PATENT SPECIFICATION

(11) 1 562 338

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(21) Application No. 23632/77 (22) Filed 3 June 1977
(31) Convention Application No. 693 462
(32) Filed 7 June 1976 in
(33) United States of America (US)
(44) Complete Specification published 12 March 1980
(51) INT CL^3 C08L 53/00, 77/00
(52) Index at acceptance
C3M 104 127AC 129AC 140 144 146 146A 153 C
C3R 22C 22D1A2 22D2A2 22D3D1 22N1A C27 C33B C8P
C9B L1B L2CX L6F

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(54) COMPOSITIONS CONTAINING HYDROGENATED BLOCK COPOLYMERS AND POLYAMIDES

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

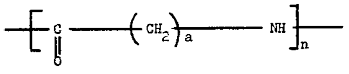
The invention relates to a composition comprising a partially hydrogenated block copolymer comprising at least two terminal polymer blocks A of a monoalkenyl arene having an average molecular weight of from 5,000 to 125,000, and at least one intermediate polymer block B of a conjugated diene having an average molecular weight of from 10,000 to 300,000, in which the proportion of the terminal polymer blocks A is between 8 and 55% by weight of the block copolymer, and no more than 25% of the arene double bonds of the polymer blocks A and at least 80% of the aliphatic double bonds of the polymer blocks B have been reduced by hydrogenation.

Block copolymers comprising at least two terminal polymer blocks of a monoalkenyl arene and at least one intermediate polymer block of a conjugated diene are known. A block copolymer of this type is represented by the structure polystyrene-polybutadienepolystyrene (SBS). When the monoalkenyl arene blocks comprise less than 55% by weight of the block copolymer, the product can be referred to as a thermoplastic elastomer. By this is meant a polymer which in the melt state is processable in an ordinary equipment for processing thermoplastics but in the solid state behaves like a chemically vulcanized rubber without chemical vulcanization having been effected.

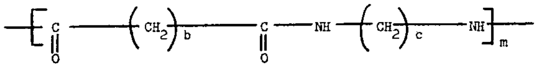
Such block copolymers are not compatible with polar polymers, such as polyamides. According to British patent specification 1,190,049 this shortcoming is removed by mixing the block copolymer with the polyamide in the presence of a salt of a metal from groups II A, III A, IV A, I B, II B, III B, IV B, V B, VI B, VII B or VIII of the Periodic System with an aliphatic carboxylic acid, hydrofluoric acid or phosphoric acid. Example 8 of the patent specification discloses a composition containing 75 parts of a three-block copolymer of butadiene and 30% by weight of styrene (1,2-vinyl content 10%, 1,4-cis content 35%), 25 parts of polycaprolactam and 2 parts of lanthanum (III) fluoride.

It has been found that an interpenetrating network can be obtained by mixing a partially hydrogenated block copolymer and a polyamide. An interpenetrating network of two polymers is a blend in which one polymer would be thought of as filling the voids of a foam of the second polymer. The interpenetrating network is not a blend in which there is molecular mixing. Although the polymers form separate and distinct phases, they are not in a form which can lead to gross phase separation causing delamination.

Now, the invention provides a block copolymer composition comprising: a) 100 parts by weight of a partially hydrogenated block copolymer comprising at least two terminal polymer blocks A of a monoalkenyl arene having an average molecular weight of from 5,000 to 125,000 and at least one intermediate polymer block B of a conjugated diene having an average molecular weight of from 10,000 to 300,000, in which the proportion of the terminal polymer blocks A is between 8 and 55% by weight of the block copolymer, and no more than 25% of the diene double bonds of the polymer blocks A and at least 80% of the aliphatic double bonds of the polymer blocks B have been reduced by hydrogenation, and b) 5 to 200 parts by weight of a polyamide having the formula

I  or

$$-\!\left[\underset{\underset{\displaystyle O}{\|}}{C}-(CH_2)_a-NH\right]_n-$$

II 

$$-\!\left[\underset{\underset{\displaystyle O}{\|}}{C}-(CH_2)_b-\underset{\underset{\displaystyle O}{\|}}{C}-NH-(CH_2)_c-NH\right]_m-$$

wherein a, b and c each vary from 4 to 12 and n and m are integers corresponding to a number average molecular weight of between 10,000 and 30,000.

