Effect of Butyl Rubber Type on Properties of Polyamide and Butyl Rubber Blends

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ABSTRACT: Polyamide-12 was blended with butyl rubber, bromobutyl rubber, and chlorobutyl rubber with and without a sulfur curing system. Mechanical properties for dynamically vulcanized blends generally exceed those made with no vulcanization. Chlorobutyl-containing blends prepared by dynamic vulcanization have higher tensile strength and elongation at break values in comparison to those made from other butyl rubbers. For a variety of polyamide/rubber blends made by dynamic vulcanization, there is very little effect of rubber percentage unsaturation and Mooney viscosity on the mechanical properties of the blends. In chlorobutyl-containing blends prepared by dynamic vulcanization, the swelling index values attributed to the rubber portion decrease as rubber content decreases, and it is likely that the polyamide phase completely surrounds the rubber particles at compositions exceeding approximately 25% poly-amide. Swelling index results can be correlated with elongation at break values for similar blends. The results of differential scanning calorimetry suggest that the polyamide phase is not a neutral component in high shear mixing with butyl rubbers with or without curing agents. Rheological studies indicate strong non-Newtonian behavior for all blends of polyamide-12 with butyl rubbers. Scanning electron microscopy on polyamide-12/butyl rubber blends indicates compatibility for butyl rubbers in the order of chlorobutyl > bromobutyl > butyl rubber. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1423–1435, 2004

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

INTRODUCTION

It is widely known that high shear melt mixing can be used to produce blends of thermoplastics and vulcanizable elastomers, resulting in thermoplastic elastomer materials and other thermoplastic vulcanizates. This mixing can be undertaken in the presence or absence of a curing system, and blends made by either method produce unique compositions with properties reflective of the component elastomers and thermoplastics. In the absence of a curing system, the phase morphology is determined by the relative concentrations of the polymeric components, the interfacial tension between them, the conditions used to process the mixture, and the viscosity differences between the components.[1] The addition of compatibilizing agents can significantly reduce the dimensions of the dispersed phase[2] in some systems.

When curing compounds are added to the blend components after sufficient melting and mixing of rubber and plastic, the process is called dynamic vulcanization, and the materials produced can be chopped, pelletized, and remelted in an injection molding or extrusion operation to make articles. Often these materials have superior properties to that of block copolymer-type thermoplastic elastomers or other blends containing uncured mixtures[3–6] and can also be readily recycled after regrinding. Substantial work has been undertaken to determine the optimum choices for rubber, plastic, and curing systems in blends made by dynamic vulcanization.[6–9] The effect of morphology on the properties of some thermoplastic vulcanizates is now becoming understood.[7]

Several publications have appeared over the years on the dynamic vulcanization of polyamide and butyl rubber systems.[10–17] In some of these blends the butyl rubber component is modified with carboxyl, anhydride, or epoxy groups.[14] Both polyamide and butyl rubber are polymers known for their barrier characteristics,[18,19] and successful blending of these polymers by dynamic vulcanization has produced thermoplastic barrier compositions for use in such applications as refrigeration hoses.[10,11,14,15] Materials made by this method consist primarily of a discontinuous phase of the cross-linked elastomeric component (butyl rubber) in a continuous matrix of the non-crosslinked thermoplastic component (polyamide).

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In previous studies undertaken on polyamide/butyl rubber blends in our laboratories[16,17] it was shown that these two normally incompatible systems can be mixed in a high shear environment with and without the presence of curing agents added. The high shear environment seems responsible for producing an interaction between the polyamide and rubber components during processing. This was confirmed by measurement of the melt viscosity and differential scanning calorimetry (DSC) of these blends, along with analysis of the extracted soluble butyl rubber component, which supports the presence of small quantities of block or graft polymers in the system.[16]

A systematic study of dynamically vulcanized polyamide-12/chlorobutyl rubber (PA/CIIR) mixtures indicates that all blends that employ curing agents show increased tensile properties, particularly elongation at break, in comparison to blends containing no curing agents. Using several different curatives (sulfur, dithiocarbamate/ZnO, and 4,4-methylenebiscyclohexylamine/MgO), it was shown that maximum mechanical properties are obtained at relatively low levels of curing agent in all systems. Hexane extraction of the mixtures and measurement of percentage insolubles along with swelling index of the rubber phase confirm that a high level of cure is likely achieved using low levels of curing agents.[17]

The objective of the present study was to examine a variety of PA/butyl rubber blends prepared with and without dynamic vulcanization. To observe the effect of the rubber properties on the blend, the butyl rubbers were varied in halogen content, halogen type, percentage unsaturation, and Mooney viscosity. Halogenation is known to enhance the rate of the cross-linking reaction over that of nonhalogenated butyl rubbers. For blends prepared by dynamic vulcanization, a vulcanizing system based on sulfur was used, because these are generally effective on butyl rubber systems, both halogenated and nonhalogenated. Varying levels of PA in PA/CIIR blends were also tested. Pure rubber compounds made from the same materials used in the blends were prepared for comparison. Selective solvation with hexane, DSC, and scanning electron microscopy (SEM) were used to examine a number of PA/rubber blends (with and without cross-linking agents) and pure rubber systems to determine the effect of blending on the morphology of the rubber component in these blends. One composition was blended in the absence of vulcanizing agents, cooled, and mixed with vulcanizing agents at a temperature below the activation of vulcanization. This blend was then compression molded and vulcanized to provide a statically cured sample that could be compared to those made by dynamic vulcanization.

EXPERIMENTAL

Materials used

Polyamide-12 (PA; Grilamid L16) was obtained from EMS-American Grilon (Sumter, SC). Butyl 068, chlorobutyl 1066, 1068, and SB5066, and bromobutyl 2222 rubber were supplied by Exxon Chemical (Sarnia, ON, Canada). Butyl 100, 301, and 402, chlorobutyl 1255, and bromobutyl X2 rubber came from Bayer Chemical (Sarnia). Zinc oxide was supplied by Zochem (Brampton, ON, Canada), tetramethylthiuram disulfide (TMTD) by H. M. Royal (Trenton, NJ), 2-mercaptobenzothiazole (MBTS) by Uniroyal Chemical (Elmira, ON, Canada), stearic acid (Emersol 150) by Cognis Canada (Toronto), and Paracin 285 wax by CasChem (Bayonne, NJ).

Sulfur curing system employed in this study

A sulfur-based curing system was used for pure rubber compounds and all blends.[20] The proportions of the curing components were as follows: 0–4 phr of sulfur (on rubber), 1.8 phr TMTD (on rubber), 0.9 phr of MBTS (on rubber), 2.4 phr of stearic acid (on rubber), and 6.0 phr of untreated ZnO (on total mass of PA and rubber).

Mixing procedure

All blends were made in a 258-cm^3-capacity 5 HP Plasticorder EPL-V5502 equipped with Prep Mixer type R.E.E.6 and type 808-2504/PSI/DTI Rheometer and temperature control (Brabender Instruments, Inc., Hackensack, NJ).

