Preparation and Characterization of Heterophase Blends of Polycaprolactam and Hydrogenated Polydienes*

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Synopsis

The preparation, analysis, testing, and structure determination of ultrahigh impact rubber-toughened polycaprolactams (nylon 6) are described. Partially unsaturated hydrocarbon rubbers were used for this purpose. They were functionalized by reaction either in solution or in bulk with maleic anhydride to give rubbery "ene" adducts containing varying amounts of pendent succinic anhydride. Tough, rigid, thermoplastic engineering resins with notched Izod impact strengths of 750–1000 J/m were prepared by briefly melt-blending these adducts with nylon 6. Properties of the blends could be affected by the type and amount of elastomer used, the anhydride content, the type of nylon, the mixing conditions and the test conditions. Fractionation by coacervation in *m*-cresol/cyclohexane of a typical resin containing 20% by weight of functionalized rubber showed approximately 35% of a rubber–nylon graft, along with a few percent of free rubber dispersed in the nylon 6 matrix. A comb-block copolymer structure for the graft and a model for its formation are proposed, consistent with analyses of the fractions. Some of the blends prepared with partially hydrogenated medium vinyl polybutadiene–maleic anhydride adducts displayed a retention of impact properties at low temperatures which was superior to that obtainable with a similarly prepared EPDM-modified nylon 6. Transmission electron microscopy of a blend containing an anhydride-modified hydrogenated medium vinyl polybutadiene showed a morphology consisting of a nylon matrix containing finely dispersed, irregularly shaped, 0.03–0.55 µm rubber domains in which were found even smaller domains of nylon.

INTRODUCTION

In the unmodified state polycaprolactam, nylon 6, resin has a sufficient combination of good tensile and flexural properties, high heat distortion temperature, and an appreciable notched Izod impact strength on the order of 50 J/m that it is considered to be among the first "engineering resins." By chemically grafting the nylon to a dispersed rubber, heterophase blends with impact strengths on the order of 1000 J/m, well in excess of so-called "high impact" resins, can be obtained, and the blends might be more properly named "ultra-high impact" resins.

Toughened blends of nylon 6 were prepared in 1974 by Ide and Hasegawa,[1] who recognized that the dispersion of polypropylene in nylon 6 was improved when the PP was first functionalized by grafting with maleic anhydride. They

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attributed this to the presence of an interfacial agent which was formed through the reaction of the anhydride with amine chain ends. The impact strengths of their blends approached ca. 250–325 J/m.

Blends of nylon 6 and rubber which show toughening have been described by Cimmino et al.,[2] Martuscelli et al.,[3] and Greco.[4] In these reports, the blends were prepared from nylon 6 and an EPM copolymer grafted with maleic anhydride in the presence of peroxide; in some cases the blends were prepared by the *in situ* polymerization of caprolactam in the presence of the grafted EPM. Borggreve et al.[5] also described rubber-toughened nylon 6 that was prepared by blending with EPDM which had been grafted with maleic anhydride.

Both crazing and shear banding are believed to occur during the fracture of plastics upon impact. Rubber contributes to the toughness of plastic blends by stopping craze growth and concentrating stresses in the rubbery domains. In 1979, Flexman recognized and described crazing and shear banding behavior upon deformation of rubber-toughened nylon 66.[6] Wu[7] and Hobbs et al.[8] also described both behaviors and proposed that shear flow or shear banding is the dominant mode of energy absorption during fracture of rubber-toughened nylon 66. Jang et al.[9] have also reported crazing and shear banding upon fracture in blends of PP and rubber. Epstein et al.[10] have recently compared impact fracture of semicrystalline and amorphous nylons, from which they proposed that shear banding is the dominant mechanism of energy absorption in amorphous polymers, while craze formation dominates in semicrystalline polymers.

In the work reported here, we investigated the properties of several heterophase nylon 6–rubber blends. We selected for this study blends of nylon 6 with the maleic anhydride adducts of hydrogenated polydiene rubbers, primarily hydrogenated polybutadienes.[11] In some instances, comparisons were also made with blends of nylon 6 and maleic anhydride adducts of ethylene–propylene–diene (EPDM) rubber. The effects of variations in the amounts and types of rubber and nylon 6, the amount of anhydride adduct, and mixing conditions were followed. We also investigated the morphologies produced on blending and the temperature dependence of the impact properties. Finally, we separated and characterized the toughened blends in order to develop a model for the grafting process and the structure of the graft component.

EXPERIMENTAL

Materials

Most blends were prepared using Firestone 203001 (SF5104) resin with $[\eta] = 1.860$, M_w ca. 28,750, and having ca. 34 μeq NH_2/g, and 41 μeq COOH/g polyamide. When other resins were used, they are noted in the text. All of the nylon resins contained a maximum of 2% methanol-extractable materials. The elastomers used were hydrogenated polybutadienes prepared in our laboratories at several levels of unsaturation, based on polymers with high (99 + %), medium (40–50%), or low (11%) vinyl contents,[11] as well as several

TABLE I
Elastomers Used in Adductions with Maleic Anhydride

Elastomer no.	Polymer description	Unsaturation level (wt %)	Vinyl in base rubber (wt %)
I	Hydrogenated medium vinyl polybutadiene	5	44.1
II	Hydrogenated medium vinyl polybutadiene	8	40
III	Hydrogenated medium vinyl polybutyadiene	12	44.1
IV	Hydrogenated medium vinyl polybutadiene	30	44.1
V	Hydrogenated low vinyl polybutadiene	12	11
VI	Hydrogenated low vinyl polybutadiene	10	11
VII	Hydrogenated high vinyl polybutadiene	10	99.5
VIII	Hydrogenated polyisoprene (Goodyear Natsyn)	2	< 2
IX	Hydrogenated block SBS (Kraton 1101)	8	< 5
X	EPDM (Nordel 1070, DuPont)	5	—
XI	EPDM (Nordel 3681, DuPont)	5	—

hydrogenated commercial polydiene elastomers, and various commercial EPDM resins, as noted. Features of several of these polymers are listed in Table I.

Procedures

Maleic Anhydride Adducts

Solution Method. The "ene" modification of rubber was carried out in a toluene solution in a 2-gal reactor. The modified rubber was recovered by desolventization on a scraped-drum dryer under a nitrogen purge. Infrared analysis was used to measure the anhydride concentration of the products (see below). The preparations are summarized in Table II.

Bulk Method. Some of the modified rubbers were also prepared in bulk by the reaction of the rubber with liquid maleic anhydride in a Werner-Pfleiderer ZSK-30 corotating twin-screw extruder, operating at temperatures of 280°C and residence time of 30–600 s. The product rubber was cooled, chopped, and dried before further use. Anhydride contents and polymer properties were similar to those obtained from the solution process, and are also noted in Table II.

Preparation of Nylon-Grafted Rubber

The toughened polyamide blends were prepared in the twin-screw extruder using a similar process, by feeding a dried mixture of polyamide and modified rubber pellets through the 30 mm extruder operating at 170–260°C, with a residence time of 120–180 s. The extrudate was cooled in water, chopped, and dried under vacuum before injection molding.