The block copolymer may be linear, radial or branched.

Methods for the preparation of such polymers are known in the art. The structure of the block copolymers is determined by the methods of polymerization. For example, linear polymers result by sequential introduction of the desired monomers into the reaction vessel when using such initiators as lithium-alkyls or dilithiostilbene, or by coupling a two segment block copolymer with a difunctional coupling agent. Branched structures, on the other hand, may be obtained by the use of suitable coupling agents having a functionality with respect to the precursor polymers of three or more. Coupling may be effected with multifunctional coupling agents such as dihalo-alkanes or -alkenes as well as certain polar compounds such as silicon halides, siloxanes or esters of monohydric alcohols with carboxylic acids. The presence of any coupling residues in the polymer may be ignored for an adequate description of the polymers forming a part of the compositions of this invention. Likewise, in the generic sense, the specific structures also may be ignored. The invention applies especially to the use of selectively hydrogenated polymers having the configuration before hydrogenation of the following typical species:

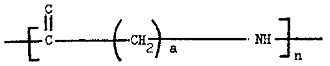
polystyrene-polybutadiene-polystyrene (SBS)
polystyrene-polyisoprene-polystyrene (SIS)
poly(alpha-methylstyrene)-polybutadiene-
    poly(alpha-methylstyrene) (α-MeSBα-MeS) and
poly(alpha-methylstyrene)-polyisoprene-
    poly(alpha-methylstyrene) (α-MeSIα-MeS)

Both polymer blocks A and B may be either homopolymer or random copolymer blocks as long as each block predominates in at least one class of the monomers characterizing the blocks as defined hereinbefore. Thus, blocks A may comprise styrene/alpha-methylstyrene copolymer blocks or styrene/butadiene random copolymer blocks as long as the blocks individually predominate in monoalkenyl arenes. The term "monoalkenyl arene" will be taken to include styrene and its analogs and homologs including alpha-methylstyrene and ring-substituted styrenes, particularly ring-methylated styrenes. The preferred monoalkenyl arenes are styrene and alpha-methylstyrene, and styrene is particularly preferred. The blocks B may comprise homopolymers of butadiene or isoprene, copolymers of butadiene with isoprene and copolymers of one of these two dienes with a monoalkenyl arene as long as the blocks B predominate in conjugated diene units. When the monomer employed is butadiene, it is preferred that between 35 and 55 mol percent of the condensed butadiene units in the butadiene polymer block have 1,2 configuration. Thus, when such a block is hydrogenated, the resulting product is, or resembles, a regular copolymer block of ethylene and butene-1 (EB). If the conjugated diene employed is isoprene, the resulting hydrogenated product is or resembles a regular copolymer block of alternating ethylene and propylene (EP).

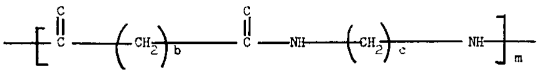
Hydrogenation of the precursor block copolymers is preferably effected by use of catalyst comprising the reaction products of an aluminium alkyl compound with nickel or cobalt carboxylates or alkoxides under such conditions as to substantially completely hydrogenate at least 80% of the aliphatic double bonds while hydrogenating no more than about 25% of the alkenyl arene aromatic double bonds. Preferred block copolymers are those where at least 99% of aliphatic double bonds are hydrogenated and less than 5% of the aromatic double bonds are hydrogenated.

The average molecular weights of the individual blocks may vary within certain limits. The block copolymer present in the composition according to the invention has at least two terminal polymer blocks A of a monoalkenyl arene having an average molecular weight of from 5,000 to 125,000 and at least one intermediate polymer block B of a conjugated diene having an average molecular weight of from 10,000 to 300,000. These molecular weights are most accurately determined by tritium counting methods or osmotic pressure measurements. The proportion of the polymer blocks A of the monoalkenyl arene should be between 8 and 55% by weight of the block copolymer, preferably between 10 and 30% by weight.