Nonvulcanized blends

PA was first added at 30 rpm mixing speed to the Brabender mixer at a target temperature of 190°C and allowed to melt for 2 min. Rubber was then added and the mixing speed 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.

Dynamically vulcanized blends

PA was first added at 30 rpm mixing speed to the Brabender mixer at a target temperature of 190°C and allowed to melt for 2 min. The rubber was then added along with 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
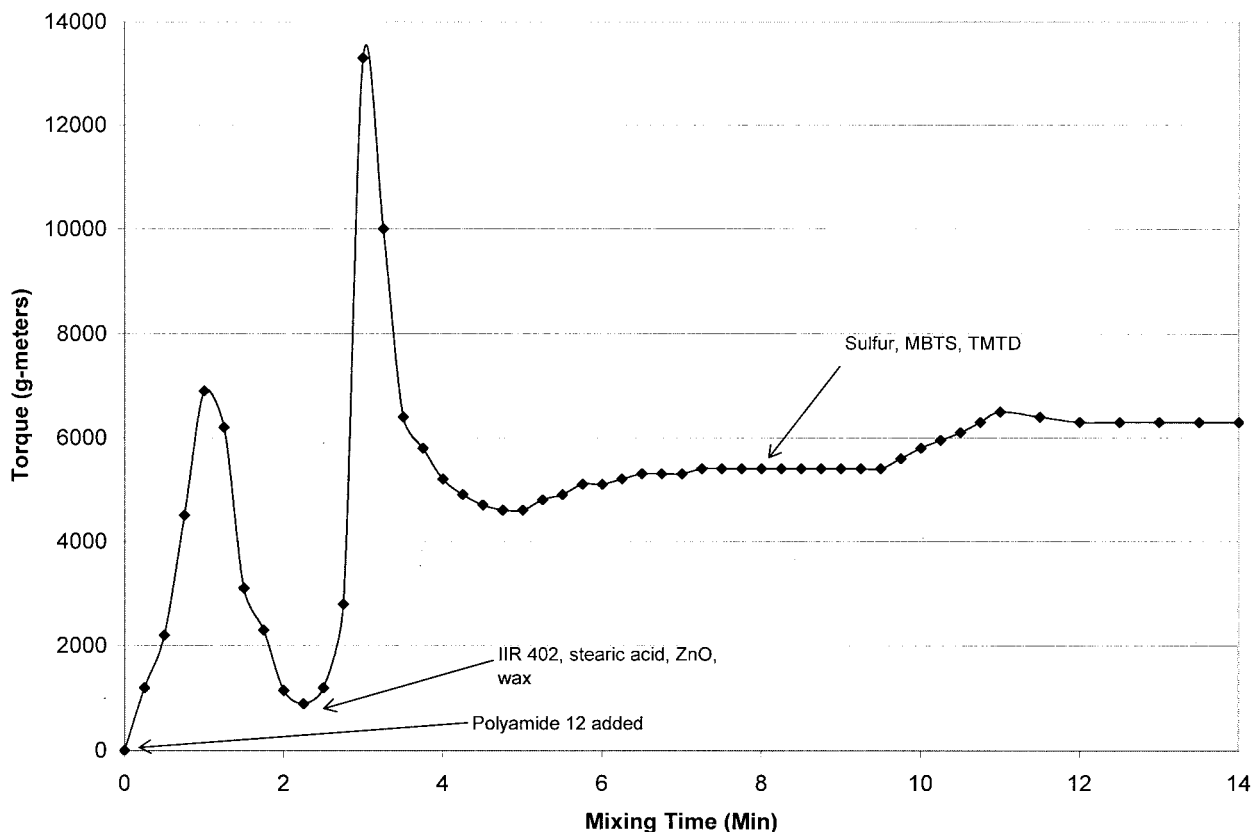
Figure 1   Torque measurement during extended mixing of 40PA/60IIR blend with sulfur curing system.

typical torque versus mixing profile for one of these blends is indicated in Figure 1. The rise in torque after 8 min of mixing is most likely due to cross-linking in the rubber phase after the active curing ingredient is added.

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

Postcured blend

This blend was made by the same procedure that was used for nonvulcanized blends. However, after removal from the mixer the blend was rapidly cooled, granulated, and then reintroduced to the Brabender mixer along with a sulfur curing system at a target mixing temperature of 60°C. The resulting mixture was masticated for 8 min. (The melt temperature did not rise above 109°C.) The mixture was then removed from the Brabender, cooled, and compression molded with static curing at 160°C for 30 min.

Rubber

Both halogenated and nonhalogenated butyl rubber were masticated at 25 rpm and a target temperature of 60°C for 3 min, after which stearic acid, zinc

oxide, and antioxidant were added and mixing was continued for an additional 2 min. MBTS and THTD were then added and mixing was continued for 3 min. Sulfur was then added and mixing was complete after an additional 2 min. The total mixing time was 10 min. The curing levels (based on rubber) were identical to those used in the dynamic vulcanization experiments. After blending was complete, the compound was compression molded at 160°C for 30 min.

Testing and characterization

Mechanical properties

For the statically cured blend the test specimens were cut from compression molded sheets. In all other blends, the mechanical properties 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 A and D) were determined by ASTM D2240.
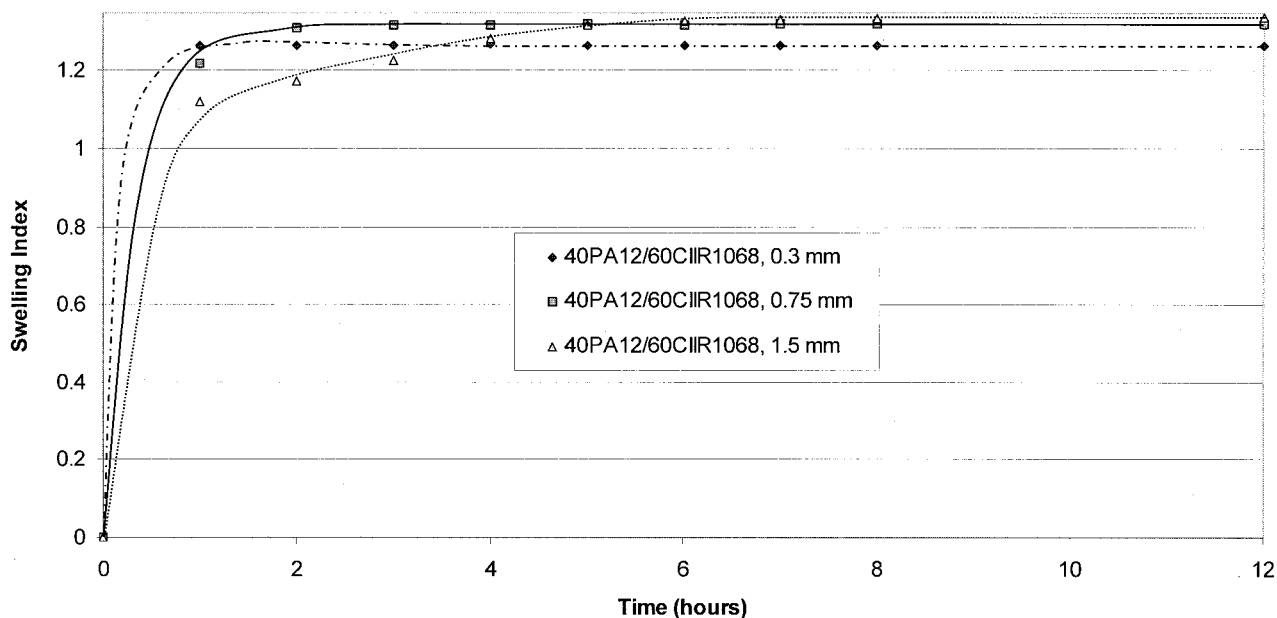
Figure 2 Effect of sample thickness on attainment of equilibrium swelling index.

