Solvent Resistance and Mechanical Properties in Thermoplastic Elastomer Blends Prepared by Dynamic Vulcanization

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ABSTRACT: Dynamic vulcanization was used to prepare thermoplastic elastomer blends of nylon (polyamide), polypropylene (PP) and polybutylene terephthalate thermoplastics with chlorobutyl (CIIR) and nitrile (NBR) rubbers. Mechanical properties of the blends were correlated against composition. Although hardness and tensile strength increase with increasing thermoplastic content for all blends, elongation at break values initially decrease and then increase in the range of 20–40% thermoplastic. For various blend compositions, the swelling behavior was evaluated with solvents that are able to dissolve the uncured rubber portion but not the thermoplastic component of the mixtures. All five systems showed swelling index values that were substantially less than the calculated "theoretical" values of swelling index. This was attributed to a caging effect of the thermoplastic component on the rubber phase, which restricts access of solvent and swelling of the rubber phase. In turn, this affects the solvent resistance of the blend. Some of the blends were evaluated by differential scanning calorimetry to assess the compatibility of the components in the blend. scanning electron microscopy was also used to determine the degree of compatibility of the two phases generated in the mixing process. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1535–1546, 2008

Key words: blends; dynamic vulcanization; polyamide; nylon; polypropylene; butyl rubber; nitrile rubber; polybutylene terephthalate; mechanical properties; differential scanning calorimetry; electron microscopy

INTRODUCTION

Over the past 2 decades high shear melt mixing has become an important method to prepare a variety of blends of thermoplastics and vulcanizable elastomers, both in the presence and absence of a curing system for the rubber phase. Unique blend compositions are now possible, some of which are commercialized, with a multiplicity of properties that reflect the component elastomers and thermoplastics in these blends. Thermoplastic elastomers (TPE) made from two or more blend components are of particular interest, and a wide variety of interesting thermoplastic/rubber combinations have now been prepared and summarized in several review articles.[1–4] Commercial thermoplastics used in these studies include polypropylene (PP), polyamides (nylon, PA), and polyesters such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). Commercial rubbers include butyl (IIR), ethylene-propylene (EPDM), and nitrile (NBR) rubbers. Several studies cover blends of PP with IIR,[5,6] EPDM,[1,7,8] and

NBR.[2,9–12] PA compositions have been prepared with NBR,[2,13–15] EPDM,[16–19] acrylate,[20,21] and various butyl rubbers.[22–27] PBT has been blended with oxazoline-modified nitrile rubber.[28]

In the absence of a curing system, the phase morphology of a blend is determined by a number of factors, including 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.[29] Addition of compatibilizing agents can significantly reduce the dimensions of the dispersed phase in some systems.[16]

Dynamic vulcanization, which results in curing of the rubber component during the mixing process, is a method used to overcome a lack of stability in some thermoplastic elastomeric blends, particularly at elevated temperatures. Crosslinking in the rubber phase during preparation of a blend reduces the size of the rubber particle,[30] and inhibits reagglomeration of the rubber particles during cool down times after mixing has stopped, as well as in subsequent use of the blend at higher temperatures.[31] During the mixing process the melt viscosity of the rubber phase increases dramatically in relation to the thermoplastic phase, which enables the thermoplastic phase to

form the continuous phase with relatively small proportions of plastic in the blend.[32] Materials of this nature can be readily recycled after regrinding, largely due to the fact that, although the vulcanized rubber particles physically interact with each other in the blend to form a loose rubber network, these interactions easily disintegrate during melt-reprocessing. The effect of morphology on the properties of some thermoplastic vulcanizates, and the mechanical and chemical factors affecting the morphology, are now becoming understood.[10,15,19,33–35]

The optimum choices for rubber, plastic, and curing systems in blends made by dynamic vulcanization have been the subject of several articles by Coran's group.[2,3,33,36] Dynamic vulcanization often produces materials having superior properties over blends containing uncured mixtures or block copolymer-type thermoplastic elastomers.[1,2,5,37] Many previously difficult combinations of materials are now possible, particularly when compatibilizing agents are also incorporated into the blend.[1] Materials of this nature generally show superior properties in permanent set, tensile strength and elongation, fatigue resistance, hot-oil resistance, melt strength, and thermoplastic fabricability.[37]

In previous studies undertaken on blends of PA and butyl rubber in our laboratories,[25–27] it was shown that these polymers, although normally incompatible, can be mixed in a high shear environment, with and without the presence of curing agents. The greatest compatibility occurs with CIIR. The high shear environment seems responsible for producing an interaction between the polyamide and rubber components during processing, resulting in the presence of small quantities of block or graft polymers in the system, which can act as compatibilizing agents.

Exposure to solvents has become a useful tool in our laboratories to understand the morphological changes taking place in blends over a range of compositions. It has been observed that experimental values of the solvent swelling indices for blends of CIIR and PA are much less than values that would be calculated for mixtures of rubber and plastic that have not gone through a high shear blending process. A similar observation was made by Jha and Bhomick for nylon/acrylate blends.[20] This effect may be due to restrictions a continuous thermoplastic phase places on the swelling of the crosslinked rubber particles. There is some evidence that phase inversion in PA/CIIR blends may occur as low as 25% PA, which would make this effect observable whenever the thermoplastic composition exceeds this relatively low value.