IR Analysis of Maleic Anhydride (MA) in Rubber

The MA functional rubber was vacuum dried for at least 1 h at 100°C under a pressure of less than 0.1 mm Hg before analysis. Samples were run on a

TABLE II
"ENE" Adducts of Rubber and Maleic Anhydride

Modified rubber	Hydrogenated elastomer type	Elastomer (no.)	Adduction		
			Temp (°C)	Time (h)	MA (wt %)
A[a]	Medium vinyl PBd	I	182–188	160	0.67
B[a]	Medium vinyl PBd	II	177–188	90	0.96
C[a]	Medium vinyl PBd	III	177	48	0.36
D[a]	Medium vinyl PBd	III	177	48	0.42
E[a]	Medium vinyl PBd	III	182	72	0.85
F[a]	Medium vinyl PBd	IV	171–177	72	0.93
G[a]	Low vinyl	V	177–190	140	1.35
H[a]	Low vinyl	VI	190	48	1.17
J[a]	Block SBS (Kraton) (1101)	X	177–185	120	0.97
K[a]	High vinyl PBd	VII	200	24	ND[c]
L[a]	EPDM	X	170	190	0.34
M[a]	EPDM	XI	170	190	0.34
N[a]	Polyisoprene	VIII	179–185	160	0.1
O[b]	Med. vinyl PBd	II	280	0.1	0.8
P[b]	Low vinyl PBd	VI	280	0.1	0.6
Q[b]	EPDM	XI	280	0.1	0.4

[a] Prepared in 1 gal reactor, toluene solvent, 5 wt % MA charge.
[b] MA adduction performed in extruder.
[c] ND = not determined.

Beckman 4220 infrared spectrometer either in 1.0 mm solution cells or as films.

Solution Method. An accurately prepared solution of 1.5–2.5% (wt/vol) of the MA modified rubber in spectrograde chloroform was used. The 2100–1600 cm^{-1} range was scanned at 300 cm^{-1}/min at least three times and the bound MA content [MA] in $\mu mol/g$ was calculated using Beer's law. The value of the extinction coefficient used was determined from undecenyl succinic anhydride as 178 mm^{-1} M^{-1}:

$$[MA] = \frac{10^6}{178lc} \log\left[\frac{T_{2000}}{T_{1790}}\right]$$

where T_{2000} is the % transmittance at 2000 cm^{-1}, T_{1790} is the % transmittance at 1790 cm^{-1}, c is the solution concentration (g/L), and l is the pathlength (mm).

Optical Ratio Method. A rapid determination of the MA content can be made using a thick cast or pressed film. For this measurement, the range from 3000 to 1500 cm^{-1} was scanned at the same rate as above. Using at least three scans, the bound % MA was calculated from the following equation:

$$\% \, MA = 0.1872 \frac{[\log(T_{2000}/T_{1790})]}{[\log(T_{2000}/T_{2720})]} + 0.0215$$

where the T's are as defined above. For a series of EPDMs modified with MA, in which the MA content was determined by the solution method, the correlation with the optical ratio method is given in the calibration curve shown in Figure 1.
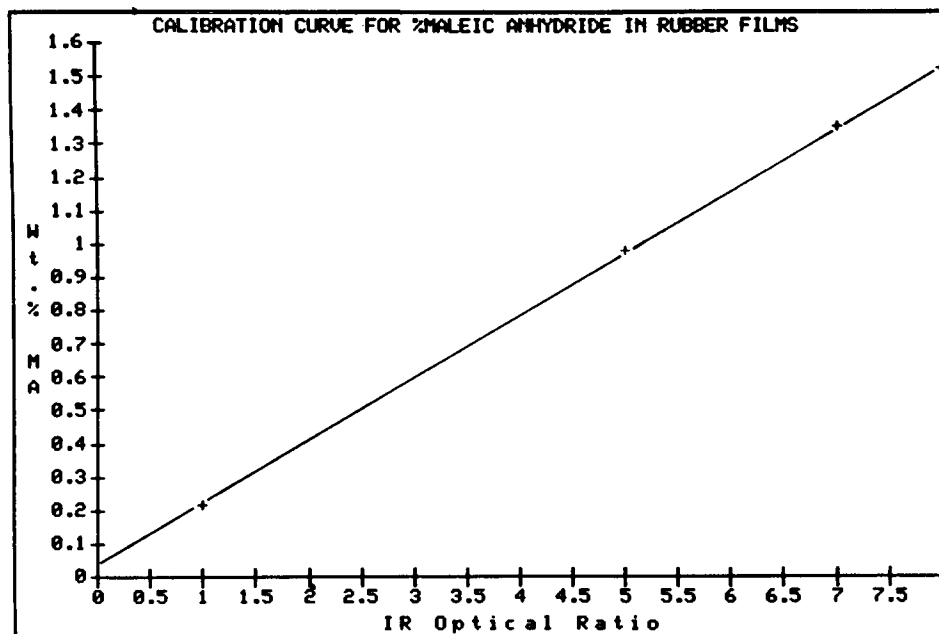
Fig. 1.   Calibration curve for determination of bound maleic anhydride from IR optical ratio in EPDM.

Tests for Physical Properties

Room Temperature Impact Tests. Notched Izod impact strength was determined per the procedure outlined as ASTM D-256.[12] Particular attention must be paid to the quality and uniformity of the notch to obtain reproducible results, as well as the location on the injection-molded bar at which the sample is cut.[10]

Low Temperature Impact Tests. Variable temperature impact strength measurements were obtained by the ASTM method, using samples which had been immersed in an isopropyl alcohol bath maintained within 0.2°C of the desired temperatures. Samples for impact testing were cut, notched, gauged, and labeled, and then immersed directly in the bath (10 min for 3.2 mm samples, 20 min for 6.4 mm samples). Samples were removed individually from the bath with forceps and tested within 10 s of their removal.

Flexural and Heat Distortion Tests. Flexural testing was performed in accordance with ASTM Procedure D-790.[13] Heat distortion temperatures were measured at two different loads by ASTM Procedure D-648.[14]

Separation and Analysis of Blends

Coacervation Fractionation Procedure.[15,16,17] The previously described coacervation procedure[17] was used. Free rubber was obtained from the first two fractions by extracting the material with refluxing toluene for 48 h.