The polyamide being present in the composition according to the invention herein referred to as nylons are represented by the following formulas:



$$-\!\!\left[\overset{C}{\overset{\|}{C}}-\left(CH_2\right)_a-NH\right]_n\!\!- \text{ or}$$



$$-\!\!\left[\overset{C}{\overset{\|}{C}}-\left(CH_2\right)_b-\overset{C}{\overset{\|}{C}}-NH-\left(CH_2\right)_c-NH\right]_m\!\!-$$

where a, b and c each vary from 4 to 12 inclusive. The nylons can be those having pendant hydrocarbon groups in place of a hydrogen attached to the nitrogen or the methylene carbons of the polymer backbone. The molecular weights (Mn — number average molecular weight) of the polyamides used in the invention are between 10,000 and 30,000, preferably between 15,000 and 25,000.

Preferred nylons are nylon 6 (polymer of epsilon amino caprolactam), nylon 6,6 (polymer of hexamethylene diamine and adipic acid), nylon 6,10 (polymer of hexamethylene diamine and sebacic acid), nylon 11 (polymer of ω-amino undecanoic acid), nylon 4 (polymer of pyrrolidone), nylon 7 (polymer of amino heptanoic acid), nylon 9 (polymer of 9-amino nonanoic acid). Nylon 6 and nylon 6,6 are particularly preferred.

The amount of polyamide employed varies from 5 to 200 phr, preferably 5 to 75 phr, more preferably 10 to 40 phr. "Phr" means parts by weight per 100 parts by weight of the partially hydrogenated block copolymer.

There are at least two means (more positive than the observance of the absence of delamination) by which the presence of an interpenetrating network can be shown. In one method, an interpenetrating network is shown when moulded or extruded objects made from the blends of this invention are placed in a solvent that dissolves away the block copolymer, and the remaining polymer structure (comprising the polyamide) still has the shape of the moulded or extruded object. If the remaining structure has the appearance of continuity then an interpenetrating network has been formed.

The second method of detecting the presence of an interpenetrating network is by measuring the tensile strength at break of the blend. This follows simply from the fact that an applied tensile stress is distributed over the available network elements. The number of elements supporting a force is decreased in the presence of a noncontributing filler. At low concentrations of the secondary heterophase (the polyamide) where an interpenetrating network is absent, islands of polyamide crystallites dilute the number of block copolymer elements bearing stress. If the concentration of polyamide is increased to a point where a continuous crystalline structure occurs throughout the block copolymer network, the second network is then capable of bearing a portion of the tensile strength and the presence of interpenetrating network is shown by increased tensile modulus and strength.

The nylon and the hydrogenated block copolymer may be blended in any manner that produces the interpenetrating network. For example, the two polymers may be dissolved in a solvent common for both and coagulated by admixing in a solvent in which neither polymer is soluble. But more preferably, a particularly useful procedure is to intimately mix the two polymers as melts of nibs and/or powder in a device which provides shear. In the case of nylon 11, milling on a 5 cm mill at 195—215°C for 10—15 minutes was sufficient to achieve a compatible blend, but was not sufficient for blending nylon 6 or nylon 66. However, good results were obtained with nylon 6 using a Banbury Laboratory Model B mixer. In order to achieve the mixing necessary for an interpenetrating network with nylon 66 it was necessary to use both the mixing obtained with a Banbury Laboratory Model B and a pass through an Ankerwerk 3-ounce reciprocating screw injection moulder. A practical way to ensure the interpenetrating network, is to blend the polymers as nibs and/or powders on a Banbury at a temperature of 10—30°C above the melting point of the highest melting polymer, followed by a processing step, i.e., extruding on a twin screw extruder, or injection moulding on a reciprocating screw machine.

The mixing or processing temperature employed varies from 200°C to 300°C.

The blend of nylon with the partially hydrogenated block copolymer may be compounded with an extending oil ordinarily used in the processing of rubber and plastics. Especially preferred are the types of oil that are compatible with the elastomeric blocks of the blocks copolymer. While oils of higher aromatics content are satisfactory, those petroleum-based while oils having low volatility and less than 50% aromatics content as determined by the clay gel method (tentative ASTM method D 2007) are particularly preferred. The oils should additionally have low volatility, preferably having an initial boiling point above 260°C.