Percentage insolubles and swelling index.

For selective solvation on PA/rubber blends, a 0.250-g sample of the blend in the form of small cut pieces (~1 mm) was suspended in reagent-grade hexane (Anachemia, Montreal, PQ, Canada) 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 to obtain equilibrium. The swelling index of a blend sample was determined by comparison of the weight of the swollen sample to its weight after drying to constant weight.

To determine the effect of exposure over time on the swelling index of blended samples, the swelling index versus time was determined for several 40PA/60CIIR blends with differing thickness of test specimen. Figure 2 indicates that equilibrium is established in less than 1 day for all samples, and the final swelling index is only marginally higher in samples with the greatest thickness. Thus, for all of the results reported in this study, the sample thickness was standardized at 1.5 mm to achieve the highest reliability in the results.

The swelling index of the rubber component in a PA/butyl rubber blend was calculated on the basis that hexane solvent, for practical purposes, neither dissolves nor swells the PA component in the blend. The swelling index (rubber component) is thus

$$\text{S.I. (rubber component)} =$$

$$\frac{\begin{pmatrix} \text{mass of rubber in sample +} \\ \text{mass of solvent after swelling} \end{pmatrix}}{\text{mass of rubber in sample}}.$$

The mass of rubber in the sample is proportional to the percentage rubber used to prepare the blend, and the mass of solvent in the sample after swelling is equal to the difference between the swollen and dry mass of the blend. By substitution, it is determined that

S.I. (rubber component)

$$= \frac{\text{S.I. (blend)}}{\text{proportion of rubber in blend}}$$

$$- \frac{\text{proportion of PA in blend}}{\text{proportion of rubber in blend}}.$$

Calculated values of S.I. (rubber component), representing normalized swelling indices for each composition, can be compared between blends of differing rubber proportions to determine the effect of increasing PA content on the swelling characteristics of the rubber component in blends.

Differential sanning calorimetry

For DSC, all PA/butyl rubber blends (with and without curing agent) were prepared at 190°C, followed by analysis on a Perkin–Elmer DSC-7 instrument (Perkin–Elmer Cetus Instruments, Norwalk, CT) according to ASTM D 3417. The melting temperature and the enthalpy of fusion for the PA phase were recorded for each sample. If multiple peaks occurred, the melting temperature refers to the highest (second) peak. For PA/CIIR blends, repetitive results in our laboratories indicate values of melting temperature and enthalpy of fusion that are within experimental error of each

TABLE I
Effects of Rubber Type on Properties of 40 PA/60 Butyl Rubber Blends[a,b]

Rubber grade	Unsaturation (%)	Mooney viscosity (@ 125°C)	Halogen content (%)	Ultimate strength (MPa)[c]	Elongation at break %[d]	Hardness Shore D	% Insolubles in hexane[e]	Swelling index — blend (hexane)[f]	Swelling index — rubber phase (hexane)[g]
(a) Blends made by dynamic vulcanization									
Butyl 068	0.8	47		9.1	93	47	97.2	1.29	1.48
Butyl 100	0.9	35		9.1	117	45	95.1	1.33	1.55
Butyl 301	1.91	49		9.1	117	48	94.0	1.30	1.52
Butyl 402	2.25	33		8.8	113	45	95.1	1.34	1.57
Chlorobutyl 1066	2% isoprene	38	1.26	13.3	281	50	97.1	1.23	1.38
Chlorobutyl 1068	2% isoprene	50	1.27	13.9	341	49	98.7	1.29	1.48
Chlorobutyl SB 5066	2% isoprene	40	1.50	13.4	266	50	96.9	1.25	1.42
Chlorobutyl 1255	1.8% isoprene	50	1.25	13.6	294	52	100.6	1.24	1.40
Bromobutyl X2	1.6% isoprene	50	2	12.2	140	51	99.5	1.30	1.50
Bromobutyl 2222	2% isoprene	37	2	12.4	141	49	98.9	1.27	1.45
(b) Blends made with no vulcanizing agents									
Butyl 402	2.25	33		10.0	81	41	42.3		
Chlorobutyl 1068	2% isoprene	50	1.27	9.4	90	42	44.9		
Bromobutyl X2	1.6% isoprene	50	2	10.7	99	45	48.3		

[a] All properties were measured at room temperature.
[b] All blends were mixed for 12.5 min, followed by injection molding at 180°C.
[c] Standard deviation of ±10%.
[d] Standard deviation of ±15%.
[e] Based on samples tested in triplicate. Standard deviation of ±2%.
[f] Based on samples tested in triplicate. Standard deviation of ±1%.
[g] Swelling index of the rubber phase calculated on the basis that the polyamide component does not swell. Solvent associates exclusively with the rubber component:

$$\text{S.I. (rubber component)} = \frac{\text{S.I. (blend)}}{\text{proportion of rubber in blend}} - \frac{\text{proportion of polyamide in blend}}{\text{proportion of rubber in blend}}.$$

other for injection molded samples and granulated pellets.

Rheology

The rheological properties of the blends were evaluated according to ASTM D5422/C.W. Brabender procedure. This procedure allows for measurement of melt viscosity at various shear rates. The Brabender Plasticorder (see mixing procedure) was attached to an extruder with a 19.05-mm-diameter screw (L/D 25/1, compression ratio 3:1), and 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.

Scanning electron microscopy

SEM was conducted using a variable-pressure LEO 1455VP microscope (Meridian Scientific Services, Stittsville, ON, Canada). Specimens were prepared by cutting with a sharp blade. The blends were mounted on aluminum stubs with carbon paint and examined without coating at low pressure using a Robinson backscatter detector.

RESULTS AND DISCUSSION

Mechanical and solution properties of blends

Several 40 PA/60 butyl rubber blends were prepared using various grades of butyl rubber, with and without cross-linking agents, and the results are summarized in Table I. A comparison was conducted among butyl (IIR), bromobutyl (BIIR), and CIIR rubbers, and the halogen level was varied from 0 to 2%. Unsaturation in the butyl rubber phase was varied from 0 to 2.25%, and Mooney viscosity varied from 33 to 50.