Digestion of Nylon–Rubber Blends in Hydrochloric Acid. The rubber content of two component nylon–rubber blends was determined in the following manner: An accurately weighed among of compound (5–10 g) was placed in a 500-mL flask containing 250 g of $6N$ hydrochloric acid. The contents of the flask were refluxed for 48 h, and then filtered. The rubber precipitate was

washed repeatedly with water, then air-dried, and finally vacuum-dried at 70–80°C for 16–18 h and weighed. Nitrogen analyses on the rubber residue indicated the degree of functionality/grafting which took place. A less detailed description of this procedure was recently reported by Chen and Kennedy.[18]

RESULTS AND DISCUSSION

Modification of Rubber with Maleic Anhydride via the Ene Reaction

The ene reaction, defined as the addition of a compound with a double bond (eneophile) to an olefin with an allylic hydrogen (ene) [reaction (1)], has been known for some time, and the subject has been reviewed[19]:

$$(1)$$
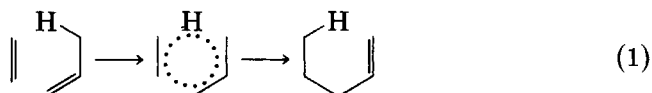
The reaction is applicable to polymers, such as unsaturated rubbers. The ene reactions of maleic anhydride (MA) with 1,4-polyisoprenes,[20] poly(dodecane-co-diene),[21] ethylene/propylene/diene (EPDM) polymers,[22] and hydrogenated polydienes[11] have previously been described.

Hydrogenated polydiene elastomers, with low levels of unsaturation, readily form an adduct with MA under ene conditions. The process thought to be involved is depicted in reaction (2). As noted, the reaction is purely thermal, requiring no initiator. The procedure may be performed in solution or in bulk as described in the Experimental section:

$$(2)$$
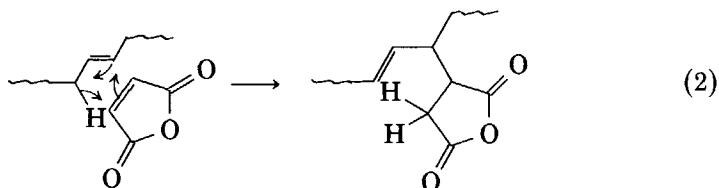
TABLE III
DSC Analysis of Selected Elastomers and Elastomer–MA Adducts

Polymer no.	Identity	T_g (K)	T_m (K)	H_f [a] (J/g)	Relative % Crystallinity[b]
XI	EPDM	232.4	328.7	11.8	4.09
Q	EPDM–MA	234.5	326.1	10.6	3.67
N	Hydrog. polyisoprene–MA	216.6	306.6	14.3	4.95
G	Hydrog. low vinyl PBd–MA	233.1	327.6	46.1	15.97
I	Hydrog. med. vinyl PBd (95% sat.)	217.5	304.4	5.6	1.94
A	Hydrog. med. vinyl PBd–MA (95% sat.)	219.6	303.9	5.6	1.94
D	Hydrog. med. vinyl PBd–MA (88% sat.)	217.5	310.91	18.7	6.48

[a] Heat of fusion.
[b] Relative to ΔH_f = 288.7 J/g for 100% crystalline polyethylene (Ref. 23).

In these experiments, MA incorporations of up to 1.5% by weight were achieved, with a typical range being 0.3–1.0% (see Table I). Typical reaction conditions for the MA adduction were 24–190 h at 170–200°C, with shorter reaction times at higher temperatures. In several cases it was necessary to estimate the bound-MA content using the optical ratio of bands at 1795 and 2740 cm^{-1}, with a calibration developed using EPDM. This was because several of the products were insoluble, as a result of either gelation or high crystallinity. Table III shows the results of DSC analyses of several of these products. Both crystallinity, which ranged from about 2 to 28%, and T_m were dependent on the microstructure. Crystallinity was changed little by adduction with MA, although the T_m was depressed slightly. Measurements of T_g may be influenced by T_m in some of the more highly crystalline polymers.

Melt Blending in the Twin-Screw Extruder

Blending is achievable by a variety of methods, the most convenient being melt-blending in a twin-screw extruder. In this process, the pendent anhydride can conceivably react with either the terminal amine groups or with the amide bonds of the nylon to give a nylon 6–rubber graft. Reactions (3) and (4) depict these respective processes. Several groups have favored the predominance of reaction (3), but have not obtained data which would rule out reaction (4).[1,2] Based on the present fractionations of toughened blends, reaction (4) can be ruled out (see below). Typical conditions for extruder blending are given in the Experimental section.

(3)

(4)
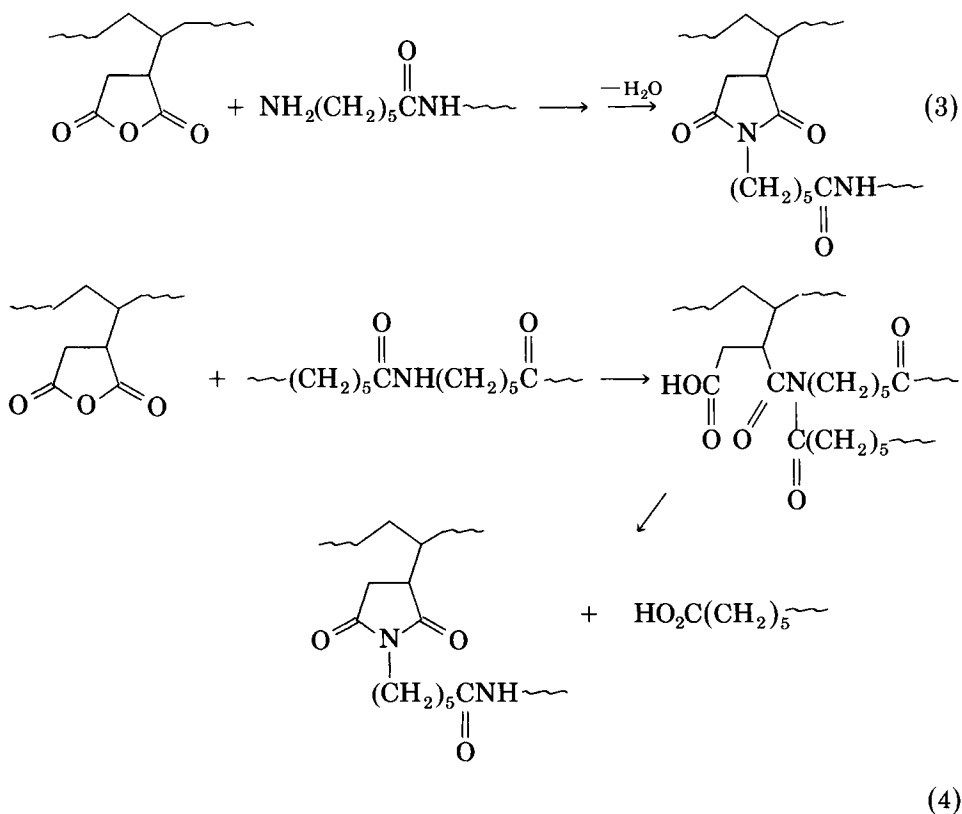
Physical Test Results

Effect of Elastomer Type

Table IV lists the results of impact and flex tests on blends of selected adducts of hydrogenated dienes with nylon 6 (20%/80%). Outstanding notched Izod impact strengths in the ultratough region (580–1100 J/m) were obtained with adducts based on hydrogenated high, medium, and low vinyl polybutadiene microstructures with greater than 70% saturation. EPDM–MA-modified resins also showed excellent properties. Some blends of nylon 6 with EPDM–MA and EPM–MA have recently been described which also show similar properties.[2,5]

No improvement in impact resistance was achieved with an MA-modified medium vinyl PBd which was saturated to only 69.4% (blend no. 7). This was presumably the result of crosslinking of the rubber during blending with nylon. The compound exhibited a grainy surface, which is thought to be due to poorly dispersed gelled rubber.

