.34%). Zinc diethyldithiocarbamate (ZDEDC), zinc dimethyldithiocarbamate (ZDMDC), and zinc dibutyldithiocarbamate

(ZDBDC) were supplied by R.T. Vanderbilt, zinc oxide (ZOCO 103) by Zochem, magnesium oxide (Maglite D) by C.P. Hall, tetramethylthiuram disulfide (TMTD) by H.M. Royal, 2-mercaptobenzothiazole (MBTS) by Uniroyal Chemical, stearic acid (Emersol 150) by Henkel, 4,4-methylenebiscyclohexylamine (MBCHA) by Aldrich, and Paracin 285 wax by CasChem.

Curing systems

Sulfur curing system

The sulfur curing system contained the following: 0–4 phr of sulfur (on CIIR) 1.8 phr of TMTD (on CIIR), 0.9 phr of MBTS (on CIIR), 6.0 phr of ZnO (on CIIR), and 2.4 phr of stearic acid (on CIIR).

Dithiocarbamate curing systems [including zinc oxide (ZnO)]

Three dithiocarbamate curing systems were used. (1) In the ZDEDC/ZnO system, the ZDEDC/ZnO ratio was 1:5.1 and the ZDEDC amount ranged from 0 to 2.8 phr (on CIIR). (2) In the ZDMDC/ZnO system, the ZDMDC/ZnO ratio was set at 1.8:9.3 phr (on CIIR) and the molar ratio was adjusted to equal a ZDEDC/ZnO content of 2.2:11.2 (on CIIR). (3) In the ZDBDC/

TABLE I
Mechanical Properties, Percentage Insolubles, and Swelling Index Values of 40PA/60CIIR Blends With Different Curatives[a,b]

Curative (phr on Rubber)	Ultimate Strength (MPa)[c]	Increase Over Control (%)	Elongation at Break (%)[d]	Increase Over Control (%)	Hardness (Shore D)	Amount of Insolubles in Hexane (%)[e]	Swelling Index (Hexane)[f]
No cure	9.4		90		42	45	
Sulfur cure							
0.8	14.4	53	330	270	49	99	1.30
1.6	14.1	50	333	270	49	100	1.31
2.4	13.9	48	341	280	49	99	1.30
3.2	14.1	50	352	290	48	99	1.29
4.0	13.7	46	344	280	48	98	1.30
ZDEDC/ZnO cure							
0.6/3.1	12.0	28	173	90	43	75	1.62
1.5/7.8	12.1	29	219	140	43	88	1.37
1.8/9.5	12.5	33	171	90	46	92	1.38
2.2/11.2	13.4	43	226	150	47	93	1.35
2.5/12.8	13.2	40	193	110	46	94	1.35
2.8/14.5	12.9	37	262	190	46	95	1.31
ZDMDC/ZnO cure							
1.8/9.3	14.2	51	248	180	47	95	1.34
ZDBDC/ZnO cure							
2.5/9.3	13.9	48	220	140	48	93	1.35
MBCHA/MgO cure							
1.3/3.3	11.0	17	152	70	46	99	1.34
2.7/6.7	11.3	20	163	80	46	100	1.33
4.0/10.0	11.2	19	116	30	48	99	1.27
5.3/13.3	11.0	17	117	30	48	100	1.24
6.7/16.7	10.8	15	100	10	49	100	1.29

[a] All properties measured at room temperature.
[b] All blends are mixed for 12.5 min, followed by injection molding at 180°C.
[c] Standard error, ±0.5.
[d] Standard error, ±12.
[e] Based on samples tested in triplicate; standard error, ± 1.
[f] Based on samples tested in triplicate; standard error, ± 0.02.

ZnO system, the ZDBDC/ZnO ratio was set at 2.5:9.3 phr (on CIIR) and the molar ratio was adjusted to equal a ZDEDC/ZnO content of 2.2:11.2 (on CIIR).

MBCHA/MgO curing system

In this system, the MBCHA amounts ranged from 0 to 6.7 phr (on CIIR), and the MgO/MBCHA ratio was 2.5.

Mixing procedure

All blends were made in a 258 cm³ capacity 5 hp Brabender mixer equipped with roller mixing blades at a target temperature of 190°C.

Nonvulcanized blends

PA was first added at 30 rpm mixing speed to the Brabender mixer and allowed to melt for 2 min. CIIR was then added, and the mixing speed was increased to 65 rpm. Mixing was continued for an additional 8 min. After a total mixing time of 10 min, the blend was removed from the mixer and cooled.

For nonvulcanized samples used in differential scanning calorimetry (DSC) analyses, mixing times were extended to obtain the desired sample.