It can be observed that percentage unsaturation and Mooney viscosity values have little effect on the mechanical properties in IIR-containing blends. Percentage isoprene and Mooney viscosity also have relatively little effect on the properties of BIIR- and CIIR-containing blends. The principal effect on properties in these blends is the presence and type of halogen in the rubber phase.

TABLE II
Effect of Method of Preparation on Properties of 30 PA/70 CIIR[a] Blends

Method	Ultimate strength (MPA)[d]	Elong. @ break (%)[e]	Hardness (Shore D)	% Insolubles in hexane[f]	Swelling index —blend (hexane)[g]	Swelling index —rubber phase (hexane)[h]
No vulcanization[b]	6.2	120	31	30.7		
Dynamic vulcanization[c]	9.4	233	40	87.7	1.44	1.63
Postcure[b]	2.1	412	21	98.3	2.05[i]	2.52

[a] Based on CIIR 1068.
[b] Test specimens prepared by compression molding.
[c] Test specimens prepared by injection molding.
[d] Standard deviation of ±10%.
[e] Standard deviation of ±15%.
[f] Based on samples tested in triplicate. Standard deviation of ±2%.
[g] Based on samples tested in triplicate. Standard deviation of ±1%.
[h] Swelling index of the rubber phase calculated on the basis that the polyamide component does not swell. Solvent associates exclusively with the rubber component:

$$\text{S.I. (rubber component)} = \frac{\text{S.I. (blend)}}{\text{proportion of rubber in blend}} - \frac{\text{proportion of polyamide in blend}}{\text{proportion of rubber in blend}}.$$

[i] Absolute value (mass of swollen sample measured in closed vessel).

For blends prepared by dynamic vulcanization, the ultimate strength values are approximately 9, 12.3, and 13.5 Mpa for IIR-, BIIR-, and CIIR-containing blends, respectively. Percentage elongation values are approximately 110, 140, and 300%, respectively. Hardness values are generally higher in blends containing halogenated rubbers. All samples are more than 95% insoluble in hexane, with the majority in the range of 98–100%. Swelling index values range from 1.23 to 1.34 for these blends. The curing reaction in these samples appears to be virtually complete, which has generally been observed in our laboratories when the sulfur content in the formulation is greater than 2.0 phr. (In a few cases the percentage of insolubles is greater than 100%; this is attributed to tenacious entrapment of traces of solvent in the blend.)

Blends made with no added vulcanizing agents exhibit lower tensile strength and percentage elongation values, especially in halogenated rubber-containing blends. As expected, the percentage of insolubles is much lower in nonvulcanized blends, but still exceeds the proportion of PA in these blends (particularly for halogenated rubbers). This may be due to phase entrapment or cross-linking in the rubber phase and is consistent with our earlier report[16] that the reactivity of the rubber component in blends produced by high shear most likely leads to some block and/or graft rubber formation between the two otherwise incompatible materials.

Table II provides a further comparison of dynamic vulcanization to nonvulcanization for 30PA/70 CIIR blends, showing a significant decrease in ultimate strength, elongation at break, and hardness in the absence of curing agents. Also listed in Table II are the results of a 30PA/70 CIIR blend prepared by static (postcure) vulcanization. Although the main interest in this blend is the comparison of swelling index, it is seen that the ultimate strength of the statically cured blend is less than that of the nonvulcanized blend.

The mechanical and solution properties for a number of selected rubber and PA samples used in the PA/rubber blends are shown in Table III. To facilitate comparisons, the same curing system was used as for the dynamic vulcanization of blends reported in Tables I and II (sulfur level 2.4 phr). For rubber samples, the tensile strength and elongation values follow in the order of BIIR > CIIR > IIR. The hardness values for halogenated butyl rubbers are generally lower than for nonhalogenated butyl rubber, in contrast to comparable hardness values for PA/butyl rubber blends (Table I). The percentage of insolubles in all rubber samples exceeds 92%, and swelling index values in hexane for the halogenated samples reach values of 3.13 and 3.38 for BIIR and CIIR, respectively.

As noted earlier, the mechanical properties of CIIR-containing blends with PA exceed those of similar BIIR-containing blends. This is an unexpected result, given the fact that the mechanical properties in tested rubber samples strongly favor BIIR (Table III). This apparent anomaly may be explained by the kinetics and reactivity of the rubber components (including grafting and chemical interaction with the PA component) in blends. Rubber curing kinetics seem to have more impact on the mechanical properties of the blends than do the mechanical properties of the rubber components themselves.

Effect of rubber content on the properties of PA/CIIR blends

CIIR has been blended with increasing proportions of PA, and the mechanical properties are listed in Table

TABLE III
Properties of Polyamide and Sulfur Cured Butyl Rubber Samples[a]

Polymer	Ultimate strength (MPA)[b]	Elongation at break (%)[c]	Hardness (Shore A)	Hardness (Shore D)	% Insolubles in hexane[d]	Swelling index (hexane)[e,f]
Polyamide-12	43.9	355			100.0	1.00
Butyl 301	1.7	336	42		95.7	2.80
Bromobutyl X-2	8.3	824	37	7	94.8	3.13
Chlorobutyl 1068	2.0	496	36	7	92.8	3.38

[a] Rubber test specimens prepared by compression molding.
[b] Standard deviation of ±10%.
[c] Standard deviation of ±15%.
[d] Based on samples tested in triplicate. Standard deviation of ±2%.
[e] Based on samples tested in triplicate. Standard deviation of ±1%.
[f] Absolute values (mass of swollen samples measured in closed vessels).

IV, along with the results of exposure of these samples to hexane solvent. As expected, in dynamically vulcanized PA/CIIR blends, the ultimate tensile strength and hardness values increase with the addition of PA to the blend. However, the percentage elongation decreases in the range of 0–20% PA with increasing PA, but increases in the range of 20–40% PA. In all of these blends the rubber phase shows extensive curing, with percentage insolubles above 96% for all blends.

Experimental values of swelling index for the blends, calculated values of swelling index (based on a physical mixture of the components), and elongation at break values versus percent PA are plotted in Figure 3. As shown, for all proportions of PA the swelling indices of blends under dynamic vulcanization are substantially less than the theoretical values. It should also be observed that the swelling index curve undergoes a change in slope at approximately 20–25% PA, which corresponds to the composition where the elongation at break curve also reaches a minimum point. The change in slope of the swelling index curve may indicate the composition where the volume of the PA phase is sufficiently large to surround the rubber particles formed during dynamic vulcanization. Using this model, the elongation at break values should dramatically decrease in the early stages as PA is introduced into the blends. At a composition where PA becomes the continuous phase, the elongation at break will reach a minimum. Further increases in PA beyond this composition will not only change the rate of decrease in swelling index, but also enhance elongation at break values.