Lower but significant improvements in impact strength were obtained from an MA adduct of hydrogenated polyisoprene which contained less than optimum anhydride and grafting (see Analysis of Blends), and an MA adduct of a hydrogenated block SBS thermoplastic elastomer.

Effect of Elastomer Content

A major determinant of impact strength in nylon–rubber blends is the amount of rubber present. It was found that impact strength increases sigmoidally with increasing modified rubber content, as shown in Figure 2. This relationship was developed using blends of nylon 6 with MA-modified EPDM. The mode of failure also changes as the amount of rubber increases, going from predominantly brittle failure at rubber levels below 10%, to ductile failure at levels above 10%. At one extreme, a blend of 50% nylon 6 and 50% MA adduct of hydrogenated medium vinyl polybutadiene (D) was flexible and could not be broken in the Izod impact test. As would be expected, the modulus and strength of the blends decreased as the rubber content was increased, as shown in Figure 3.

Effect of Anhydride Content

The amount of anhydride incorporated into the elastomer was found to have little effect on impact properties of the nylon blends, provided that a sufficient level of rubber was used, a minimum level of anhydride above about 0.2% was present, and the anhydride was not allowed to hydrolyze appreciably. The data compiled in Table V for samples 24–33, a series of blends of nylon 6 with EPDM–MA adducts, showed an insignificant increase in impact strength with increasing MA content between 0.2 and 0.6% by weight. The lower impact strength of sample 29 compared with sample 30, both with 0.33% MA, was due to partial hydrolysis of the MA adduct used in 29 as a result of storage in moist air for over 1 week before blending with nylon. Apparently the grafting reaction is more efficient with anhydride than with diacid. An even greater effect can be seen with blends 22 and 23, where the MA adduct

TABLE IV
Properties of Blends of Nylon 6 with Various MA-Modified Rubber

Blend no.	Type of elastomer		Elastomer content	Notched Izod imp strength[a] (J/m)		Flexural modulus (GPa)	Heat distortion temp (°C)	
				3.2 mm	6.4 mm		455 Pa	1.82 kPa
1	None		0	0.80	0.68	2.40[a]	127	54
2	High vinyl PBd	(K)	15	827.7	240.3	1.49[a]	102	58
3	Med. vinyl PBd	(A)	20	934.5	801.0	0.82[b]		
4	Med. vinyl PBd	(B)	20	1036.0	982.6	—		
5	Med. vinyl PBd	(C)	20	822.4	694.2	—		
6	Med. vinyl PBd	(D)	20	1014.6	982.6	1.63[a]	88	55
7	Med. vinyl PBd	(F)	20	46.5	38.4	0.74[b]		
8	Low vinyl PBd	(G)	20	955.9	801.0	1.52[a]	84	55
9	Low vinyl PBd	(H)	20	875.8	614.1	—		
10	Polyisoprene	(N)	20	110.0	99.9	1.65[a]	95	55
11	Block SBS	(J)	20	97.2	79.0	1.11[b]		
12	Med. vinyl PBd	(O)	20	1030.6	849.1	1.80[a]		
13	Low vinyl PBd	(P)	20	955.9	704.9	1.88[a]		
14	EPDM	(Q)	20	843.7	763.6	1.76[a]		

[a] Tested dry as molded, room temperature.
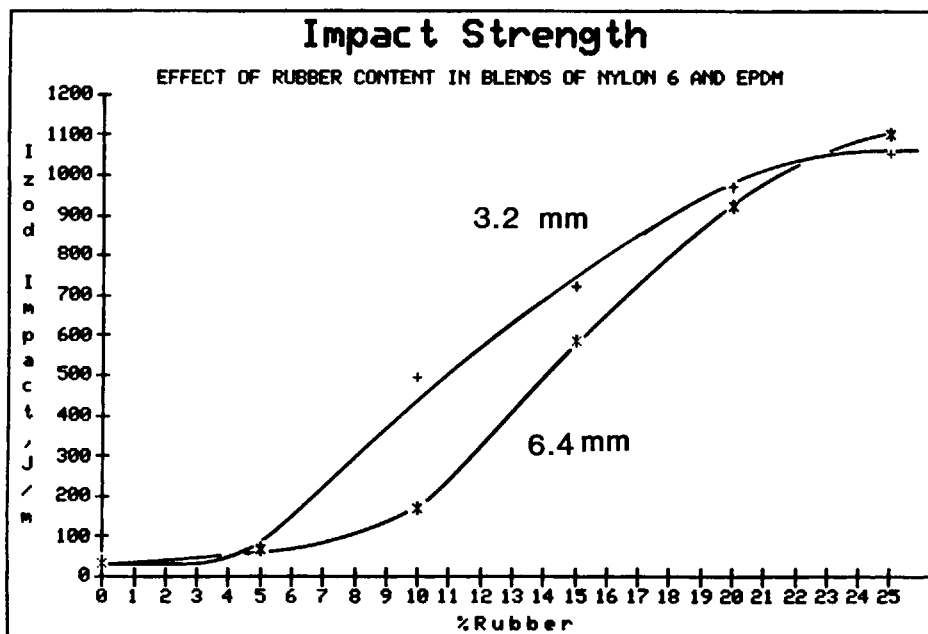[b] Tested after standing in humid air.

Fig. 2.   Effect of rubber content on notched Izod impact strength in blends 1 and 15–19, containing nylon 6 and increasing amounts of MA-modified EPDM (L).
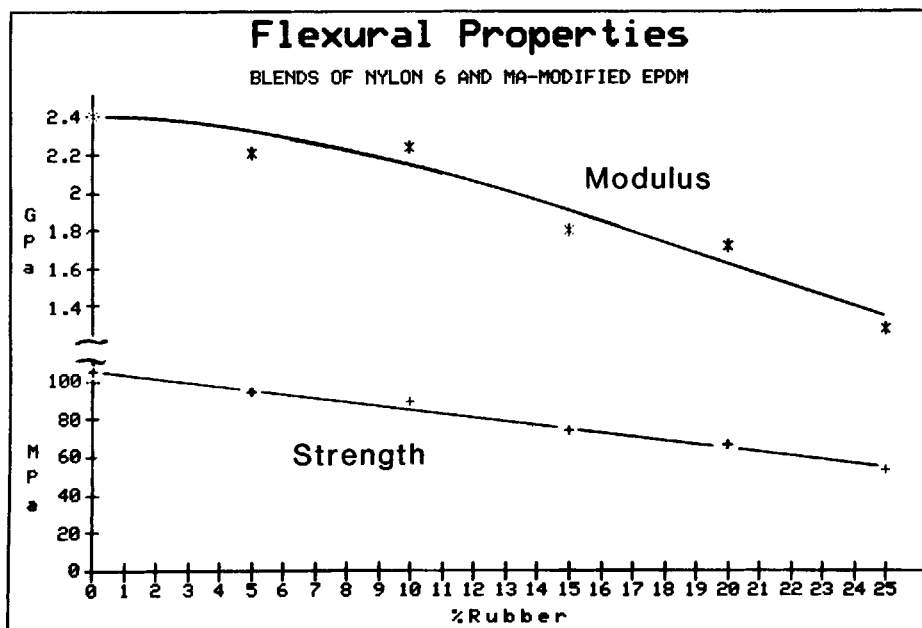

Fig. 3.   Flexural properties of blends 1 and 15–19, containing nylon 6 with increasing amounts of MA-modified EPDM (L).