Dynamically vulcanized blends

PA was first added at 30 rpm mixing speed to the Brabender mixer and allowed to melt for 2 min. CIIR was then added along with the stearic acid, metal oxides, and wax, and the mixing speed was increased to 65 rpm. Mixing was continued for an additional 6 min. After a total mixing time of 8 min, the active curing agent was added and allowed to mix for 4.5 min (total mixing time of 12.5 min). The blend was then removed from the mixer and cooled. For blends used in rheology evaluation, stearic acid and wax were left out of the blend formulation. A typical torque versus mixing profile for one of these blends is indicated in Figure 1. The rise in torque after 8 min of

TABLE II
DSC and Hexane Solubility Results for Polyamide-12/Chlorobutyl Rubber Blends (Nonvulcanized)[a]

Mixing Time (min)	Melting Temp (°C)[b]	Enthalpy of Fusion (J/g of Nylon)[c]	% Insolubles[d]
40 PA/60 CIIR (reference)			
0	178.9	54.2	
40 PA/60 CIIR (no curatives)			
8	178.2	52.5	
12.5	177.4	51.5	45
15	177.4	52.6	
17.5	177.9	52.7	
20	177.5	53.5	
25	178.3	53.5	
30	178.3	54.9	41

[a] Based on samples tested in duplicate.
[b] Expected error, ±0.15°C.
[c] Enthalpy calculated based on weight of polyamide present in blend; expected error, ±1%.
[d] Standard error, ±1.

mixing is most likely due to crosslinking in the rubber phase after the active curing ingredient is added.

All dynamically vulcanized blends used for injection molding contained 0.8 phr Paracin 285 wax (on CIIR).

Testing and characterization of samples

Mechanical properties of blends were tested on specimens prepared directly by injection molding, with all zones adjusted to 180°C. A computerized Instron 4400 Universal Testing Machine was used to determine stress/strain characteristics on injection-molded samples according to the American Society for Testing and Materials procedure D638 (ASTM D638). Hardness values (Shore D) were determined by ASTM D2240.

For selective solvation on PA/CIIR blends, a 0.25 g sample of the blend in the form of small cut pieces (~ 1 mm) was suspended in reagent-grade hexane (Anachemia) and shaken for 48 h. This procedure was followed by centrifugation of the insoluble material

and determination of the percentage insolubles. Swelling index was determined on molded or pressed samples, ~ 1 cm square and 1.5 mm thick, that were immersed in hexane for 4 days. The swelling index was determined by comparison of the weight of the swollen sample to its weight after drying to constant weight.

Blends prepared by ASTM D 3417 were analyzed by DSC with a Perkin Elmer DSC-7 instrument. PA as well as PA/CIIR mixtures (with and without curing agent) were blended at 190°C, and samples were withdrawn from the mixture at specified time intervals and examined by DSC. The melting temperature and the enthalpy of fusion for the PA phase were recorded for each sample. A reference sample consisting of 40 parts PA and 60 parts CIIR, placed together in the DSC pan, was also evaluated. In each case, if multiple peaks occurred, the determination of melting temperature and enthalpy of fusion referred to the highest (second) peak. Results in our laboratories show that melting temperature and enthalpy of fusion values for injec-

TABLE III
DSC and Hexane Solubility Results for 40 PA/60 CIIR Blend with 2.2 phr ZDEDC/11.2 phr ZnO During Dynamic Vulcanization[a]

Mixing Time (min)[b]	Melting Temp (°C)[c]	Enthalpy of Fusion (J/g of Nylon)[d]	% Insolubles[e]	Swelling Index[f]
8	178.1	52.8	53	2.65
12.5	176.9	51.2	89	1.56
15	176.1	52.4	91	1.35
17.5	176.0	52.2	91	1.38
20	175.6	49.6	91	1.32
25	175.7	53.2	90	1.37
30	175.7	52.4	90	1.35

[a] Based on samples tested in duplicate.
[b] Curing agent added at the 8 minute mark.
[c] Expected error, ±0.15°C.
[d] Enthalpy calculated based on weight of polyamide present in blend; expected error, ±1%.
[e] Standard error, ±1.
[f] Standard error, ±0.02.

TABLE IV
DSC Data for PA/CIIR Blends with Different Curing Systems[a,b,c]

Curative	Melting Temp (°C)[d]	Enthalpy of Fusion (J/g of Nylon)[e]
None	177.7	55.2
Amine 1.3 phr	176.6	48.9
Amine 6.7 phr	175.1	45.8
Sulfur 0.8 phr	175.8	51.4
Sulfur 7.0 phr	175.3	53.9
ZDEDC 0.6 phr	177.9	52.5
ZDEDC 2.2 phr	176.4	50.1
ZDEDC 2.8 phr	175.8	51.0

[a] All samples produced after 12.5 min of blending.
[b] Specimens for this evaluation were injection molded prior to measurement by DSC.
[c] Based on samples tested in duplicate.
[d] Expected error, ±0.15°C.
[e] Enthalpy calculated based on weight of polyamide present in blend; expected error, ±1%.

tion molded and noninjection molded samples are within experimental error for PA/CIIR blends. The blends containing PA, CIIR, and curing agent were also analyzed for percentage insolubles and swelling index of the rubber phase.