The amount of oil employed may vary from 0 to 50 phr (phr = parts by weight per hundred parts by weight of block copolymer), preferably from 5 to 30 phr.

The blend of nylon with the partially hydrogenated block copolymer may be further compounded with a polymeric alpha-olefin resin, or a flow promoting resin such as an alpha-methylstyrene resin, a vinyl toluene/alpha-methylstyrene resin or an end-block plasticizing resin. The polymers of alpha-olefins include both high and low density polyethylene, isotactic and atactic polypropylene and polybutene-1. The preferred poly-alpha-olefin is isotactic polypropylene, which is a crystalline polypropylene.

The amount of the additional resin may vary from 0 to 100 phr, preferably from 5 to 25 phr.

Further the composition may contain fillers, antioxidants, stabilizers and other compounding ingredients.

Elastomeric compositions prepared in accordance with this invention are suitable for most purposes where rubbers and flexible thermoplastics such as polyurethanes are employed, such as in mechanical goods, thermoformed articles, insulations, etc. The compositions may be injection moulded, blow moulded, or extruded. Other moulded articles as well as films, sheets, and textile coatings may be produced. The compositions may be cast from solvents to form films or spun into fibers or coated on both objects. Moulding compositions having the usual plastic end uses may be prepared, particularly when the monoalkenyl arene polymer blocks constitute a high percentage of the weight of the block polymer. Contemplated plastic end uses encompass mouldings, mechanical goods, extruded objects such as films, sheets, and fibers. The present invention is especially useful in applications where fabricated articles are subjected to high temperature oxidative environments such as automotive under-the-hood applications or electrical power applications.

To illustrate the instant invention, the following illustrative examples are given.

Example I

The following two tables set out blends of polystyrene/hydrogenated polybutadiene/polystyrene block copolymer with low and medium viscosity nylon 6 and low viscosity nylon 66. These blends are prepared by mixing the components on a Banbury Model "B" Laboratory mixer at approximately 400°C for seven minutes, until a smooth blend was obtained, followed by injection moulding in a reciprocating screw Ankerwerk injection moulding machine at 260°C.

Block copolymer A has block molecular weights of 25,000—100,000—25,000; block copolymer B has block molecular weights of 9,000—47,000—9,000; and block copolymer C has block molecular weights of 6,000—35,000—6,000.

The formulations and results are presented below in Tables 1, 2 and 3.

TABLE 1

COMPOSITION OF TEST SAMPLES

	Block Copolymer			Polyamide			Resins							
Sample Number	A	B	C	Nylon 6 low vis.	Nylon 6 med. vis.	Nylon 6,6 low vis.	Polypropylene med. mf	high mf	Acrylic[1] Resin	Poly-[2] vinyl Toluene Resin	Ethylene[3] Vinyl-acetate Copolymer	Plasticizer[4] Oil	Stabilizer[5] AO, UV	Pigment[6] Carbon Black
1131	50	–	50	–	–	–	–	10	–	–	–	20**	2	5
1132	–	50	50	–	–	–	–	10	–	–	–	–	2	5
1136	–	50	50	30	–	–	–	10	–	–	–	–	2	5
1149	50	50	–	45	–	–	15	–	–	–	–	20	2	5
1150	50	50	–	30	–	–	15	–	30	–	–	20	2	5
1151	50	50	–	60	–	–	15	–	–	–	–	20	2	5
1152	–	100	–	45	–	–	15	–	–	–	–	–	2	5
1153	–	100	–	30	–	–	10	–	–	–	–	–	2	5
1154	25	75	–	45	–	–	15	–	–	–	–	10	2	5
1155	–	100	–	30	–	–	15	–	15*	–	–	–	2	5
1156	–	–	100	30	–	–	10	–	–	–	–	–	2	–
1157	–	–	100	30	–	–	–	10	–	–	–	–	2	–
1158	–	–	100	30	–	–	–	–	–	10	–	–	2	–
1163	–	50	50	–	–	30	–	10	–	–	–	–	2	5
1165	–	100	–	30	–	–	–	–	–	10	–	–	2	–
1166	–	100	–	30	–	–	–	–	–	10	10	–	2	–
1168	–	50	50	–	30	–	10	–	–	–	–	–	2	–
1169	–	100	–	–	30	–	10	–	–	–	–	–	2	–

[1] Acryloid KM–611 and * Acryloid K–120N resins, Rohm and Haas.