TABLE V
Effect of Anhydride Concentration on Impact Properties of Blends
of Nylon 6 with MA-Modified EPDM

Blend no.	MA (wt %)	Rubber (%)	Notched Izod impact strength at RT (J/m)	
			3.2 mm	6.4 mm
20	0	15	51.8	47.0
21	0.12	15	202.9	160.2
22	1.1	15	507.3	395.2
23	1.48	15	998.6	694.2
24	0.33	18	833	726.2
25	0.20	20	—	747.6
26	0.27	20	—	779.6
27	0.29	20	—	758.3
28	0.31	20	—	817
29	0.33	20	—	608.8
30	0.33	20	—	790.3
31	0.35	20	—	731.6
32	0.44	20	—	747.6
33	0.52	20	—	779.6

used in 22 was allowed to hydrolyze similarly. Although a higher concentration of anhydride was initially present in both rubbers, the 15% rubber in these blends is closer to the minimum level of toughener sufficient for ultrahigh impact strength.

Effect of Nylon Type

Examples 34–36 of Table VI show the effect of varying amine end-group content on impact strength. The impact strength appears to be greater when the amine end concentration is high, presumably reflecting the efficiency of grafting of the rubber–MA adduct to the nylon.

Effect of Mixing Conditions

In early experiments using a Welding Engineers twin screw extruder, two passes of 4 min residence time at 260°C were necessary to obtain blends with optimum properties. Further mixing did not improve properties, and properties deteriorated when more than four passes through the extruder were made,

TABLE VI
Effect of Polyamide Amine End-Group Content on Impact Properties of Blends
of Nylon 6 with MA-Modified EPDM (0.35 wt % Bound MA, 15% Rubber)

Blend no.	Amine concentration (μeq NH_2/g resin)	Notched Izod impact strength at RT (J/m)	
		3.2 mm	6.4 mm
34	9	555.4	133.5
35	27	720.9	587.4
36	34	731.6	651.5

TABLE VII
Effect of Mixing Conditions on Impact Strengths of Blends of 85% Nylon 6
with 15% MA-Modified EPDM

Blend no.	MA adduct of EPDM	Number of passes	Extruder temp (°C)	Notched Izod impact strength (J/m)	
				3.2 mm	6.4 mm
37	Nordel 1040	1	260	106.8	106.8
38		2	260	688.9	555.4
39	Nordel 1070	1	260	106.8	96.1
40		2	260	571.4	149.5
41	Nordel 1070	1	280	614.1	464.6
42		2	280	587.4	523.3
43		3	280	635.5	539.3
44		4	280	635.5	534
45		5	280	608.8	496.6
46		6	280	550	464.6

presumably the result of degradation of the nylon. The data are summarized in Table VII. A single pass at residence times of greater than 100 s was sufficient to obtain optimum properties using the Werner–Pfleiderer twin screw extruder. Borggreve et al.[5] have shown that the particle sizes and interparticle distances in nylon 6/EPDM-MA blends can be controlled by varying the extruder temperature. The brittle–tough transition temperatures of the resulting blends varied directly with the particle sizes, even though the blends had equal amounts of the identical functionalized rubber.
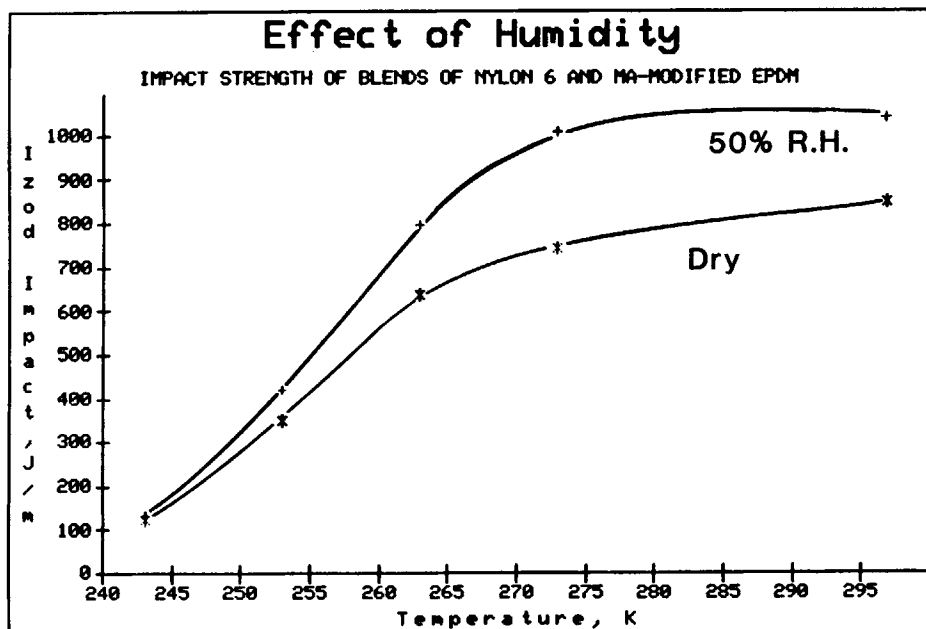

Fig. 4.   Notched Izod impact strength of blend 47, containing 80% nylon 6/20% MA-modified EPDM (L), tested dry as molded and at 50% RH.

TABLE VIII
Variable Temperature Impact Resistance of Hydrogenated Polydiene Rubber–Nylon Blends
(MA Adducts Prepared in Bulk)

Test temp (K)	Example no., MA adduct	Notched Izod impact strength, 6.4 mm (J/m)		
		12, Med. vinyl PBd(O)	13, Low vinyl PBD(P)	14, EPDM(Q)
297		849.1	704.9	822.4
273		902.5	331.1	715.6
263		865.1	213.6	635.5
253		913.1	192.2	582.1
243		352.4	117.5	256.3
233		202.9	112.1	144.2

Effect of Test Conditions

Humidity. Flexural and impact properties were significantly affected by the humidity conditions under which the test samples were stored. Measured impact strengths were typically lower for dry samples (Fig. 4).