Scanning electron microscopy (SEM) was conducted using a variable pressure LEO 1455VP microscope. Specimens were prepared by fracture after immersion in liquid N_2. The blends were mounted on aluminum stubs with carbon paint, and examined without coating at low pressure using a Robinson Backscatter Detector.

The rheological properties of the blends were evaluated according to the ASTM D5422/C.W. Brabender procedure. This procedure allows for measurements of melt viscosity at various shear rates. A Brabender plasticorder extruder equipped with a 19.05 mm diameter screw (L/D, 25:1; compression ratio, 3:1) was used. This extruder was equipped with capillary dies D (L/D 10) and E (L/D 15), for evaluation at extruder speeds of 10, 20, and 30 rpm. Melt temperature at the capillary was maintained at 205°C.

RESULTS

Mechanical and solution properties of blends

The mechanical and solution properties of PA/CIIR blends with different types and quantities of curatives are summarized in Table I. With only 0.8 phr sulfur in the system, the tensile strength increases by > 50% and the elongation by 270%, in comparison to the case where no curing agents are present. Hardness also increases with the addition of a small amount of sulfur. Further additions of sulfur to the blends do not dramatically change any of the mechanical results. (Sulfur curing systems are known to be used at levels as low as 0.5 phr sulfur[12]). The crosslinking of the

rubber phase may be affected by other components in the curing system.

Similar results are achieved for ZDEDC/ZnO vulcanization, and mechanical properties reach a plateau at approximately 1.5 phr ZDEDC. As curing agent is increased from zero to 2.2 phr ZDEDC, tensile strength and elongation values increase by > 40% and 150%, respectively. Hardness values reach a plateau at 2.2 phr ZDEDC. In the MBCHA/MgO system, a plateau is reached at ~ 1.3 phr MBCHA, in spite of the fact that the patent literature[2] normally recommends ~ 4 phr of this curative. At 1.3 phr MBCHA, the tensile strength and elongation values exceed those in blends prepared with no vulcanization agents by ~ 20% and ~ 150%, respectively. Further increases of this curative result in a loss of percent elongation at break.

Overall, the highest values of ultimate strength (14.4 MPa) and elongation at break (352%) are obtained with the sulfur curing system. Hardness is dependent on the degree of cure and varies from 42 Shore D in the nonvulcanized system to 49 in the vulcanized system. The lowest values of hardness occur in the ZDEDC/ZnO cure system.

The percentage insolubles and swelling index values for each of these samples (Table I) reach a plateau at relatively low levels, particularly in the sulfur and MBCHA/MgO curing systems. This result indicates that the rubber phase is crosslinked with low quantities of curing agent in these blends. The highest values of swelling index and lowest percentage insolubles are observed for ZDEDC/ZnO vulcanization, indicating lower crosslink densities for the rubber phase at relatively low ratios of curing agent. Swelling index values for the MBCHA/MgO cure system reach the lowest values of any of the curing systems, and these are paralleled by lower ultimate strength and elongation at break values.

For all three curing systems the tensile strength and elongation at break values generally reach a plateau

TABLE V
Effect of Mastication on the DSC Results for Polyamide

Mixing Time (min)	Melting Temp (°C)[a]	Enthalpy of Fusion (J/g)[b]
Polyamide-12		
0	179.3	53.5
2	180.2	56.3
8	180.0	57.2
12.5	180.3	60.1
15	179.9	58.6
17.5	180.5	56.8
20	179.9	57.8
25	180.2	57.5
30	179.7	59.8
Polyamide-12 with 1.3 phr ZDEDC/6.6 phr ZnO		
30	180.1	59.2