The present study was undertaken to determine if the observation of a continuous PA phase as low as 25% in PA/CIIR blends could be generalized and

applied to a variety of other rubber/plastic combinations prepared by dynamic vulcanization. Such observed phenomena may have significant practical value in relation to overall chemical resistance in blends, particularly when the rubber phase is vulnerable to attack. Three thermoplastics PA, PP, and PBT were studied in combination with two rubbers, CIIR and NBR, and five blend combinations were produced at different proportions of rubber and plastic. The completed blends were molded, and tested for mechanical properties, exposure to solvents, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials used

Polyamide-12 (Grilamid L16) was obtained from EMS-American Grilon (Sumter, SC), polypropylene (Profax 6524) from Exxon Mobil Chem (Houston, TX), and polybutylene terephthalate (PBT 1700A) from Celanex Ticona (Bishop, TX). Chlorobutyl 1068 rubber was supplied by Exxon Chemical (Sarnia, ON, Canada), and nitrile rubber (Krynac 3345C) by Bayer Chemical (Sarnia, ON, Canada). Zinc oxide (ZOCO 172) was supplied by Zochem (Brampton, ON, Canada), zinc diethyldithiocarbamate (ZDEDC) by R.T Vanderbilt (Norwalk, CT), peroxide (Trigonox 101-45B-pd) by Akzo-Nobel (McCook, IL), and antioxidants (Flectol TMQ by Flexys America (Akron, OH), Naugard PHR by Crompton (Middleburg, CT), and A/O 2264 by Aldrich (Milwaukee, WI)). Stearic acid (Emersol 150) was supplied by Cognis Canada (Toronto, ON), Paracin 285 wax by CasChem (Bayonne, NJ), Sartomer (SR-525) by Sartomer (Weschester, PA), and magnesium oxide (Maglite D) by the C.P. Hall Co (Memphis, TN). Reagent-grade hexane was supplied by Anachemia (Montreal, QC, Canada), and reagent-grade chloroform by Caledon Labs (Georgetown, ON, Canada).

Curing systems employed in this study

Chlorobutyl rubber-based systems

A ZDEDC/ZnO-based curing system was used for pure rubber compounds and all blends containing this rubber. The proportions of the curing components were 2.2 phr of ZDEDC (on rubber), and 6.70 phr ZnO (based on total polymer).

Nitrile rubber-based systems

For blends with PA, the curing system employed 2.50 phr of Sartomer and 2.1 phr of peroxide (both based on rubber); for blends with PP, the curing sys-

TABLE I
Properties of Polyamide/Chlorobutyl Rubber Blends[a,b]

Blend ratio (PA/CIIR)	Mechanical properties				Effect of exposure to solvents			
	Ultimate strength (MPa)[c]	Elong. at break (%)[d,e]	Modulus (Mpa)[f]	Shore D hardness[g]	Swelling index (hexane)[h]	Swelling index (CHCl$_3$)[i]	% Insol. (hexane)[j]	% Insol. (CHCl$_3$)[k]
0/100					2.93	6.51	99.9	99.6
15/85	1.8	252	3.7	12	3.59	8.33	68.4	67.0
20/80	4.7	168	16.3	22	2.55	5.60	81.3	78.9
25/75	7.0	165	35.8	30	1.88	3.90	92.0	90.8
30/70	9.7	196	74.4	37	1.59	3.18	95.6	94.3
35/65	11.0	210	77.5	46	1.45	2.66	97.2	97.2
40/60	12.3	195	91.7	49	1.34	2.34	99.1	98.3
50/50	14.6	94				2.06		97.2
100/0	35.3	110			1.00	1.08	99.5	104.8

[a] Blends prepared by dynamic vulcanization, formulation: nylon 12 (L16), chlorobutyl 1068, ZDEDC 2.2 phr (on rubber), [ZnO 6.70 phr, stearic acid 1.44 phr, paracin wax 0.55 phr, (based on total polymer)].
[b] Samples injection molded, except for 0/100 which was compression molded.
[c] Average SD of 4%.
[d] Elongation at break values based on bench marks.
[e] Average SD of 5%.
[f] Average SD of 13%.
[g] Average SD of 4%.
[h] Average SD of 0.7%.
[i] Average SD of 1.3%.
[j] Average SD of 0.2%.
[k] Average SD of 0.4%.

tem employed 2.50 phr of Sartomer (based on rubber) and 2.50 phr of MgO (based on total polymer). For blends with PBT, the curing system employed 1.66 phr of Sartomer (based on rubber).

Complete formulations are listed in Tables I–V.

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

TABLE II
Properties of Polypropylene/Chlorobutyl Rubber Blends[a,b]

Blend ratio (PP/CIIR)	Mechanical properties				Effect of exposure to solvents			
	Ultimate strength (MPa)[c]	Elong. at break (%)[d,e]	Modulus (Mpa)[f]	Shore D hardness[g]	Swelling index (hexane)[h]	Swelling index (CHCl$_3$)[i]	% Insol. (hexane)[j]	% Insol. (CHCl$_3$)[k]
0/100					2.93	6.51	99.9	99.6
17.5/82.5	3.1	136	13	20	2.62	5.16	87.6	86.8
20/80	3.6	146	19	25	2.45	5.05	89.2	87.8
25/75	4.4	128	30	26	2.30	4.48	89.3	88.0
30/70	5.5	124	41	31	2.09	3.84	91.7	91.6
35/65	7.9	198	67	38	1.87	3.43	94.3	93.0
40/60	9.1	244	79	43	1.77	2.97	94.5	94.2
50/50	12.4	278			n/a	2.47		95.7
100/0	31.8		138	71	n/a	1.26	94.1	99.7

[a] Blends prepared by dynamic vulcanization, formulation: polypropylene, chlorobutyl 1068, ZDEDC 2.2 phr (on rubber), [ZnO 6.70 phr, stearic acid 1.44 phr, paracin wax 0.55 phr, A/O2264 0.33 phr (based on total polymer)].
[b] Samples injection molded, except for 0/100 which was compression molded.
[c] Average SD of 4%.
[d] Elongation at break values based on bench marks.
[e] Average SD of 5%.
[f] Average SD of 13%.
[g] Average SD of 4%.
[h] Average SD of 0.7%.
[i] Average SD of 1.5%.
[j] Average SD of 0.4%.
[k] Average SD of 0.4%.