[2] Piccotex 120 resin PICCO.

[3] Ultrathene 641 resin, USI Chemical.

[4] "Indopol" ® H–50 oil, Amoco Chemical and ** SHELLFLEX® 790 oil, Shell Chemical.

[5] 0.5 phr each hindered phenol and dilaurylthiodipropionate antioxidants, benzotriazole and hydroxybenzoate UV stabilizers.

[6] 1:1 dispersion of SRF black in high mf ethylene-vinylacetate copolymer.

TABLE

PHYSICAL PROPERTIES 1)

Sample Number	Hardness Shore D	Gardner Impact, cm/0.45kg 50	50–125	225	Stiffness 3) kg/cm²/rad.	Ross % Cut 0.5 Kc	Flex Growth 10 Kc
		(–30°C)	(23°C)	(23°C)			
1131	18	V. good	good	100% cut	–	–	–
1132	26	V. good	–	–	–	–	–
1136	38	Cracked	good	sl. cut deforms	401/548	–	–
1149	35	Cracked	fair-good	sl. cut deforms	–	–	–
1150	32	Cracked	fair-good	sl. cut deforms	–	–	–
1151	40	Cracked	fair-good	sl. cut deforms	–	600	900
1152	43	Cracked	fair-good	sl. cut deforms	–	–	–
1153	37	Cracked	fair-good	sl. cut deforms	–	200	900
1154	39	Cracked	fair-good	sl. cut deforms	–	–	–
1155	42	Cracked	fair-good	sl. cut deforms	–	–	–
1156	41	Cracked	fair-good	deforms	–	–	–
1157	38	Cracked	fair-good	deforms	–	–	–
1158	38	V. good	fair	deforms	–	–	–
1163	40	–	fair-good	–	–	0	400
1165	40	–	fair-good	–	–	200	900
1166	43	–	fair-good	–	–	–	–
1168	–	–	fair-good	–	–	0	700
1169	–	–	fair-good	–	–	–	–

1) All properties measured on injection moulded samples at 23°C. unless otherwise specified.

2) Compositions are given in Table 1.

3) Tinius – Olson stiffness measured normal and parallel to flow respectively.

4) 1 hour at 149°C.

5) Die C angle tear measured normal and parallel to flow respectively.

6) Microdumbells measured parallel to flow.

2

OF TEST SAMPLES 2)

Over Stability 4) Shrinkage	Distortion	Angle 5) Tear, kg/2,5cm	Flexural modulus of Elasticity, kg/cm^2			Tensile Properties 6) M_{100}, kg/cm^2	T_b, kg/cm^2	E_b, %
			(70°C)	(23°C)	(-30°C)			
V. high	severe	133/128	–	–	–	–	–	–
V. high	severe	149/135	–	–	–	–	–	–
None	None	149/158	352	1280	–	77	172	500
–	–	–	–	654	–	70	70	250
–	–	–	–	478	–	–	–	–
–	–	126/117	–	1266	–	77	81	110
–	–	–	–	1195	–	91	134	380
–	–	180/158	–	1055	–	–	–	–
–	–	–	–	886	–	–	–	–
–	–	–	–	1814	–	84	84	500
None	None	–	–	1308	–	–	–	–
None	None	–	352	1694	–	–	–	–
None	None	–	260	–	–	–	–	–
None	None	225/180	–	1076	–	112	190	460
None	None	180/135	–	1514	–	70	162	470
None	None	–	–	–	–	70	190	550
–	–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–	–