[a] Experimental error not exceeding ±0.2 °C.
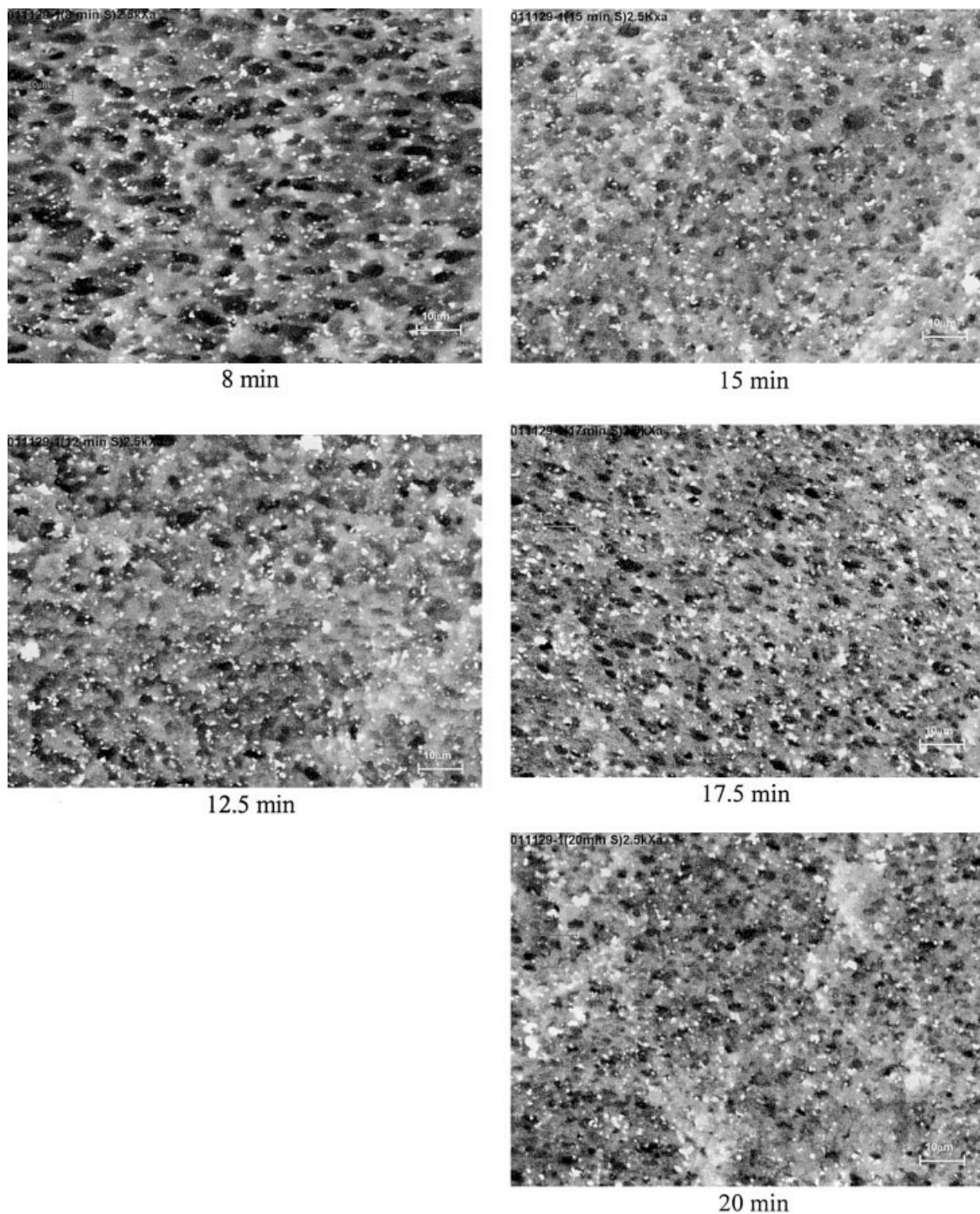[b] Standard deviation of 1.5 J/g.

Figure 2 SEM micrographs for fractured cross sections of 40PA/60CIIR blends with 2.2 phr ZDEDC/11.2 phr ZnO curing agent after different blending intervals.

when the percentage insolubles and swelling index of the rubber phase reach their maximum values. ZD-MDC and ZDBDC vulcanizations achieve higher values of percentage insolubles and higher tensile strength and elongation at break values than comparable ZDEDC vulcanizations.

Separate tests, not presented in Table I, show that CIIR cured by 2.2 phr ZDEDC/11.2 phr ZnO has a

tensile strength of 2 MPa and elongation at break of 575%.

DSC experiments undertaken on blends during dynamic vulcanization

A number of blends of PA and CIIR were tested by DSC. The melting points and heats of fusion results for

30 min
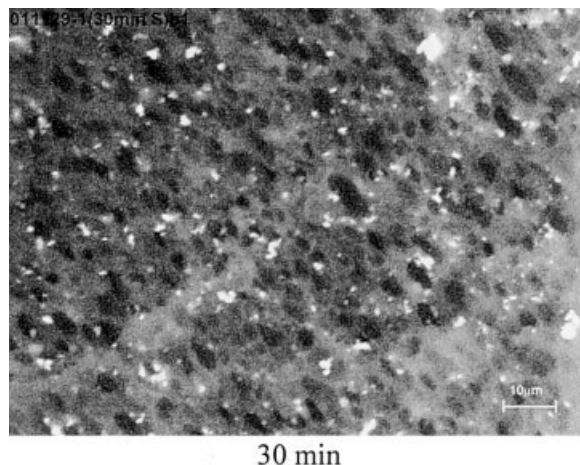
Figure 2 *(Continued from the previous page)*