TABLE IV
Effect of Rubber Level on Properties of PA/CIIR Blends[a,b,c]

Blend	Ultimate strength (MPA)[d]	Elongation @ break (%)[e]	Hardness (Shore D)	% Insolubles in hexane[f]	Swelling index —blend (hexane)[g]	Swelling index —rubber phase (hexane)[h]
0PA/100CIIR[i]	2.0	496	7	92.8	3.38[j]	3.38
15PA/85 CIIR	2.9	188	18	81.1	2.20	2.43
20PA/80 CIIR	5.6	154	25	84.1	1.77	1.97
25PA/75 CIIR	7.7	180	36	86.8	1.55	1.74
30PA/70 CIIR	9.4	233	40	87.7	1.44	1.63
40PA/60 CIIR	13.9	341	49	98.7	1.29	1.48

[a] All properties measured at room temperature.
[b] All blends except for pure rubber are mixed for 12.5 min, followed by injection molding at 180°C.
[c] Based on CIIR 1068.
[d] Standard deviation of ±10%.
[e] Standard deviation of ±15%.
[f] Based on samples tested in triplicate. Standard deviation of ±2%.
[g] Based on samples tested in triplicate. Standard deviation of ±1%.
[h] Swelling index of the rubber phase calculated on the basis that the polyamide component does not swell. Solvent associates exclusively with the rubber component:

$$\text{S.I. (rubber component)} = \frac{\text{S.I. (blend)}}{\text{proportion of rubber in blend}} - \frac{\text{proportion of polyamide in blend}}{\text{proportion of rubber in blend}}.$$

[i] Compression molded sample.
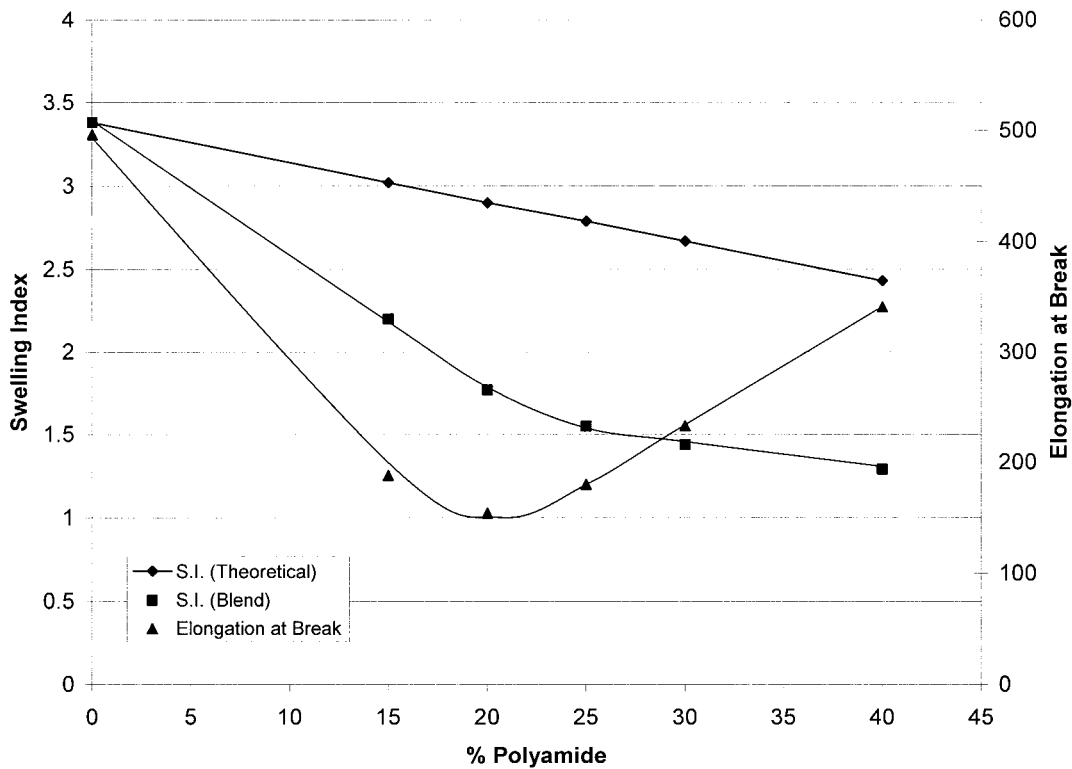[j] Swelling index determined from swollen mass weighed in closed vessel.

Figure 3 Swelling index and elongation at break of dynamically vulcanized blends.

To demonstrate the effect of blending on the swelling index of the rubber phase itself, the normalized swelling index results (based on the rubber component in the blends) were plotted versus percentage PA in Figure 4. As shown, the swelling index of the rubber phase is markedly reduced as PA is added to the blend. This reduction is likely explained by a "caging effect" on the rubber phase, in which increased PA has
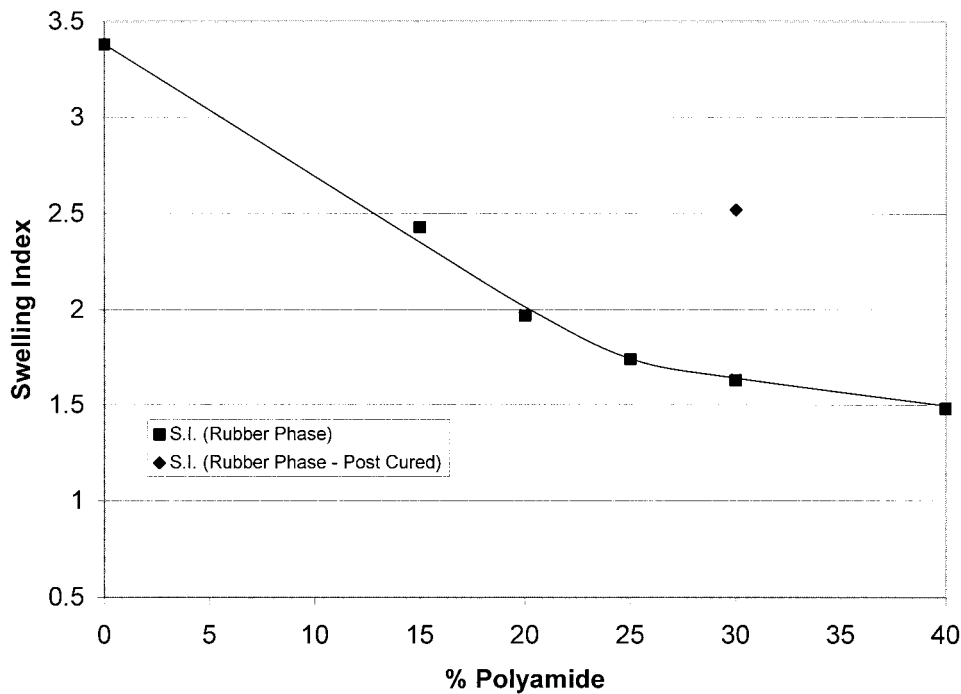

Figure 4 Swelling index of the rubber phase in PA/CIIR blends.