TABLE III
Properties of Polyamide/Nitrile Rubber Blends[a,b]

Blend ratio (PA/NBR)	Mechanical properties				Effect of exposure to solvents	
	Ultimate strength (MPa)[c]	Elong. at break (%)[d,e]	Modulus (Mpa)[f]	Shore D hardness[g]	Swelling index (CHCl$_3$)[h]	% Insol. CHCl$_3$[i]
0/100	2.7	140	1.8	21	5.99	96.6
15/85	7.9	129	13	35	5.48	95.3
20/80	9.1	136	16	39	4.70	94.7
25/75	12.2	173	16	41	4.77	95.3
30/70	14.0	179	16	45	4.19	94.8
35/65	16.4	170	25	49	3.75	93.9
40/60	18.2	190	23	49	3.37	97.0
100/0					1.08	104.8

[a] Blends prepared by dynamic vulcanization, formlation: nylon 12 (L16), nitrile, [Sartomer 2.50 phr, peroxide 2.1 phr, antioxidant TMQ 1.66 phr, all based on rubber], [stearic acid 1.44 phr, paracin wax 0.55 phr, based on total polymer].
[b] Samples injection molded, except for 0/100 which was compression molded.
[c] Average SD of 4%.
[d] Elongation at break values based on bench marks.
[e] Average SD of 5%.
[f] Average SD of 13%.
[g] Average SD of 4%.
[h] Average SD of 2.4%.
[i] Average SD of 1.9%.

and temperature control (Brabender Instruments, Hackensack, NJ).

Blends based on polyamide

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 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.

TABLE IV
Properties of Polypropylene/Nitrile Rubber Blends[a,b]

Blend ratio (PP/NBR)	Mechanical properties				Effect of exposure to solvents	
	Ultimate strength (MPa)[c]	Elong. at break (%)[d,e]	Modulus (Mpa)[f]	Shore D hardness[g]	Swelling index (CHCl$_3$)[h]	% Insol. (S.I.) CHCl$_3$[i]
0/100	2.3	572	0.7	12	34.61	45.7
15/85	2.6	28	16.9	27	10.59	87.1
20/80	2.7	18	22.6	29	9.83	87.7
25/75	3.9	30	33.6	33	8.75	87.4
30/70	4.9	38	43.5	38	7.75	87.3
35/65	7.2	30	78.1	41	7.14	88.1
40/60	5.9	40	54.9	46	6.23	87.3
50/50	11.1	42			4.80	91.0
100/0	31.8		138.0	71	1.26	99.7

[a] Blends prepared by dynamic vulcanization, formlation: polypropylene, nitrile, [sartomer 2.50 phr, A/O 2264 1.67 phr, naugard PHR 0.83 phr, based on rubber], [stearic acid 1.44 phr, paracin wax 0.55, MgO 2.50 phr, based on total polymer].
[b] Samples injection molded, except for 0/100 which was compression molded.
[c] Average SD of 4%.
[d] Elongation at break values based on bench marks.
[e] Average SD of 5%.
[f] Average SD of 13%.
[g] Average SD of 4%.
[h] Average SD of 4.2%.
[i] Average SD of 1.3%.

TABLE V
Properties of Polybutylene Terephthlate/Nitrile Rubber Blends[a,b]

Blend ratio (PBT/NBR)	Mechanical properties				Effect of exposure to solvents	
	Ultimate strength (MPa)[c]	Elong. at break (%)[d,e]	Modulus (Mpa)[f]	Shore D hardness[g]	Swelling index (CHCl$_3$)[h]	% Insol. (S.I.) CHCl$_3$[i]
0/100	2.3	572	0.7	12	24.43	79.0
15/85					16.16	89.2
20/80	2.6	36	13.2	29	9.39	86.6
25/75	3.6	46	17.4	31	7.97	93.1
30/70	7.2	96	26.7	39	6.29	94.0
35/65	9.4	124	36.0	40	5.59	94.8
40/60	12.1	138	48.1	42	4.95	95.3
50/50	17.9	198			3.39	97.6
100/0	53.1	44	458.4	74	1.15	102.4

[a] Blends prepared by dynamic vulcanization, formulation: PBT, nitrile, [stearic acid 1.44 phr, paracin wax 0.55 phr, based on total polymer], [antioxidant TMQ 1.56 phr, sartomer 1.56 phr, based on rubber].
[b] Samples injection molded, except for 0/100 which was compression molded.
[c] Average SD of 4%.
[d] Elongation at break values based on bench marks.
[e] Average SD of 5%.
[f] Average SD of 13%.
[g] Average SD of 4%.
[h] Average SD of 4.2%.
[i] Average SD of 1.3%.

Blends based on polypropylene

PP was first added at 30 rpm mixing speed to the Brabender Mixer at a target temperature of 190°C, and allowed to melt for 4 min, with antioxidant addition at 3 min. Rubber was added at 4 min and additional antioxidant along with stearic acid and wax at 5 min, and the mixing speed was increased to 65 rpm. Metal oxides were added at 7 min, and Sartomer (when needed) at 8 min. Total mixing time was 12 min. The blend was then removed from the mixer and cooled.

Blends based on polybutylene terephthalate

PBT was first added at 30 rpm mixing speed to the Brabender Mixer at a target temperature of 235°C, and allowed to melt for 3 min. Rubber and antioxidant were added over a period from 3 to 5 min, and the mixing speed was increased to 65 rpm. Stearic acid, wax, and Sartomer were added over the period from 5 to 6 min. Total mixing time was 9 min. The blend was then removed from the mixer and cooled.

Pure rubber samples

For each blend combination investigated in this study, a pure rubber composition was prepared with a formulation that was identical to blends containing this rubber.

Chlorobutyl rubber was masticated at 25 rpm and a target temperature of 50°C for 3 min, after which

stearic acid and zinc oxide were added. At the 8 min-mark ZDEDC was added and mixing was continued for an additional 2 min. The total mixing time was 10 min. After blending was complete, the compound was compression molded at 160°C for 30 min.

Nitrile rubber was masticated at 25 rpm and a target temperature of 90°C for 3 min, after which A/O was added. Stearic acid was added at the 4 min-mark, Paracin wax at 4.5 min, SR-525 at 6 min, and peroxide at 8.5 min. Mixing was continued for an additional 3.5 min for a total blend time of 12 min. After blending was complete, the compound was compression molded at 210°C for 30 min.