PA in PA/CIIR mixtures are shown in Tables II–IV. When no curatives are used (Table II), a comparison of DSC results with those of an unblended reference sample of PA and CIIR shows very little change. In contrast, when 2.2 phr of ZDEDC/ZnO curing agent is added to the system (Table III), there is a steady decrease in the peak temperature for the first 15 min of mixing, after which time no additional significant change is observed. During the blending period, the percentage of insolubles in the blends increases after the ZDEDC agent is added at the 8-min mark. The swelling index of the rubber phase drops rapidly and reaches a plateau at ∼ 15 min of mixing. (Swelling index values in Tables I and III cannot be directly compared because the samples in Table I have gone through an additional injection molding step prior to measurement of swelling index.)

A comparison of DSC results for PA/CIIR blends containing different curing systems after 12.5 min of blending, followed by injection molding at 180°C, is made in Table IV. The results show that the melting temperature of the PA phase is affected by the amount of curative added. Reductions in peak temperature of up to 2.5°C are seen at the higher levels of curative in each blend. Enthalpy of fusion results of the PA phase are similar for the sulfur and ZDEDC systems; the amine/MgO curing system results in the lowest values of enthalpy of fusion.

The reduction in PA melting temperature when PA and CIIR are dynamically vulcanized suggests that the PA phase be likely affected during the rubber curing process. This effect is not seen in PA/CIIR mixtures without curing agent.

To compare PA/CIIR mixtures with PA homopolymer, the homopolymer was masticated for up to 30 min and then examined by DSC (results are shown in Table V). There is an initial small increase in melting temperature after the compounding operation is begun, followed by very little further change over 30 min of mixing. There is a small increase in the enthalpy for all masticated samples. Furthermore, when a ZDEDC/ZnO curing system is added to PA (without CIIR present) and the blending operation is continued for a 30-min period, there is very little change in the melting temperature and enthalpy. Thus, the curing agent on its own has very little effect on PA during blending.

SEM micrographs of PA/CIIR blends

Fractured cross sections of 40:60 blends of PA/CIIR with 2.2 phr ZDEDC/11.2 phr ZnO curing agent over selected time intervals between 8 min and 30 min of blending are shown in Figure 2. The white dots in each of the photographs are indicative of the ZnO component in the blend. This curing agent is already well dispersed throughout the blend at 8 min, including uniform dispersion across both phases in the mixture. The gray and black portions of the micrographs most likely indicate the PA and CIIR phases, respectively, and it is evident that the CIIR phase becomes smaller over time. At 8 and 20 min of blending, the particles are in the size ranges of 10 and 1–2 μm, respectively. The largest reduction in size occurs between the 8- and 12-min marks (4 min after adding the curative).
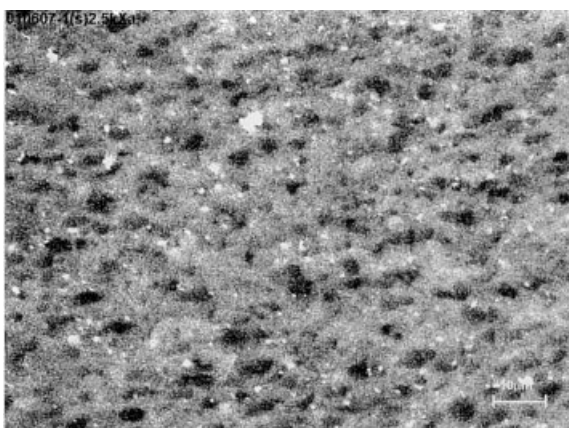
A number of fractured cross sections of PA/CIIR blends containing increasing quantities of the ZDEDC/ZnO curing system (0.6–2.8 phr ZDEDC) after 12.5 min of mixing are shown in Figure 3. The discrete phase size is as large as 5 μm at low levels of curing agents (0.6 phr) and ∼ 1–2 μm at higher levels (2.8 phr).