TABLE V
Effect of Sulfur Level on Properties of 40 PA/60 Butyl Rubber Blends[a,b,c]

Sulfur level (phr)	Ultimate strength (MPA)[d]	Elongation at break (%)[e]	Hardness (Shore D)	% Insolubles in hexane[f]	Swelling index of the blend (hexane)[g]	Swelling index— rubber phase (hexane)[h]
(a) Blends containing butyl rubber (IIR 301)						
0	9.2	87	46	99.6	1.46	1.79
0.8	9.6	118	46	107.1	1.34	1.57
1.6	9.4	119	48	106.8	1.32	1.53
2.4	9.1	117	48	94.0	1.30	1.50
3.1	9.0	105	46	96.8	1.30	1.50
4.0	8.6	103	44	94.9	1.30	1.50
(b) Blends containing chlorobutyl rubber (CIIR 1068)						
0	13.2	250	49	97.8	1.26	1.43
0.4	13.4	260	52	100.0	1.26	1.43
0.8	14.4	330	49	98.6	1.27	1.45
1.6	14.1	333	49	100.7	1.29	1.48
2.4	13.9	341	49	98.7	1.29	1.48
3.2	14.1	352	48	99.0	1.29	1.48
4.0	13.7	344	48	98.4	1.29	1.48

[a] All samples contain 1.8 phr TMTD, 0.9 phr MBTS, and 2.4 phr stearic acid, based on the rubber content, and 6.0 phr ZnO based on the overall blend.
[b] All properties measured at room temperature.
[c] All blends are mixed for 12.5 min, followed by injection molding at 180°C.
[d] Standard deviation of ±10%.
[e] Standard deviation of ±15%.
[f] Based on samples tested in triplicate. Standard deviation of ±2%.
[g] Based on samples tested in triplicate. Standard deviation of ±1%.
[h] Swelling index of the rubber phase calculated on the basis that the polyamide component does not swell. Solvent associates exclusively with the rubber component: S.I. (rubber component) = S.I. (blend)/(proportion of rubber in blend) − (proportion of polyamide in blend)/(proportion of rubber in blend).

the effect of increasing the protective sheath around the discontinuous rubber phase, restricting its volume expansion in the presence of solvents compatible with the rubber phase. Although the swelling pressure of the rubber phase becomes very high, as expected in cross-linked rubber systems,[21] the rubber phase is not able to overcome the counterpressure exerted by the continuous PA phase. A result of this nature might be expected for dynamic vulcanization. An alternative explanation may be that the continuous PA phase reduces the extent to which the solvent can enter the rubber phase to cause swelling, although this effect is presumed to be much less significant since equilibrium values of swelling index are achieved relatively quickly (see Figure 2). A further possibility is that PA may catalyze the cross-linking reaction in the rubber phase to increase the density of the polymer network, which would result in lower values of swelling index with increasing proportions of PA.

A useful comparison of swelling index can be seen in Table II for two 30PA/70CIIR samples—one by dynamic vulcanization and the other by static vulcanization (postcuring). The rubber phase in the postcured sample has interacted with PA during the intense mixing cycle; however, the rubber phase in this sample is not affected as much by the caging effect,

since curing of the rubber phase takes place after the mixing cycle is complete, leaving rubber the mostly continuous phase of the blend and a lower residual swelling pressure. As a result, the swelling index of the rubber phase has a higher value (2.52) than in the dynamically prepared blend (1.63). (The comparison is also seen in Figure 4).

Effect of the sulfur curing system on the properties of PA/butyl rubber blends

The results of a series of dynamic vulcanization experiments in which sulfur levels are adjusted from 0 to 4.0 phr (on rubber), with other components in the curing system retained at standard levels, are given in Table V. In IIR-containing blends the swelling index values decrease with increasing sulfur level up to ~0.8 phr sulfur. Ultimate tensile strength and percentage elongation values increase with small additions of sulfur. The optimum cure is likely at 0.8 phr sulfur, but higher levels of sulfur have relatively little effect on the properties. In CIIR-containing blends, dynamic vulcanization can be achieved without the addition of sulfur to the formulation. However, maximum values of percentage elongation are achieved when sulfur

TABLE VI
DSC Results for Polyamide/Butyl Rubber Blends[a]

Sample	% Polyamide	No Curing Agents		Dynamic vulcanization	
		Melting temp. (°C)[b]	Enthalpy of fusion (J/g of polyamide)[c]	Melting temp. (°C)[b]	Enthalpy of fusion (J/g of polyamide)[c]
PA	100	178.7	58.8	180.1	59.2
PA/IIR 402	40	177.8	61.6	176.0	54.4
PA/BIIR X2	40	173.8	58.6	174.0	50.3
PA/CIIR 1068	40	176.5	59.6	174.6	48.1
PA/CIIR 1068	30	175.9	56.2	172.4	49.9

[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%.

level is at or above 2.4 phr. The sulfur level has relatively little effect on the tensile strength and hardness.

Overall, the results in Table V indicate that the accelerators and moderators normally present in a sulfur curing system (MBTS, TMTD, and ZnO) have the capability to promote dynamic vulcanization, with and without the presence of added sulfur. However, the properties of the system are generally improved with additions of sulfur to the formulation; thus, most of the blended materials produced in this study have been made with 2.4 phr sulfur in the curing system.

Results of DSC experiments undertaken on blends of PA and butyl rubber with and without dynamic vulcanization

The results of DSC experiments for a number of blends of PA with IIR, BIIR, and CIIR are shown in Table VI. With all three of the rubber samples the melting temperature of the PA phase is reduced during intensive mixing of the polymers. However, the melting temperature is further reduced when mixing is undertaken in the presence of curing agents (dynamic vulcanization). The enthalpy of fusion values of the PA phase remain fairly similar to those of virgin polyamide-12 in nonvulcanized mixtures with rubber. However, a substantial reduction in this property is noted in the presence of curing agents.

The results show that reductions in peak temperature of up to 2.5°C can be observed in simple mixtures of rubber and PA. These results exceed the results of previous tests on PA/BIIR[16] and PA/CIIR[17] blends. Reduced values of melting temperature in the PA phase indicate that this phase is not a neutral component during the blending process, but likely undergoes chemical and/or physical interaction with the rubber phase during the mixing and curing processes. There also may be chain scission and molecular weight reduction in the PA phase. Further reductions in the PA melting temperature and enthalpy of fusion under dynamic vulcanization indicate even greater

changes in the crystalline PA phase when curing agents are present.

Rheology of PA/butyl rubber blends

The Brabender 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, three nonvulcanized 40PA/60 butyl rubber blends, and three dynamically vulcanized butyl rubber blends, cured with a sulfur curing system. The results of the experiments are shown in Figure 5.