Testing and characterization

Mechanical properties

In all blends the mechanical properties were tested on specimens prepared directly by injection molding using an Arburg type 200U-D or 221K instrument. In PA/CIIR blends all zones were adjusted to 180°C, while in PA/NBR blends the zones were set at 215, 225, and 180°C, respectively. In PP-based blends, zones were adjusted to 190, 200, and 220°C; in PBT-based blends, the zones were adjusted to 255, 290, and 230°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.
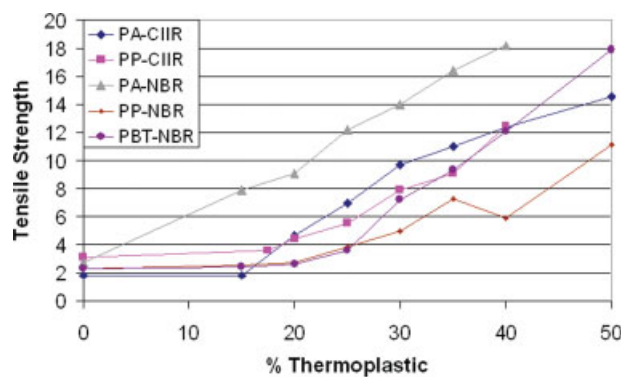
Figure 1 Tensile strength versus % thermoplastic. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Swelling index and percentage insolubles

For swelling index determination on plastic/rubber blends, a molded or pressed specimen, ~ 1 cm^2 and 1.5-mm thick, was immersed in reagent-grade hexane or reagent-grade chloroform for 4 days to obtain equilibrium. (Equilibrium swelling in rubber samples and blends is reached in less than 1 day, and thickness of samples has only a marginal effect on the final result.[27]) 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. The % insolubles were determined by comparison of the weight after drying to the original weight of the sample.

Differential scanning calorimetry

Several rubber/plastic blends prepared by injection molding were analyzed on a Perkin–Elmer DSC-7 instrument (Perkin–Elmer Cetus Instruments, Norwalk, CT) according to ASTM D 3417. The melting temperature and enthalpy of fusion values for the thermoplastic phase were recorded for each sample. If multiple peaks occurred, the melting temperature referred to the highest (second) peak. For PA/CIIR blends, it has been shown by repetitive results in our laboratories that the values of melting temperature and enthalpy of fusion are within experimental error of each other for injection molded samples and granulated pellets.

Scanning electron microscopy

SEM was conducted using a variable pressure LEO 1455VP microscope (Meridian Scientific Services, Stittsville, ON, Canada). Specimens were prepared either by cutting with a sharp blade at room temperature, or fracturing at low temperature. After exposure to OsO$_4$, the blends were mounted on alumi-

num stubs with carbon paint, and examined without coating at low pressure using a Robinson Backscatter Detector.

RESULTS AND DISCUSSION

Mechanical properties of blends

Tables I–V list the results of dynamic vulcanization experiments on PA/CIIR, PP/CIIR, PA/NBR, PP/NBR, and PBT/NBR blends, with the proportion of the hard phase ranging from 15–50% thermoplastic for most combinations. Values for 100% rubber and 100% plastic compositions are also listed in these tables, each obtained under similar heat and/or chemical treatment as blends of the two.

In all five plastic/rubber combinations, the tensile strength values increase as the proportions of thermoplastic increase in the blends (Fig. 1). As well, the modulus and hardness values increase with increasing proportion of thermoplastic. Elongation at break values, on the other hand, drop rapidly as thermoplastic is introduced to a pure rubber compound and reach a minimum value at ~ 20–25% plastic. At higher levels of thermoplastic all blends show consistent increases in elongation at break values until blend proportions reach about 50 : 50. (see Figs. 2–6).

The elongation at break results in this study parallel the results of Kumar et al.[13] on PA/NBR blends, where increasing PA content produced increasing % elongation values up to 60% PA. Another study by Oderkerk et al.[18] on PA/EPDM blends suggests that thin ligaments of the Nylon 6 matrix deform plastically during stretching, and are part of the elastic restoring forces in the rubber particles and the Nylon matrix after stress is relieved from test samples. A similar observation has been made by Van Duin[38] for PP/EPDM blends. Applying these observations to the present study, thin plastic layers between rubber particles begin to dominate with increasing proportions of the thermoplastic component. As elastic
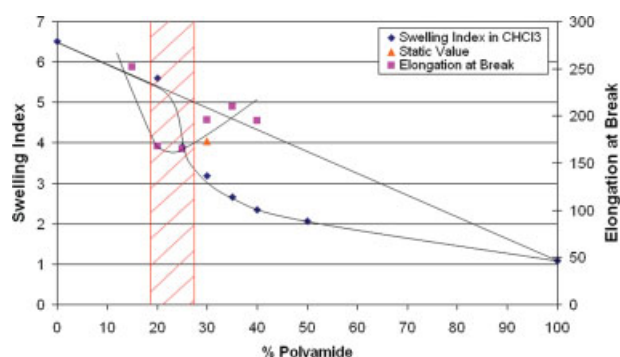

Figure 2 Swelling index and elongation at break for PA/CIIR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
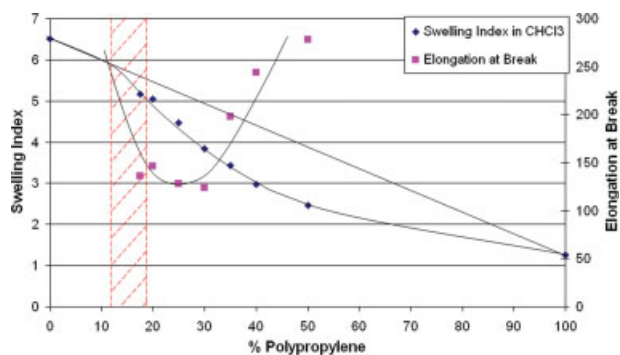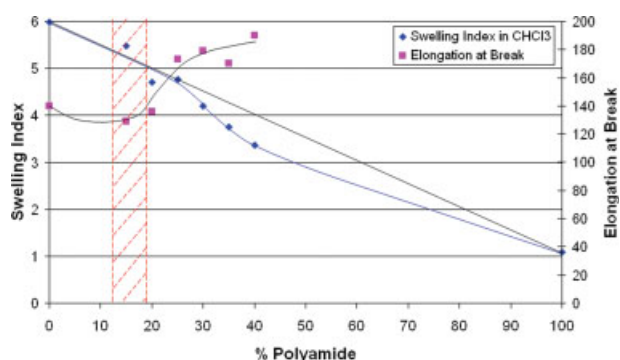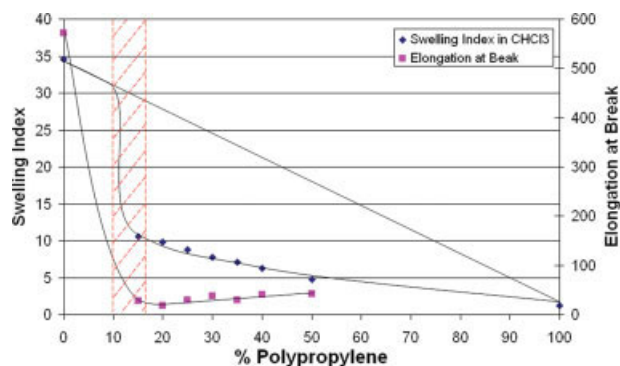
Figure 3 Swelling index and elongation at break for PP/ CIIR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 Swelling index and elongation at break for PP/ NBR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