A comparison of the three curing systems employed in this study at 12.5 min of blending, using near optimum levels of curing agent for each system, is shown in Figure 4. The smallest phase size exists in the ZDEDC system and the largest phase size in the sulfur system.
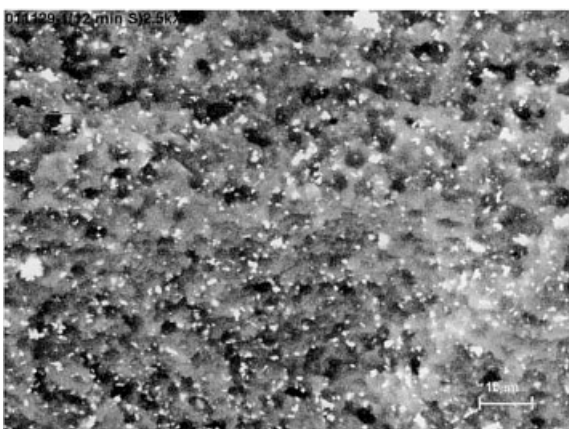
Rheology of PA/CIIR blends

The Braebender rheological procedure used in this study allows one to obtain apparent melt viscosity values at various shear rates, in contrast to a standard melt flow index that is determined at a very low shear rate. Rheological properties were measured for PA homopolymer, a nonvulcanized 40 PA/60 CIIR blend, and three dynamically vulcanized 40 PA/60 CIIR blends. The curing agents and levels (based on rubber content) for these blends were sulfur (4 phr), ZDEDC/ZnO (2.8:14.5 phr), and MBCHA/MgO (6.7:16.7 phr). The results of the experiments are shown in Figure 5.
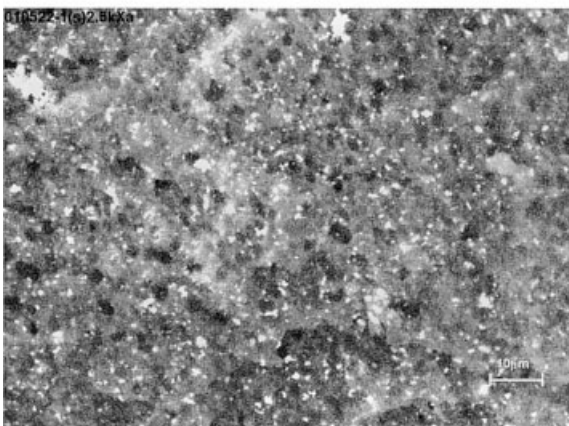
As CIIR is added to PA, the viscosity of the blend increases. The blends containing curing agents are higher in viscosity than those that do not have curing agents. The blend cured with MBCHA/MgO has the highest overall viscosity, which is substantially higher than those of blends prepared with the ZDEDC/ZnO

cantly affected by shear rate. The viscosity greatly decreases as shear rate increases, indicating a higher degree of non-Newtonian behavior in dynamically vulcanized blends. A comparison of Figures 4 and 5 also seems to indicate that there is no correlation between the melt viscosity of blends and the particle size of the dispersed phase.
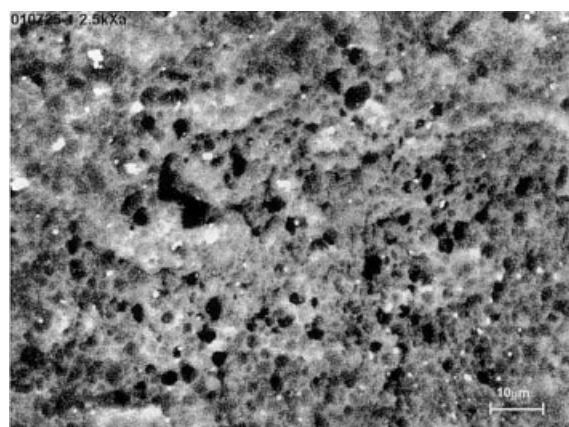

Figure 3 SEM micrographs for fractured cross sections of 40PA/60CIIR blends after 12.5 min with different levels of ZDEDC/ZnO curing agent.
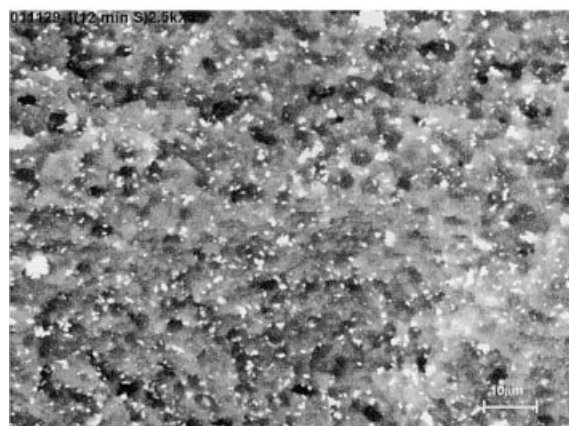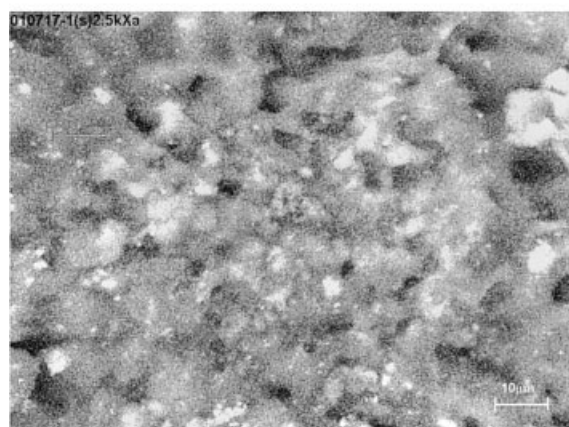
or sulfur curing systems. This high viscosity may indicate some interaction between the PA component and the MBCHA/MgO curing system, which may lead to an increase in viscosity of the PA phase.