The addition of rubber (IIR, BIIR, or CIIR) to PA causes an increase in the viscosity of the mixture, but all three blends show a similar dependence of viscosity on shear rate. Further increases in viscosity are observed as curing agents are added to these blends. In blends containing curing agents there are substantial differences in the viscosity versus shear rate dependencies for the different butyl rubbers. The highest viscosity is observed for blends containing CIIR, followed by BIIR and IIR. All of the plots of viscosity versus shear rate for PA/rubber blends show a substantial reduction in viscosity with shear rate, both vulcanized and nonvulcanized. Thus, there is a high degree of non-Newtonian behavior in both nonvulcanized and dynamically vulcanized blends.

Scanning electron microscopy on PA/butyl rubber blends

During the SEM process on blends of PA with butyl rubbers, the rubber component of the blend is etched, exposing the PA portion of the sample. Figure 6 contains the SEM micrographs of dynamically vulcanized blends of PA with IIR, BIIR, and CIIR. Evidence of orientation is visible in the micrographs of the samples
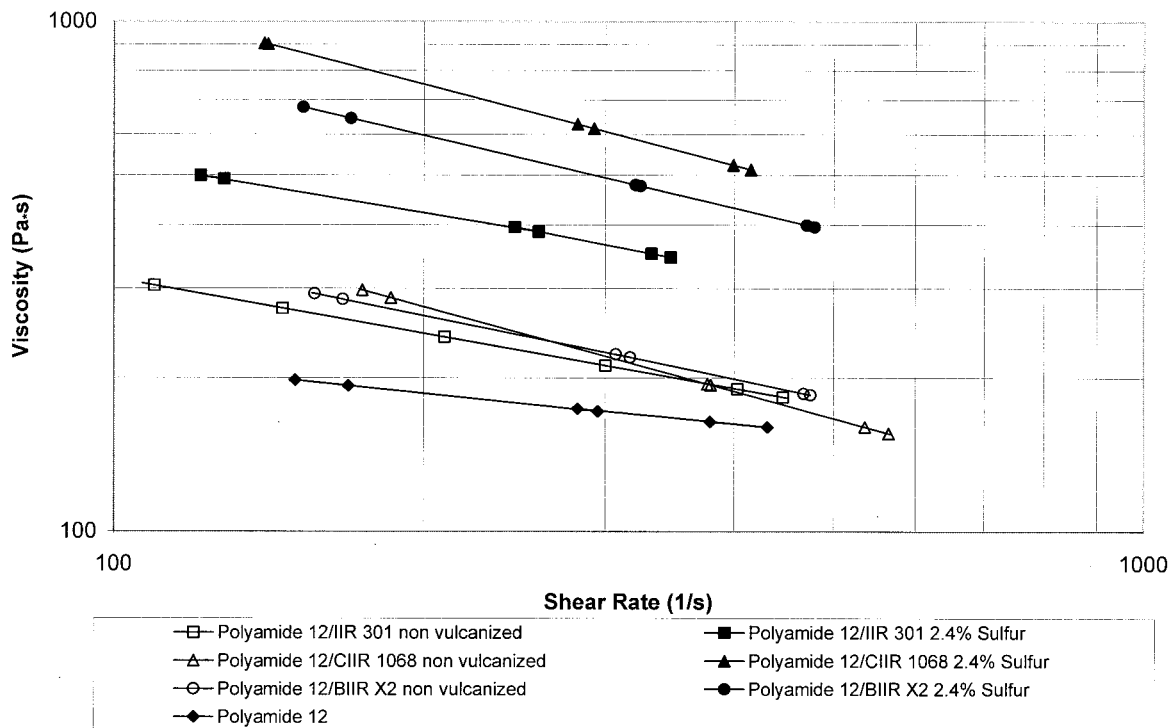
Figure 5 Rheological properties of 40PA/60 butyl rubber blends at 205°C.

containing BIIR and CIIR and is likely the result of the material mixing pattern prior to cooling.

As shown in Figure 6, the blends containing halogenated rubbers show good dispersion, with an average rubber phase particle size in the range of 2–4 μm. In contrast, the average particle size of IIR-containing blends is 4–8 μm. The smaller particle size of the rubber phase in halogenated rubber-containing blends may explain the improved mechanical properties of these materials in comparison to blends with IIR. Blends containing smaller rubber particles will, on average, allow for greater surface contact between the rubber particles in the blend, thus enhancing the interaction of the dispersed rubber phase in the blend. This also explains why equilibrium is rapidly established during exposure to solvent during the swelling index test.

CONCLUSION

In PA/butyl rubber blends produced by dynamic vulcanization the greatest effect on tensile properties is the presence or absence of halogenation in the rubber. Both ultimate strength and percentage elongation decrease in the order of CIIR > BIIR > IIR in blends containing 40% PA. This is an unexpected trend, because BIIR in pure rubber compounds has a much higher tensile strength than either CIIR or IIR.

Percentage unsaturation and Mooney viscosity values seem to have little effect on the mechanical properties in any of the blends made with CIIR, BIIR, or IIR.

Tensile strength and percentage elongation values for nonvulcanized blends are lower than for similar dynamically vulcanized blends, especially for those containing halogenated butyl rubbers.

In CIIR-containing blends the ultimate tensile strength and hardness values generally increase as PA is increased, within the range covered by the experiments.

When accelerators are present in a sulfur-based curing system, the mechanical properties of PA/butyl rubber blends are relatively insensitive to the amount of elemental sulfur used in the formulation.

Swelling index values of the rubber component in these blends indicate that the rubber phase is crosslinked in blends prepared by dynamic vulcanization, even at very low levels of elemental sulfur. This may be partly due to the inclusion of ZnO in the formula, a common vulcanizing agent in halogenated butyl rubber systems.

The normalized swelling index (rubber phase only) in PA/CIIR blends decreases with increasing proportion of PA in the blends. The reduction in swelling index is rapid and close to linear from 0 to 20% PA, followed by a second almost linear region with lower slope from 20 to 40% PA.