Temperature. Impact resistance generally decreases with decreasing temperature, a phenomenon which appears to be attributable to glass transitions of the rubber phase. Low-temperature impact resistance was measured for three resins of this study. The results summarized in Table VIII show that excellent impact properties were retained at 243 K for the medium vinyl-modified resin, with notched Izod impact strengths of 128–187 J/m (6.4 mm). High impact properties were also obtained with the hydrogenated low vinyl PBd–MA, 96 J/m (6.4 mm, notched). Figure 5 readily shows the differentiation between hydrogenated medium vinyl PBd and hydrogenated low vinyl PBd in nylon, with impact strengths dropping off much less rapidly at low temperature in the case of the former resin. The hydrogenated medium vinyl modified resin also compares favorably against EPDM–MA, showing essentially no change in impact resistance to 253 K, and 40% higher impact strength than the EPDM–MA modified resin at 233 K. High impact properties were retained by all three resins even at 233 K. The low temperature behavior appears to follow T_g as measured by DSC for the three elastomers used in these blends (see Table III). T_g values reported elsewhere for very similar polymers (EPDM, 221 K[24]; 42% 1,2-HPBD, 212 K[25]; 8% 1,2-HPBD, 243 K[25]) agree qualitatively with our values, but place EPDM and medium vinyl HPBD closer together. The T_{B-T} [5] estimated from Figure 5 occurs slightly lower for the blend with 44% vinyl HPBD than with EPDM, although the impact strength of the EPDM blend deteriorated more rapidly above T_{B-T}. The range of T_{B-T} is very similar to that reported by Borggreve et al.[5] The superior low temperature properties of hydrogenated medium vinyl PBd-modified nylon 6 represents an advantage over EPDM-modified nylon 6.

Analysis of Blends Compositions

The blending and grafting of anhydride-modified rubber with nylon should give rise to three major fractions: graft rubber-nylon, **3**, ungrafted (free)

Comparison of Rubber Modifiers
EFFECT ON IMPACT STRENGTH WITH TEMPERATURE

Fig. 5. Temperature dependence of notched Izod impact strength in blends 12–14, containing 80% nylon 6 and 20% of various MA-modified elastomers, tested dry as molded.

nylon, **1**, and ungrafted (free) rubber, **2**, according to (5).

$$(x - z) \, 2 + (y - z) \, 1$$

$$\text{(5)}$$

This equation is written showing reaction with amine ends and just one attachment to the modified rubber. Several graft sites are, in fact, obtainable. The relative amount of **3** formed in the blending determines the graft efficiency, upon which the physical properties of the blends depend. It is possible to separate **1**, **2**, and **3**, using solvent separation techniques, in order to characterize the composition and the basis for observed properties. One separation scheme using phenol/tetrachloroethane was found to be unsuitable for poorly grafted blends of nylon 6 and hydrogenated diene rubber–MA adducts. However, the coacervation procedure gave satisfactory separations; a detailed description has been published elsewhere.[26]

The approximate nylon content of the respective fractions was determined from C, H, N analyses. The results for graft and free rubber content in compounds from various sources are summarized in Table IX. The graft and

TABLE IX
Fractionation of Nylon 6//Hydrogenated Rubber–MA Blends

Reference Number	Rubber–MA Adduct	Bound (wt %)	Rubber charged (%)	Impact strength, 6.4 mm (J/m)	Free rubber (wt %)	Graft (wt %)	Nylon in graft (wt %)	% Modifier in fractions 1 and 2
2	Hydrog. high 1,2 PBd–MA (K)	ND	15	240.3	1.3	37.2	69.0	86.7
6	Hydrog. med. 1,2 PBd–MA (D)	0.42	20	982.6	2.9	35.6	57.6	90.0
12	Hydrog. med. 1,2 PBd–MA (O)	ca. 0.8	20	849.1	6.2	35.7	61.6	99.5
13	Hydrog. low 1,2 PBd–MA (P)	ca. 0.6	20	704.9	1.1[a]	32.7[a]	68.8[a]	56.5[a] 77.1[b]
10	Hydrog. polyisoprene–MA (N)	ca. 0.1	20	101.5	10.2	17.0	53.3	91.0
14	EPDM–MA (Q)	ca. 0.4	ca. 22	1068	6.2	39.0	59.5	100

[a] Neglecting 6% insoluble residue (fraction 11).
[b] Including 6% insoluble residue (fraction 11, 68% rubber).

free rubber were usually concentrated in the first two fractions, unless the rubber had become gelled or was otherwise insoluble. Free rubber was calculated according to

$$F = \text{wt \% free rubber} = \frac{100}{m_c} \frac{(m_r m_i)}{(m_s)} \qquad (6)$$

where m_c = total mass of compound fractionated, m_r = mass of residue, m_i = mass of fraction i, and m_s = mass of sample of fraction i used for extraction.

The total graft was estimated as the sum of fractions 1 and 2, minus the free rubber present, as shown by

$$G = \text{wt \% graft} = \text{wt \% fraction 1} - \text{wt \% free rubber} + \text{wt \% fraction 2} \qquad (7)$$

The percentage of nylon in the graft was estimated using the nitrogen analyses of graft-containing fractions and the wt % graft, according to

$$\text{wt \% nylon in graft} = \frac{\sum [(\text{wt \% } N)/12.39]_i (F_i + G_i)}{\sum G_i} \qquad (8)$$

The complete results are given in Table X, which showed in most cases a substantial graft fraction in the blends, ranging from 32.7 to 39.0 wt % of the total compound. The graft composition was fairly uniform, consisting of 53–69 wt % grafted nylon. Free (ungrafted, soluble) rubber contents ranged from 1.1 to 6.2%, except in the hydrogenated polyisoprene compound with a very low anhydride functionality, which had 10.2% free rubber. In that case, there was only 17.0% rubber–nylon graft in the blend. Material balances on the graft and free rubber showed that 77–100% of the functional modifiers charged were accounted for in the first two fractions, except in the case of hydrogenated low vinyl polybutadiene, where a substantial amount of insoluble rubber or graft (ca. 6%) constituted a residue after fractionation. This was due to the insolubility of the more highly crystalline rubber. In the blends which were fractionated, impact strengths were a function of both grafting efficiency and the total amount of modifier charged.

Viscosities were determined for one of the resins fractionated. The results, determined in m-cresol at 25°C, are listed in Table XI. Molecular weights were calculated from the Mark–Houwink equation, using the constant $K = 0.0032$ dL/g and exponent $\alpha = 0.62$.[27] The molecular weight of the free nylon fraction from the mixture of nylon, rubber, and nylon-g-rubber was about 6% higher than that of untreated nylon. If significant, this increase could reflect the partial removal of low molecular weight nylon in the first two fractions, or it may be due to the presence of some nylon–rubber–nylon species. Whatever the effect, its magnitude is small. The molecular weight data suggests that scission of polyamide chains [reaction (4)] is not as important as the reaction with amine chain ends [reaction (3)] during the grafting process.