Plots of viscosity versus shear rate show moderate reduction in viscosity with shear rate for PA and nonvulcanized PA/CIIR blends. In contrast, the melt viscosity of dynamically vulcanized blends is signifi-

Figure 4 SEM micrographs for fractured cross sections of 40PA/60CIIR blends after 12.5 min with different curing agents.
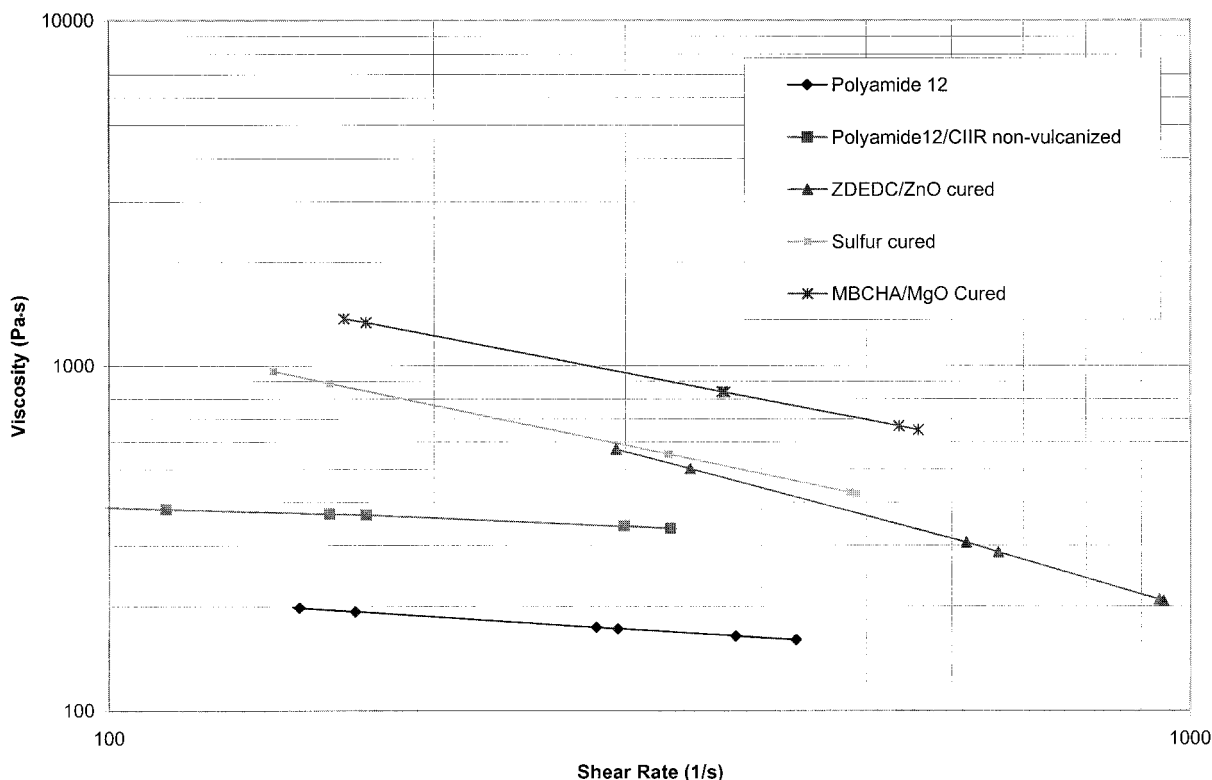
Figure 5 Rheological properties of 40PA/60CIIR blends at 205°C.

DISCUSSION

Dynamic vulcanization in each of the cure systems in this study provides improved tensile and elongation properties for injection-molded samples compared with blended systems containing no curing agents. The best mechanical properties results are obtained with the sulfur curing system, which provides up to 53% improvement in tensile strength and 270% improvement in elongation at break. All curing agents increase the hardness in these blends, but this result is much smaller proportionately than the improvement in tensile properties.