extension and recovery is greatest in thin PA sections, their presence at higher plastic levels may increase the ability of the blend to elongate under tension.

The physical properties in all of the blend combinations considered in this study vary from soft and rubbery in blends enriched in rubber, to hard and plastic-like in blends enriched in thermoplastic. Materials that can serve as useful thermoplastic elastomers generally have properties that are intermediate between those of the rubber and plastic components. Our results suggest that the best compromise between toughness, hardness, and extensibility in the blends that were studied occurs in the range of 30–40% thermoplastic.

Exposure of blends to solvents

In addition to physical properties, Tables I–V list the effect of exposure of the blends to various solvents. The values of swelling index and % insolubility in each of these tables represent equilibrium values, obtained after immersion in the solvent for 4 days. (Equilibrium values are generally achieved in less than 1 day.[27]) All blends that contained CIIR were

exposed to both hexane and chloroform, as both are excellent solvents for uncured CIIR. Referring to Tables I and II it can be seen that values of % insolubility in CIIR-containing blends are fairly equivalent for both solvents, whereas values of swelling index obtained with chloroform are much higher than hexane-based values. The disparity in swelling index values can be attributed primarily to differences in density between the two solvents. NBR-containing blends were not exposed to hexane, as this solvent is a nonsolvent for uncured NBR, while chloroform is one of the better solvents for NBR.

Percent insolubility values increase with higher proportions of thermoplastic for all blend combinations considered in this study. Compounds containing 100% CIIR show high values of % insolubility and appear to be the exception to this result, but this is explained by the different preparation method used for pure rubber samples, i.e., compression curing.

Swelling index and elongation at break values are plotted versus composition in Figures 2–6 for all combinations of rubber and plastic. Each figure also shows the straight line theoretical swelling index
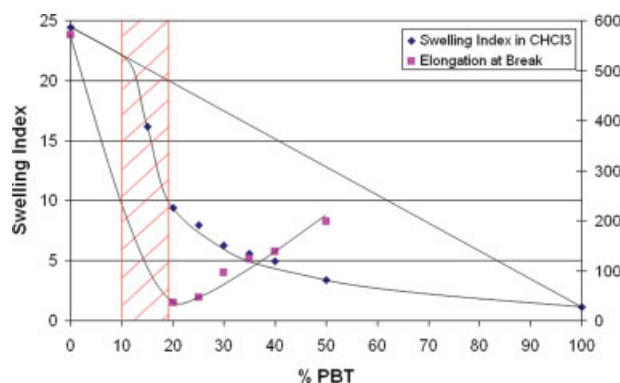

Figure 4 Swelling index and elongation at break for PA/ NBR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 Swelling index and elongation at break for PBT/NBR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VI
Compatibility Factors for Polymers Used in the Study

Polymer	Critical surface tension for wetting[a] (mN/m)	Solubility parameter[b] $(MPa)^{1/2}$
PA	39	19
PP	28	16.5
PBT	39	21.6
CIIR	27	16.7
NBR	39	21.4

[a] Values taken from Ref. 1, this paper.
[b] Values taken from Ref. 39, this paper.

predicted for simple dry-mixtures of the two components in the blend. As % thermoplastic increases in blends of PA/CIIR, PP/CIIR, PA/NBR, PP/NBR, and PBT/NBR, the swelling index values fall significantly below the theoretical line. This behavior parallels previous observations on PA/CIIR blends in this laboratory.[27] This has also been observed in nylon-6/acrylate rubber blends by Jha and Bhowmick, who attributed behavior of this nature to the restriction placed by the nylon-6 phase on the swelling of the acrylate rubber particles, as well as a reduction in the mobility of acrylate rubber chains created by nylon grafts at the acrylate/nylon interface.[20] Mousa has also observed that solvent swelling of the rubber phase in PP/EPDM blends is limited by the thermoplastic phase.[7]

The swelling index behavior for several of the blends in this study suggests that swelling index values fall below the theoretical line after a minimum % thermoplastic has been achieved. The suggested composition range over which phase inversion takes place in Figures 2–6 is indicated by hashed lines. Phase inversion may begin as low as 10–20% thermoplastic in several blends (particularly PP and PBT containing blends). In PA-containing blends, phase inversion more likely occurs between 20 and 30% thermoplastic. In all cases phase inversion appears to be accompanied by both a reduction in swelling index values and an increase in elongation at break values. Phase inversion at low % thermoplastic has been observed in at least one other system. Using rheology, Joubert et al.[34] observed that phase inversion took place with 20% PP in a PP/EVA system.

A comparison of dynamic vulcanization to static vulcanization was provided in one case for a 30/70 PA/CIIR blend using identical formulations for both methods of vulcanization. The swelling index of the static blend is higher than the one produced under dynamic vulcanization (Fig. 2), which is likely due to the fact that the morphology of the static sample consists primarily of a rubber continuous phase. The rubber phase in this sample will not experience

nearly as great a restriction on its swelling behavior as would a dynamically vulcanized sample of similar composition in which the thermoplastic phase has become the continuous phase.