Digestion of several selected blends in 6N HCl led to the recovery of a rubbery residue having approximately the same mass percentage as that

TABLE X
Fractionation by Coacervation of Nylon 6/Ma-Modified Rubber Blends[a]

Compound	Rubber–MA adduct	Fraction isolated		
			Cumulative	
		wt %	%	% nylon
6	Hydrog. med. vinyl PBd (D)	27.9	27.9	43.9
		10.6	38.5	77.8
		4.6	43.1	90.6
		6.0	49.1	89.4
		8.6	57.7	83.8
		8.0	65.7	91.4
		5.3	71.0	91.7
		9.9	80.9	90.4
		0.0	80.9	—
		0.7	81.6	ND
12	Hydrog. med. vinyl PBd, (O) adduct prepared in extruder	33.9	33.9	48.3
		8.0	41.9	77.2
		15.3	57.2	84.1
		14.6	71.8	92.1
		4.6	76.4	ND
		10.0	86.4	96.0
		3.3	89.7	95.2
		4.0	93.7	85.2
		0.0	93.7	—
13	Hydrog. low vinyl PBd, adduct prepared in extruder (P)	2.0	95.7	ND
		3.3	3.3	87.2
		10.0	13.3	87.6
		24.7	38.0	79.1
		11.4	49.4	84.8
		3.3	52.7	ND
		5.3	58.0	85.15
		7.4	65.4	94.92
		7.4	72.8	93.62
		0.0	72.8	—
		9.4	82.2	34.87[b]
		6.0	88.2	31.32[b]
10	Hydrog. polyisoprene (N)	21.9	21.9	25.4
		5.3	27.2	73.4
		7.9	35.1	88.0
		9.3	44.4	87.6
		6.6	51.0	91.0
		5.9	56.9	86.5
		5.3	62.2	92.6
		24.5	86.7	93.6
		7.3	94.0	92.2
14	EPDM, adduct prepared in extruder (Q)	1.3	95.3	ND
		39.9	39.9	48.2
		5.3	45.2	74.7
		10.0	55.2	88.0
		9.3	64.5	89.4
		6.0	70.5	84.4
		4.6	75.1	91.9
		6.6	81.7	91.8
		16.6	98.3	93.3
		2.0	100.3	ND
		0.0	100.3	—

[a] See Figure 2 for solvent compositions.
[b] Insoluble rubber or graft-containing residue in last two fractions.

TABLE XI
Molecular Weight Distribution of Nylon Fraction from Example No. 2,
with Rubber–MA Adduct K

Fraction identity	Cumulative (wt %)	Nylon (%)	$[\eta]^a$	Estimated mol wt[b]
Nylon 6, unreacted (example 1)	—	100	1.860	28,751
Nylon-6-g-rubber, Unfractionated (example 2)	—	—	1.677	24,328
Free rubber and graft, fraction 1	27.9	63.3	1.614	22,870
Graft and nylon 6, fraction 2	38.5	76.5	0.982	10,262
Nylon 6, fraction 3	43.1	86.8	0.988	10,363
Nylon 6, fraction 4	49.1	88.3	1.068	11,750
Nylon 6, fraction 5	57.7	89.1	1.165	13,518
Nylon 6, fraction 6	65.7	83.7	1.311	16,354
Nylon 6, fraction 7	73.7	82.6	1.500	20,322
Nylon 6, fraction 8	95.9	85.2	2.308	40,721
Nylon 6, fraction 9	96.9	ND[c]	ND	ND
Nylon 6, fraction 10	100.2	ND	ND	ND
Fractions 3–10	61.5		1.934	30,618

[a] Calcd from $[\eta] = 1/c\,[0.75 \ln (RV) + 0.25 (RV - 1)]$

[b] Calcd from $[\eta] = KM^d$ for $K = 0.0032$ dL/g, $\alpha = 0.62$, m-cresol, 25°C.

[c] ND = not determined.

charged in the blend. The nitrogen contents of the rubbery residue were consistent with the amounts of bound maleic anhydride known to be present in the starting adducts, assuming hydrolysis to the pendent succinimide of aminocaproic acid. This assumption was verified by melt-blending nylon 6 with undecenylsuccinic anhydride, a model for the rubber–MA adduct, and digestion under the same conditions, followed by extraction and elemental analysis. A stoichiometry consistent with an average of 0.92 aminocaproic acid units per alkenylsuccinimide was determined, indicating that the digestion proceeds to the last unit of pendent polycaprolactam. As an example of the comb-block graft copolymer structure this represents, rubber modifier D(M_n = 120,000, 0.42% by weight bound anhydride) would have an average of about five pendent succinimidyl polycaprolactam sidechains per rubber chain when fully grafted. The calculated nylon content of 54.5% in this graft agrees well with the 57.6% found. A structure such as 4, suggested by the analysis of the graft copolymer isolated from blend 6, should be typical of the graft components of the other blends as well.