TABLE 3

COMPOSITION AND PHYSICAL PROPERTIES OF TEST SAMPLES

Sample Number	Block Copolymer 1)	Nylon 6 2)	Nylon 6,6 2)	Stabilizer 3)	Hardness Shore D	Properties at 23°C		
						Stiffness 4) kg/cm^2/rad.	× 10^{-3}	Gardner Impact 125cm/0.45kg
						(N)	(P)	
1228	100	–	50	1.7	41	0.56	0.59	Excellent
1229	100	–	100	1.7	60	1.1	1.5	Very Good
1230	100	–	150	1.7	65	1.7	1.9	Poor
1231	100	–	200	1.7	68	2.1	2.6	Poor
1232	100	100	–	1.7	52	0.8	0.9	Excellent
1233	–	100	–	–	77	–	–	Poor

1) Hydrogenated S–B–S, nominal weight 65 M, approximately 28% styrene.

2) Medium viscosity type 6 resin, low viscosity type 6,6.

3) 0.2 phr hindered phenol antioxidant, 0.5 phr each dilaurylthiodipropionate antioxidant, benzotriazole and hydroxybenzoate UV stabilizers.

4) Tinius – Olsen stiffness measured normal (N) and parallel (P) to direction of flow during injection moulding.

Example II.

A 112.5 kg sample of a nylon 6, polystyrene/hydrogenated polybutadiene/polystyrene block copolymer blend having the following composition and properties was made by blending on a Werner-Pfleiderer twin screw extruder, model ZSK 83/700, at zone temperatures ranging from 200°—240°C then injection moulding test parts on a Stokes reciprocating screw injection moulding machine at 230—275°C.

Composition

Ingredients	phr
Block Copolymer [1]	50
Block Copolymer [2]	50
Nylon 6 Resin [3]	30
Polypropylene [4]	10
Carbon Black Concentrate [5]	5
Antioxidants [6]	1
UV Stabilizers [7]	1

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[1] Nominal molecular weight 65m, approximately 28% w polystyrene.
[2] Nominal molecular weight 47m, approximately 28% w polystyrene.
[3] Low viscosity nylon 6 resin.
[4] Medium melt flow polypropylene nibs.
[5] 1/1 dispersion of SRF black in EVA.
[6] Equal amounts of a hindered phenol and dilaurylthiodipropionate.
[7] Equal amounts of a benzotriazole and a hydroxybenzoate.

Physical Properties[1]

Property	ASTM Method	Result
Specific Gravity	—	0.96
Tensile and Hardness Properties		
Hardness, Shore A Points	—	91
Hardness, Shore D Points	—	36
Tensile Strength at Break, kg/cm² 23°C	D—412	155
Elongation at Break, % 23°C	D—412	350
Modulus at 100% Elongation, kg/cm² 23°C	D—412	91
Modulus at 300% Elongation, kg/cm² 23°C	D—412	141

Property	ASTM Method	Result
Flexural Properties		
Modulus of Elasticity, kg/cm^2 23°C	D—790	1266
70°C		352
−30°C		3164
Tinius-Olson Stiffness, kg/cm^2/rad	D—747	422—562
Tear Strength		
Die Angle Tear, kg/linear 2.5cm	D—624	144—247.5
Abrasion Resistance		
Tabor H—18, cc/1000 rev.	D—1044	1.90
Impact Resistance		
Gardner 50cm/0.45 kg	—	good
125cm/0.45 kg		good
200cm/0.45 kg		fair-good
(−30°C) 50cm/0.45 kg		fair-good
Elastic Nature		
Tensile Hysteresis, 100%		
Elongation	—	
First cycle loss, %		70
Equilibrium loss, %		40

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1) Properties were measured on ASTM plaques or Ross Flex bars which were injection moulded on a Stokes reciprocating screw machine at 7.2—274°C.

Example III.

100 parts of a hydrogenated SBS resin having polystyrene blocks with a number average molecular weight of 10,000 and a hydrogenated butadiene block with a number average molecular weight of 50,000 with 0.2 phr IONOL® were blended with 50 parts of a nylon 11, ("Rilsan"® BMNO from Aquitaine Chemical) on a 2" Farrell mill for 10—15 minutes at 195—215°C. The blend processed well on the mill, and compression moulded tensile bars did not show delamination. A satisfactory interpenetrating blend is obtained. The physical properties were:

Tensile at break	74.5 kg/cm^2
Elongation at break	400%
Modulus at 300% elong.	54.8 kg/cm^2
Set at break	15%

Example IV.