Elongation at break values reach a minimum in PA/CIIR blends at ~20% PA, which corresponds to the composition where the swelling index versus per-
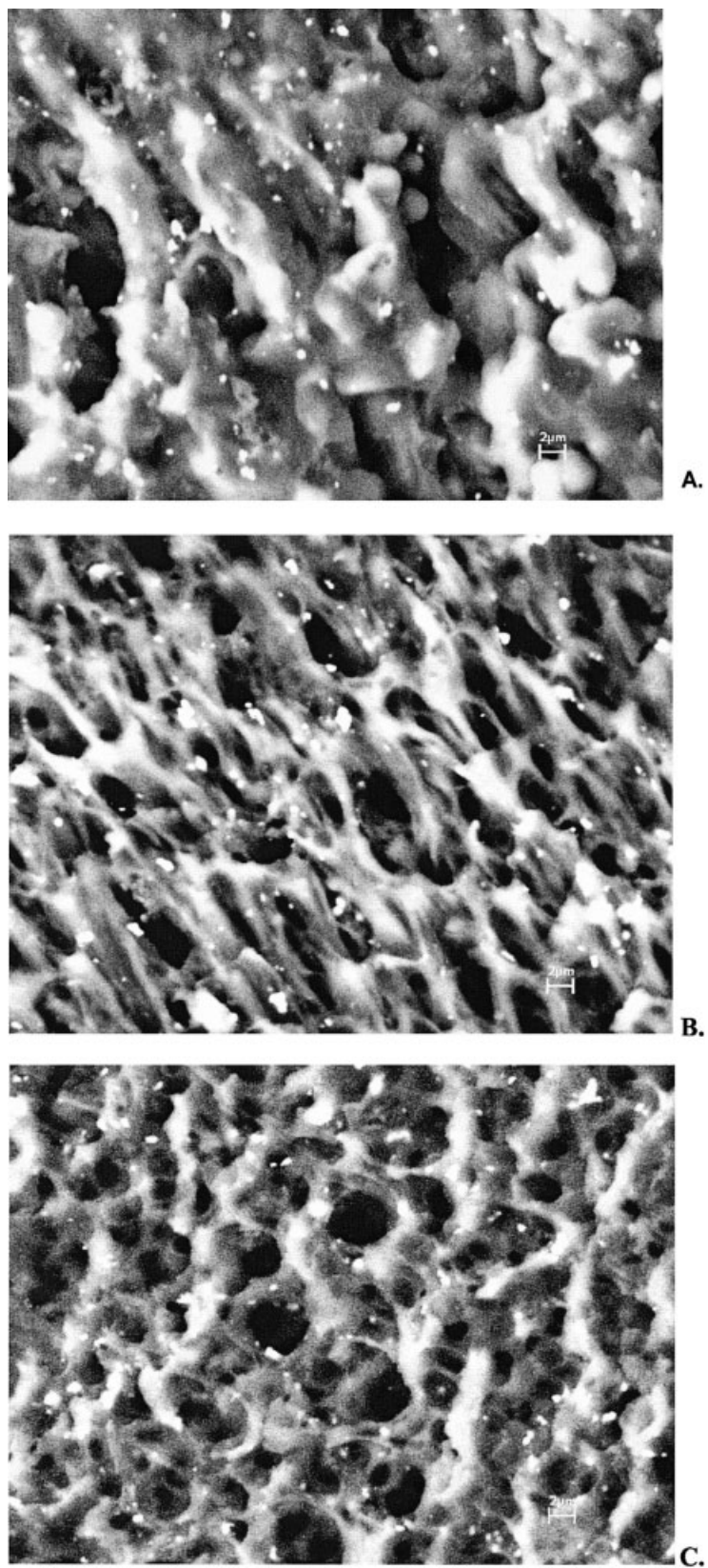
Figure 6 SEM of etched specimens of dynamically vulcanized blends of PA with (a) IIR,(b) BIIR, and (c) CIIR.

centage PA curve undergoes a change in slope. This may indicate the composition where the phase volume of the PA phase is large enough to completely encase the rubber phase.

The swelling index for a statically vulcanized specimen is significantly higher than for a blend of identical composition prepared by dynamic vulcanization. This is likely due to a large caging effect on the rubber phase in dynamically vulcanized materials.

DSC experiments reveal a reduction of up to 2.5°C in melting temperature of the PA phase for PA/butyl rubber blends, indicating that some interaction with the rubber occurs during blending.

Nonvulcanized blends of all three butyl rubbers with PA show similar increases in viscosity with respect to PA and significant non-Newtonian behavior. The viscosity is further increased with dynamic vulcanization for the same compositions, and these blends also display similar non-Newtonian behavior. Blend viscosities for three butyl types are in the order of CIIR > BIIR > IIR (similar order for most mechanical properties).

Etched surface micrographs of PA/butyl rubber blends by SEM show lower particle size for halogenated rubber specimens, indicating greater compatibility in blends with these rubbers.

REFERENCES

1. Coran, A. Y.; Chung, O.; Laokijcharoen, P. Kautschuk Gummi Kunststoffe 1998, 51, 342.

2. Ma, J.; Feng, Y. X.; Xu, J.; Xiong, M. L.; Zhu, Y. J.; Zhang, L. Q Polymer 2002, 43, 937.

3. Coran, A. Y.; Patel, R. P. In Holden, G.; Legge, N. R.; Quirk, R.; Schroeder, H. E., Eds., Thermoplastic Elastomers; Hanser/Gardner: Cincinnati, OH, 1996.

4. U. S. Patent 4,130,534 (1978), Coran, A. Y.; Patel (to Monsanto Co., Ltd.).

5. Coran, A. Y. Rubber Chem Technol 1995, 68, 351.

6. Coran, A. Y. Plastics Engineering 61 (Handbook of Elastomers, 2nd ed.) 2001, 265.

7. Chung, O.; Coran, A. Y. SPE ANTEC 60th 2002, 3, 3192.

8. Coran, A. Y.; Patel, R. P. Rubber Chem Technol 1981, 54, 892.

9. Coran, A. Y.; Patel, R. P.; Williams, D. Rubber Chem Technol 1982, 55, 116.

10. Japan Patent 3,265,662 (1991), Mizuno, H.; Hasegawa, M.; Imamura, T.; Nobuyo, K. (to Japan Synthetic Rubber Co., Ltd.).

11. U. S. Patent 4,987,017 (1991), Sato, H.; Shimada, H.; Sakeguchi, A.; Takemura, Y.; Nishi, T.; Ono, H.; Nagano, M.; Miyachi, T. (to Japan Synthetic Rubber Co., Ltd.).

12. Japan Patent 8,906,043 (1989), Aonuma, K.; Sugi, N. (to Nippon Zeon Co. Ltd.).

13. Venkataswamy, K. Polym Mater Sci Eng 1998, 79, 94.

14. U. S. Patent 5,159,014 (1992), Tsutsumi, F.; Morikawa, A.; Hasegawa, M.; Oshima, N. (to Japan Synthetic Rubber Co., Ltd.).

15. Goto, S-I.; Kenzo, K.; Yamamoto, T.; Yamashita, S. J Appl Polym Sci 1999, 74, 3548.

16. Van Dyke, J. D.; Gnatowski, M.; Koutsandreas, A.; Burczyk, A.; Duncan, S. J Appl Polym Sci 2003, 89, 980.

17. Van Dyke, J. D.; Gnatowski, M.; Koutsandreas, A.; Burczyk, A. J Appl Polym Sci 2003, 90, 871.

18. DeLassus, P. In Kroschwitz, J., Ed,, Kirk-Othmer Encyclopedia of Chem Technology, 4th ed.; Wiley: New York, 1991; Vol. 3, p 931.

19. Kresge, E.; Wang, H-C. In Kroschwitz, J., Ed., Kirk-Othmer Encyclopedia of Chem Technology, 4th ed.; Wiley: New York, 1991; Vol. 8, p 934.

20. Butyl and Halobutyl Compounding Guide for Non-Tyre Applications; Bayer Polysar Technical Centre: Antwerp, 1992.

21. Rigbi, Z. Kautshuk Gummi Kunststoffe 1991, 44, 915.