4
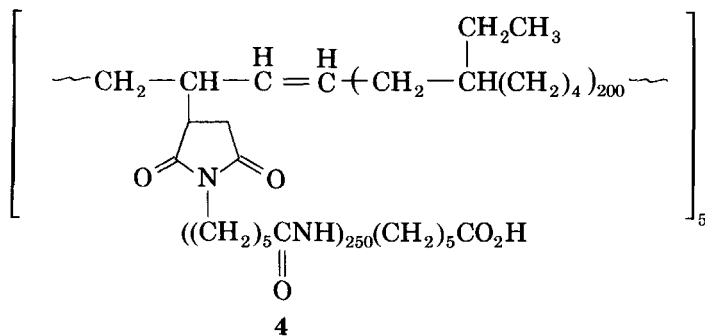
Morphology

Cimmino et al. reported that, by use of scanning electron microscopy (SEM), they found very large (20–25 μm), poorly bound rubber particles in blends of nylon 6 and unfunctionalized EPM. They could see no distinct particles in blends made with functionalized EPM.[2] The morphology of the rubber dispersed in nylon of the present blends was determined by transmission electron microscopy of OsO_4-stained, microtomed sections of several blends at 10,000–33,000 $\times$ magnification. Photomicrographs of nylon 6 toughened with an anhydride adduct of hydrogenated medium vinyl polybutadiene are shown in Figure 6. The rubber domains were finely dispersed in the nylon matrix, no large domains above 1.5 μm were observed, and the typical size range was about 0.03–0.6 μm. The functionality of the rubber stabilizes the dispersion obtained from the extruder such that agglomeration does not occur on cooling, with the mixing conditions being important factors in establishing the dispersion. Apparently, the particle size range of the rubber domains in ultrahigh impact nylon is too small to have been detectable by SEM.[2] The blend represented in Figure 6 had an interesting morphology, in that within the 0.03–0.55 μm rubbery domains of this resin were found even smaller domains, or inclusions, of nylon. Inclusions were not observable by TEM in a blend of nylon with EPDM–MA, although another group has very recently
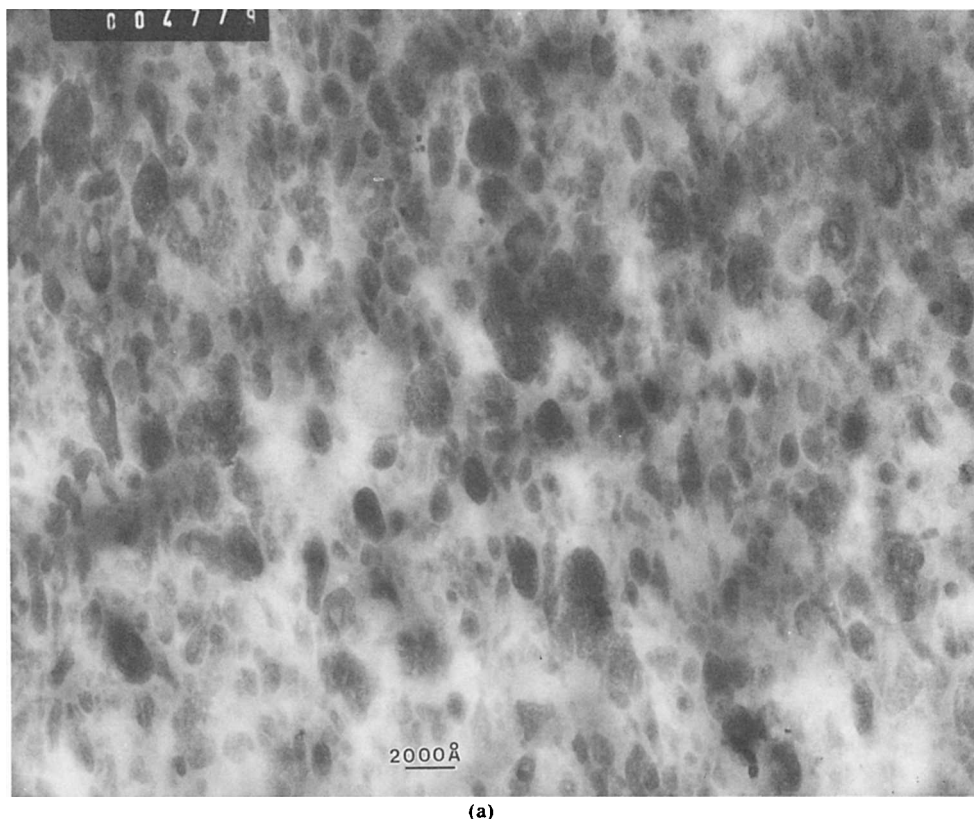
(a)

Fig. 6. Transmission electron micrograph of blend of 80% nylon 6/20% MA-adduct of hydrogenated medium vinyl polybutadiene (OsO_4-stained): (a) at 20,000 $\times$ magnification; (b) at 33,000 $\times$ magnification, showing nylon 6 inclusions (light areas) inside rubbery domains (dark areas).
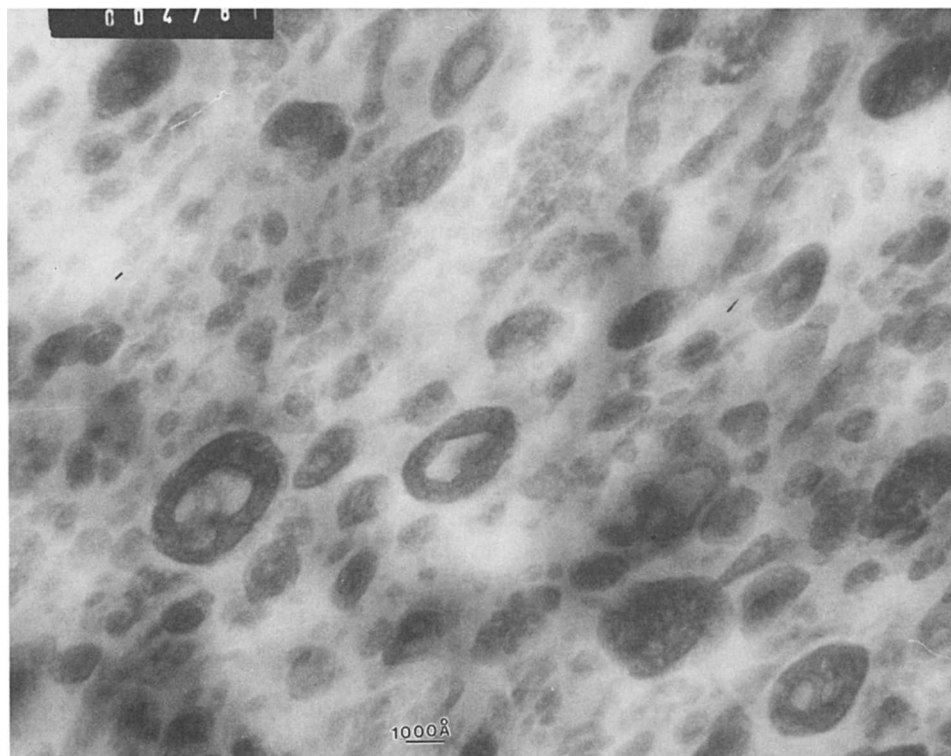
(b)

Fig. 6. (*Continued from the previous page.*)

reported the presence of inclusions at 40 vol % of the rubber phase in blends of nylon 6 with EPR-*g*-MA toughener, using different staining techniques.[28] The inclusions may be the result of the comb-block structure, which forces some of the pendent nylon segments into the center of the rubbery domains formed from the coiled copolymers.

SUMMARY

Toughened nylons have been prepared by blending nylon 6 with the maleic anhydride adducts of partially unsaturated rubbers. The resulting blends are typically rigid thermoplastics with ultrahigh impact strengths. The blends exhibit a heterophase morphology, consisting of approximately 60% free nylon, 5% free rubber, and 35% of a rubber-*g*-nylon comb-block copolymer. The block copolymer has about five nylon chains pendent from each functionalized rubber molecule. This was found to occur almost exclusively by the reaction of amine-ended nylon with the anhydride modification, to give rise to imide graft sites.

From variations in the materials and conditions used for the preparation of rubber-toughened nylon-6, the following observations were made:

1. A minimum level of incorporation of about 0.2% maleic anhydride appears to be necessary to stabilize the morphology produced during the high shear mixing. The morphology is that of a very finely dispersed rubber in a nylon matrix.

2. Anhydride functionalization can be made in elastomers having high levels of unsaturation (40% or higher). However, thermal crosslinking of the rubber occurred rapidly during melt blending with nylon-6 when the unsaturation level exceeded 12%.

3. A variety of rubbers with different T_g's and levels of partial crystallinity have been successfully modified with maleic anhydride and blended with nylon. Some of the toughened blends had outstanding low temperature impact strengths.

4. The physical properties of the nylon–rubber blends varied from slightly toughened nylons to very flexible rubberlike materials as the nylon level was varied from 95 to 50%. The grafted blends with high rubber content were remoldable without loss of properties. Further blending of the high rubber blends with homopolyamides produced resins which were toughened in proportion to the overall rubber content.

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