The properties obtained by blending are dependent on the curing system used. The dithiocarbamate system closely follows the sulfur system, with a 43% maximum improvement in tensile strength and 150% maximum improvement in elongation. The amine curing system (MBCHA/MgO) provides the lowest improvement in tensile strength (20%) and elongation (80%). The lower values observed in this curing system may be due to interaction of curing agent with the PA phase during the vulcanization process.

It is surprising to note that the sulfur system retains the largest particle size of the three curing agents. This result is in contrast to the observation of Coran and Patel[5] that lower particle size for polypropylene/EPDM blends is usually associated with increased elongation at break. It also appears that relatively little curing agent is required to increase the mechanical properties of blends of PA with CIIR. Indeed, in all cases, these properties of the blends level out at relatively low quantities of the curing system.

The SEM results show that an increase in blending time decreases the phase size of both PA and CIIR phases, particularly during the first 15 min of mixing. In addition, it has been shown that the phase size decreases with increasing amounts of curing agent, despite the fact that the mechanical properties reach a plateau at relatively low values of curing agent.

The DSC results reveal that PA is not a neutral component during the blending process. Although the ZDEDC/ZnO curing system has virtually no effect on the blending of PA alone, the effect of this curing system is quite pronounced in 40PA/60CIIR blends. As dynamic vulcanization time increases in PA/CIIR blends containing a curing system, the melting temperature of the PA phase decreases for the first 15 min of blending, and then remains unchanged for the second 15 min of blending. This result is likely associated with a chemical and/or physical interaction between the PA and CIIR phases during curing. The decrease in the melting point of PA is not likely due to the degradation of PA during dynamic vulcanization, because shear degradation of the PA phase would continue rather than level off after 15 min.

The dynamic vulcanization process significantly affects the rheological properties of PA/CIIR systems, resulting in increased viscosity at low shear rates and increased dependence of viscosity on shear rate. For

dynamically vulcanized blends, viscosity greatly decreases as shear rate increases. Furthermore, different curing systems may affect viscosity in different ways. The MBCHA/MgO curing system increases viscosity more than the other curing systems evaluated, indicating a possible interaction with the PA component of the blend. There also seems to be a lack of correlation between particle size of the dispersed phase and the melt viscosity of the blends.

The swelling index values for 40PA/60CIIR blends are all fairly similar except for ZDEDC/ZnO at the lowest loading (Table I) and shortest cure time (Table III). Although PA is not soluble in hexane, results in our laboratories have shown that samples of this polymer increase by at least 1% by weight when immersed in hexane. We thus expect that there is sufficient diffusion in and out of a blend of PA and CIIR to allow for swelling of the rubber phase. Z. Rigbi[13] reported that high swelling pressures are developed in crosslinked rubber systems. It is expected that these pressures are sufficiently high that the PA phase cannot completely restrict the swelling of the particulate rubber phase in these blends.

Finally, it is interesting to contrast the results of 40PA/60CIIR TPE blends with those for cured samples of pure CIIR. The latter samples, with a sulfur curing system, produce tensile strengths of 2 MPa and elongation at break values of 575%. Dynamic vulcanization of PA/CIIR blends not only preserves the rubbery nature of the materials, but also produces a thermoplastic elastomer. In addition, much higher tensile strengths and reasonable elongation at break values are achieved (14 MPa and 350%, respectively).

CONCLUSIONS

1. A comparison of mechanical properties for injection molded samples of dynamically vulcanized PA/CIIR blends, prepared under similar conditions but with different curatives, show that all samples have improved properties when curatives are present compared with when no curatives are present. The best mechanical properties are obtained with a sulfur-based cure and the lowest with an MBCHA/MgO-based cure. In particular, the sulfur-based system tends to give better values of percentage elongation.
2. Mechanical properties generally increase during vulcanization and reach a plateau at relatively low quantities of vulcanization agent.
3. The process of dynamic vulcanization not only affects the CIIR phase but also the PA phase. This effect is demonstrated by reduced values of peak melting temperature in the PA phase and small changes in the enthalpy of fusion.
4. During the vulcanization process, a progressive decrease in the particle size of both phases is observed with mixing time, particularly with addition of vulcanization agent. Both the type and amount of vulcanization agent added to the system affect the decrease in particle size.
5. The dynamic vulcanization process significantly affects the rheological properties of the PA/CIIR system, resulting in increased viscosity at low shear rates and increased dependence of viscosity on shear rate. For dynamically vulcanized blends, viscosity greatly decreases as shear rate increases. Furthermore, different curing systems may affect viscosity in different ways. The MBCHA/MgO curing system increases viscosity more than the other curing systems evaluated, indicating possible interaction with the PA component of the blend. The particle size of the dispersed phase in these blends does not seem to correlate with the melt viscosity of these blends.

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