Critical surface tension for wetting and solubility parameters provide an indication of compatibility in polymer systems, and values of these parameters are listed in Table VI. Higher degrees of compatibility between the two phases are expected to decrease the particle size of the dispersed phase. This, in turn, may have an effect on the behavior of the swelling index versus composition line. For example, a high level of compatibility is suggested for PA/NBR blends, which may be one reason why swelling index values do not deviate greatly below the theoretical line in this system, in contrast to the other blend combinations.

Results of DSC experiments

The DSC results on pure resins and 40/60 plastic/rubber blends, produced from reheating peaks, are shown in Table VII. For each of the blends, the thermoplastic phase displays a discrete melting temperature, indicating that plastic and rubber phases are separate in all of the blends. A typical DSC plot for a PA/CIIR combination is included in Figure 7. Adding CIIR or NBR rubber to two of the three thermoplastics used in this study causes a reduction in the melting temperature of the plastic phase, indicating that the thermoplastic phase is affected during intensive mixing of these blends. The enthalpy of fusion values for each of the thermoplastic phases are fairly similar to those of their parent values, except for PBT/NBR blends, which may be due to degradation. Possible effects on the thermoplastic phase that may be taking place during dynamic vulcanization are MW reduction, graft formation, and changes in crystallization behavior. Previous results in this laboratory suggest that grafting between PA and butyl rubber takes place during blending.[25] Naskar et al.[40] also observed PP-EPDM graft links in the

TABLE VII
DSC Results—Thermoplastic Phase

Resin or blend combination[a]	T_m (°C)	ΔH_f (J/g plastic)
PA	178.7	60.6
PA/CIIR	174.9	58.1
PA/NBR	176.5	58.5
PP	163.3	80.9
PP/CIIR	161.6	83.1
PP/NBR	161.5	80.6
PBT	223.1	38.1
PBT/NBR	224.4	113.9

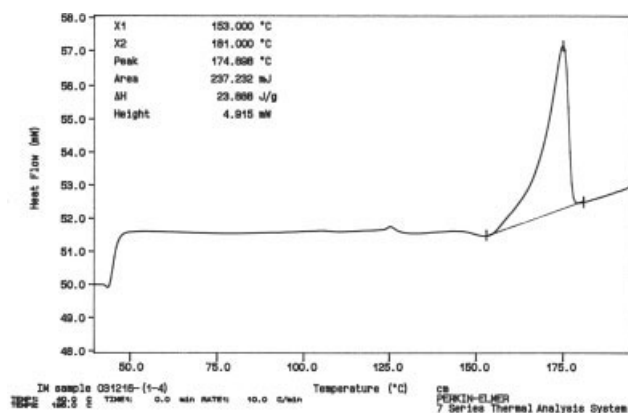[a] Blend compositions are 40/60 plastic/rubber.

Figure 7 DSC plot of a 40/60 PA/CIIR blend.

dynamic vulcanization of PP/EPDM blends. Lindsey et al. observed lower Tm values for LDPE in DSC cooling scans of LDPE/EPDM blends, and attributed this to partial solubilization of EPDM rubber with LDPE.[41] Their explanation may have only partial relevance in polymer blends such as these, where the polymeric substituents may have completely different solubility parameters.