Example II is repeated but a poly(alpha-methylstyrene)/hydrogenated butadiene/poly(alpha-methylstyrene) block copolymer is used in place of the SEBS. A satisfactory interpenetrating blend is obtained.

Example V.

Example II is repeated except a polystyrene/hydrogenated polyisoprene/polystyrene block copolymer is substituted for the SEBS. A satisfactory interpenetrating blend is obtained.

Example VI.

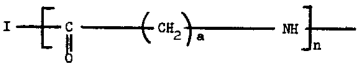
Example II is repeated except a poly(alpha-methylstyrene)/hydrogenated polyisoprene/poly(alpha-methylstyrene) block copolymer is substituted for the SEBS. A satisfactory interpenetrating blend is obtained.

The Examples show that impact strength, elasticity and flexibility are greatly reduced at nylon contents substantially over 50%, based on total blend, and that nylon/hydrogenated ABA blends are vastly superior in resistance to heat distortion at high temperatures in comparison to the neat selectivity hydrogenated ABA-type block copolymers.

WHAT WE CLAIM IS:—

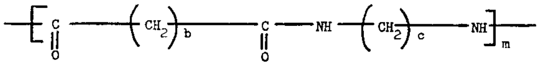
1. A block copolymer composition comprising: a) 100 parts by weight of a partially hydrogenated block copolymer comprising at least two terminal polymer blocks A of a monoalkenyl arene having an average molecular weight of from 5,000 to 125,000, and at least one intermediate polymer block B of a conjugated diene having an average molecular weight of from 10,000 to 300,000, in which the proportion of the terminal polymer blocks A is between 8 and 55% by weight of the block copolymer, and no more than 25% of the arene double bonds of the polymer blocks A and at least 80% of the aliphatic double bonds of the polymer blocks B have been reduced by hydrogenation, and

(b) 5 to 200 parts by weight of a polyamide having the formula

I 

$$-\!\!\left[\underset{\underset{O}{\|}}{C} - (CH_2)_a - NH\right]_n\!\!-$$

or

II 

$$-\!\!\left[\underset{\underset{O}{\|}}{C} - (CH_2)_b - \underset{\underset{O}{\|}}{C} - NH - (CH_2)_c - NH\right]_m\!\!-$$

wherein a, b and c each vary from 4 to 12 and n and m are integers corresponding to a number average molecular weight of between 10,000 and 30,000.

2. A composition as claimed in claim 1, in which the proportion of the terminal polymer blocks A of the monoalkenyl arene is between 10 and 30% by weight of the block copolymer.

3. A composition as claimed in claim 1, in which the polyamide has a number average molecular weight of between 15,000 and 25,000.

4. A composition as claimed in any one of the preceding claims, in which the polyamide is present in an amount of from 5 to 75 parts by weight on 100 parts by weight of the block copolymer.

5. A composition as claimed in claim 4, in which the composition contains from 10 to 40 parts by weight of the polyamide on 100 parts by weight of the block copolymer.

6. A composition as claimed in any one of claims 1—5, in which the composition contains an extending oil in an amount of no more than 50 parts by weight on 100 parts by weight of the block copolymer.

7. A composition as claimed in claim 6, in which the composition contains an extending oil in an amount of from 5 to 30 parts by weight on 100 parts by weight of the block copolymer.

8. A composition as claimed in any one of the preceding claims, in which the composition contains a polymeric alpha-olefin resin, or a flow promoting resin in an amount of no more than 100 parts by weight on 100 parts by weight of the block copolymer.

9. A composition as claimed in claim 8, in which the composition contains a polymeric alpha-olefin resin, or a flow promoting resin in an amount of from 5 to 25 parts by weight on 100 parts by weight of the block copolymer.

10. A composition as claimed in any one of the preceding claims, substantially as hereinbefore described.

11. Articles prepared by using a composition as claimed in any one of the preceding claims.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.