Scanning electron microscopy on rubber/plastic blends

Figures 8–11 contain SEM micrographs of dynamically vulcanized blends of PA, PP, and PBT with CIIR and NBR. As can be seen, blends that contain 15–20% thermoplastic largely consist of a continuous phase based on rubber. There is some evidence of formation of an interlocking network at 20%. In contrast, blends with 40% thermoplastic all show a discrete rubber phase with an average rubber phase particle size in the range of 1–3 μm for PA/NBR blends, 10–30 μm for PP/NBR blends and 0.5–3 μm for PBT/NBR blends. Blends of thermoplastics with CIIR are more difficult to observe, because their lower level of unsaturation makes them more difficult to stain. As well, the dense particles of ZnO used for curing make it somewhat difficult to see the rubber particles. Nevertheless, it appears that the rubber phase is of the order of 2–4 μm in PA/CIIR blends and 1–3 μm in PP/CIIR blends. The particle size results suggest that the size of the discrete rubber phase at 40% thermoplastic is smaller when the components are matched in interfacial tension and solubility parameter, as expected. Thus, higher compatibility of the components gives rise to smaller discrete phase size, as is suggested for blends in the absence of dynamic vulcanization.[14] 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.
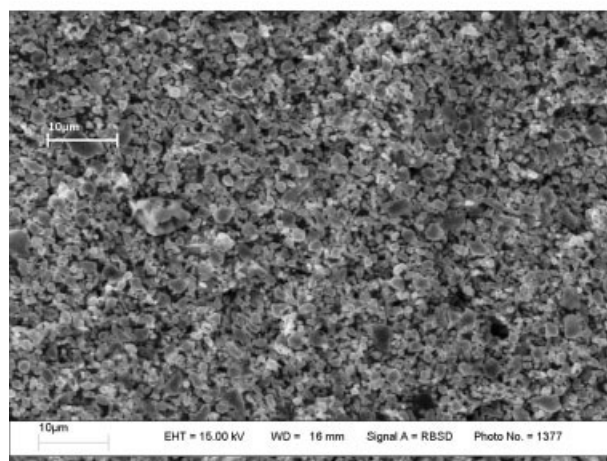
The results of SEM and exposure to solvents present a consistent picture of the morphological changes taking place in a variety of dynamically vulcanized
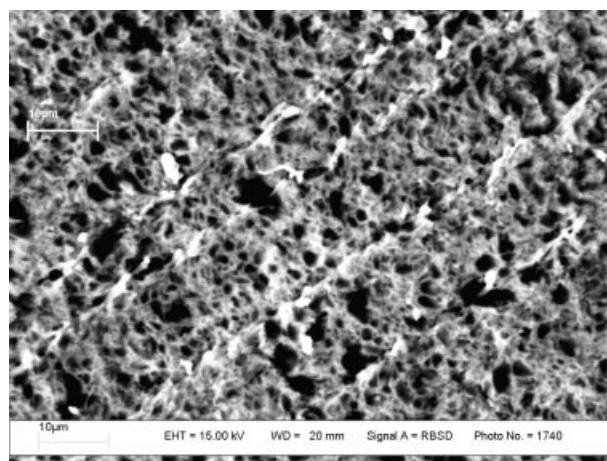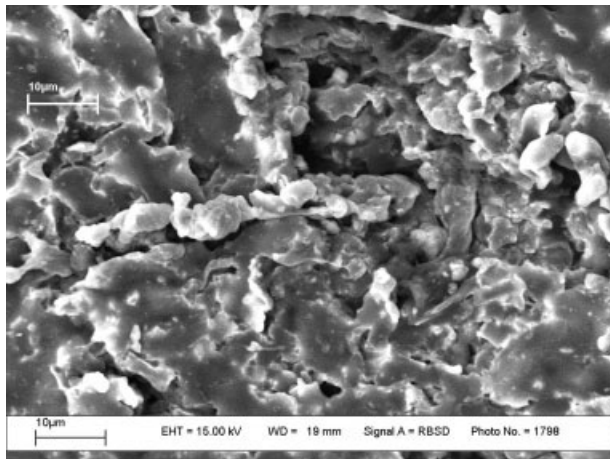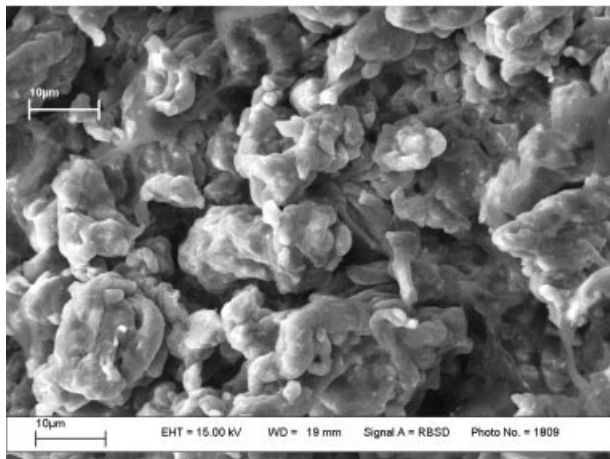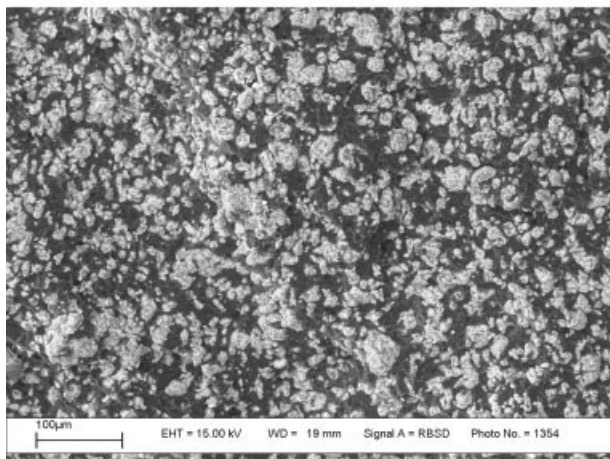

(a)
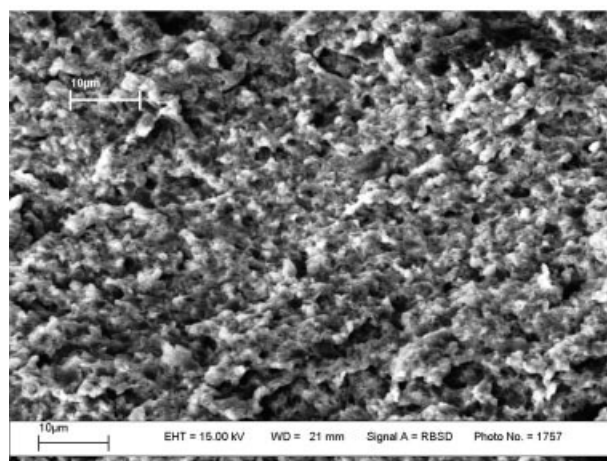
(b)

(c)

Figure 8 SEM of etched specimens of dynamically vulcanized PA/NBR blends (a) PA/NBR ratio: 15/85, (b) 20/80, and (c) 40/60.

(a)

(b)

(c)

Figure 9 SEM of etched specimens of dynamically vulcanized PP/NBR blends (a) PP/NBR ratio: 15/85, (b) 20/80, and (c) 40/60.

rubber/plastic blends over the range of 0–50% thermoplastic. As thermoplastic is introduced to the rubber compound, the continuous phase undergoes

phase inversion from rubber to plastic over a range of 10–30% thermoplastic, depending on the thermoplastic/rubber combination. When the thermoplastic component forms the continuous phase, the discrete rubber phase is provided with a plastic sheath surrounding the discrete rubber particles, which can restrict its volume expansion in the presence of solvents compatible with the rubber phase. A result of this nature might be expected for dynamic vulcanization. Although the swelling pressure in crosslinked rubber systems can become very high,[42] the counter-pressure of the continuous plastic phase in these blends acts as a negative influence in the volume expansion of the rubber phase. The success of the rubber particles to expand in the presence of solvents will depend on the choice of plastic and rubber, as well as shear history, presence of compatibilizing agents, and other factors that can affect the morphology of the blends.
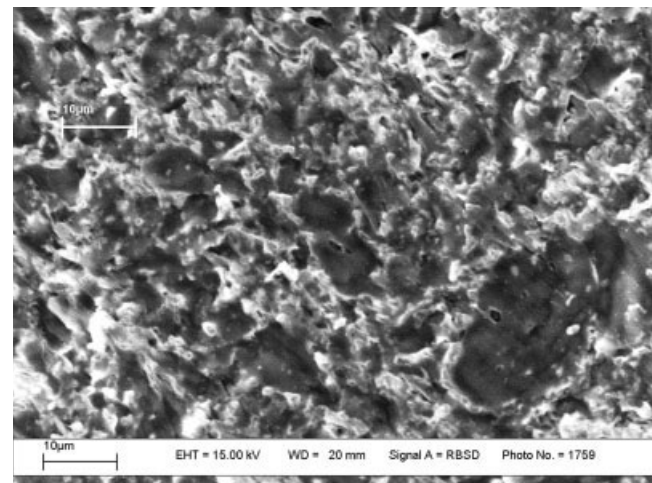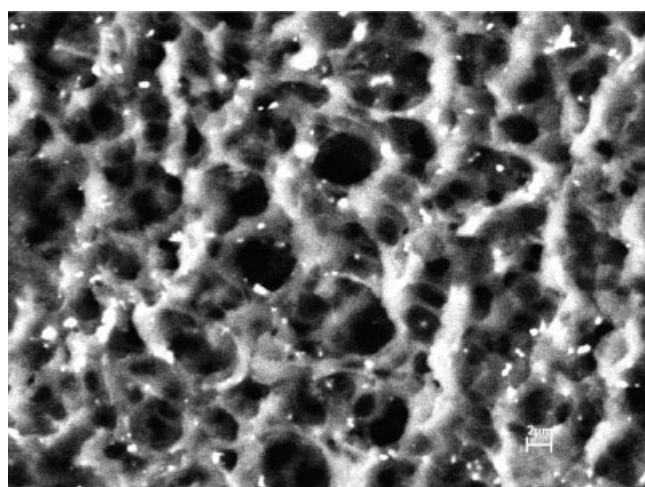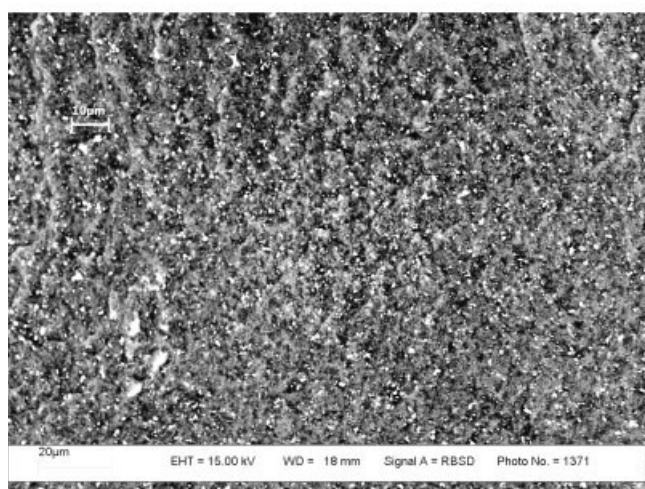

(a)
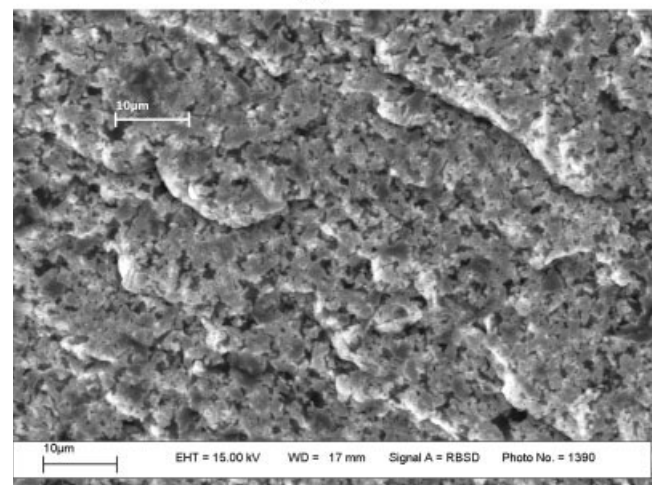
(b)

Figure 10 SEM of etched specimens of dynamically vulcanized PBT/NBR blends (a) PBT/NBR ratio: 20/80 and (b) 40/60.

Figure 11 SEM of etched specimens of dynamically vulcanized PA/CIIR and PP/CIIR blends of 40/60 ratio (a) PA/CIIR and (b) PP/CIIR.

Solvent resistance is an important issue in TPE blends, particularly those formed from mixtures of two or more component polymers. Although overall solvent resistance should be best when both the rubber and plastic components are resistant to solvents, an advantage is gained for mixtures of this type when they are exposed to solvents specific to the rubber component. If the rubber particles are surrounded by a thermoplastic sheath in blends of this nature, the TPE blend can be protected to some degree from attack by solvents that are aggressive to the rubber phase. Preliminary tests on NBR-containing blends indicate that solvents, which attack the rubber phase are much less effective when thermoplastics are introduced as blend agents. Thus, the barrier properties of blends can be enhanced by the appropriate choice of thermoplastic.

CONCLUSIONS

1. Dynamic vulcanization was used to produce a variety of rubber plastic blends in systems consisting of PA/CIIR, PP/CIIR, PA/NBR, PP/NBR, and PBT/NBR.
2. In all blends, the ultimate tensile strength and hardness values increase as the proportion of thermoplastic is increased, in the range of 0–50% thermoplastic.
3. Elongation at break values in all blends reach a minimum at 15–25% thermoplastic, which likely corresponds to the composition where the phase volume of the plastic phase is large enough to cause phase inversion.
4. In all of the tested blends, when the composition favors a continuous thermoplastic phase, the equilibrium swelling index values of the blends are significantly less than the expected "theoretical" values, based on blend composition only. This is attributed to a "caging effect" of the thermoplastic phase on the rubber phase at higher thermoplastic compositions.
5. DSC experiments reveal a reduction of up to 2.5°C in melting temperature of the thermoplastic phase in several of the blends, indicating that the plastic phase undergoes physical and chemical changes during the dynamic vulcanization process.
6. Etched surface micrographs of several plastic/rubber blends by SEM show that phase inversion occurs in the range of 20–40% thermoplastic.
7. At similar plastic/rubber proportions, increased compatibility in blends can be correlated with reduced particle size in the discrete phase. Increased compatibility may produce less caging effect on the rubber phase.

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