

DESCRIPTION

ORIENTED THERMOPLASTIC ELASTOMER FILM
AND PROCESS FOR PRODUCING THE SAME

5 Technical Field

 The present invention relates to an oriented thermoplastic elastomer film having reduced permeability and improved fatigue resistance and also to a method of preparing the same. More particularly, the present
10 invention relates to a process for producing a thermoplastic elastomer film composition with enhanced planar orientation for reduction in gas permeability and a process for producing a pneumatic tire using the same.
Background Art

15 EP722850B1 disclosed a low-permeability thermoplastic elastomer composition that is superior as a gas-barrier layer in pneumatic tires. This thermoplastic composition comprises a low-permeability thermoplastic matrix such as polyamides or blends of polyamides, in
20 which a low-permeability rubber such as brominated poly(isobutylene-co-p-methylstyrene) (i.e., or BIMS) is dispersed. Subsequently, in both EP857761A1 and EP969039A1, viscosity ratio between the thermoplastic matrix and the rubber dispersion was specified in order
25 to achieve phase continuity in thermoplastic and fine rubber dispersions. Criticality of smaller rubber dispersions was recognized in EP969039A1 in these thermoplastic elastomers for delivering acceptable durability especially for their usage as innerliners in
30 pneumatic tires.

 Further improvement in impermeability of these low-permeability thermoplastic elastomers could be achieved by imposing planar orientation. In WO 0214410, introduction of orientation into a thermoplastic
35 elastomer film for property enhancement and for permeability reduction was disclosed conceptually. No experimental data were provided in this patent

application. Further, the process specified in this application involves bi-axial orientation of cast film through drafting, tentering, and heatsetting by assuming the film in discussion has the strain hardening characteristics and suitable stretching dynamics. In the present invention, the planar orientation in a thermoplastic elastomer cast film is imposed simply by the film casting and/or film blowing process and film blowing for the improvement in film properties. This thermoplastic elastomer film does not have the suitable stretching dynamics for it to be oriented by a sequential bi-axial orientation process.

Summary of Invention

The objects of the present invention are to provide an oriented thermoplastic elastomer film having a reduced gas permeability and improved fatigue resistance and also to provide a method of preparing the same.

In accordance with the present invention, there is provided an oriented thermoplastic elastomer film having reduced permeability and improved fatigue resistance comprising a dynamically vulcanized polymer blend of (A) a halogenated isobutylene elastomer and (B) polyamide, the film is produced by casting or blowing the above polymer blend under the condition such that a shear rate at a die lip for casting or blowing is regulated to control the molecular arrangement in the film, whereby the planar birefringence (PBR) of the resultant film becomes greater or equal to 0.002, preferably the PBR is 0.004 or more.

Disclosure of Invention

In this specification and in the claims which follow, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise.

The present invention relates to an oriented thermoplastic elastomer film having reduced permeability and improved fatigue resistance and to a method of

preparing the same.

More particular, the present invention relates to film casting and blowing processes for producing a thermoplastic elastomer film with enhanced planar orientation and a process for producing a pneumatic tire using the same.

The preferred planar birefringence of the oriented thermoplastic elastomer film is greater or equal to 0.002. The orientation could be imposed by either increasing wind-up speed during casting and blowing or increasing the blow-up ratio during film blowing.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be better understood from the description set forth below with reference to the accompanying drawing of Fig. 1, which shows the correlation between the planar orientation of the film and the permeability thereof.

The thermoplastic elastomer composition is a blend of a halogenated isobutylene elastomer and a polyamide, which is subjected to dynamic vulcanization.

The term "dynamic vulcanization" is used herein to connote a vulcanization process in which the engineering resin and a vulcanizable elastomer are vulcanized under conditions of high shear. As a result, the vulcanizable elastomer is simultaneously crosslinked and dispersed as fine particles of a "micro gel" within the engineering resin matrix.

Dynamic vulcanization is effected by mixing the ingredients at a temperature which is at or above the curing temperature of the elastomer in equipment such as roll mills, Banbury[®] mixers, continuous mixers, kneaders or mixing extruders, e.g., twin screw extruders. The unique characteristic of the dynamically cured compositions is that, notwithstanding the fact that the elastomer component may be fully cured, the compositions can be processed and reprocessed by conventional rubber processing techniques such as extrusion, injection

molding, compression molding, etc. Scrap or flashing can be salvaged and reprocessed.

In a preferred embodiment the halogenated isobutylene elastomer component include copolymers of isobutylene and
5 para-alkylstyrene, such as described in European Patent Application 0 344 021. The copolymers preferably have a substantially homogeneous compositional distribution. Preferred alkyl groups for the para-alkyl styrene moiety include alkyl groups having from 1 to 5 carbon atoms,
10 primary haloalkyl, secondary haloalkyl having from 1 to 5 carbon atoms and mixtures thereof. A preferred copolymer comprises isobutylene and para-methylstyrene.

Suitable halogenated isobutylene elastomer components
15 include copolymers (such as brominated isobutylene-paramethylstyrene copolymers) having a number average molecular weight M_n of at least about 25,000, preferably at least about 50,000, preferably at least about 75,000, preferably at least about 100,000, preferably at least
20 about 150,000. The copolymers may also have a ratio of weight average molecular weight (M_w) to number average molecular weight (M_n), i.e., M_w/M_n of less than about 6, preferably less than about 4, more preferably less than about 2.5, most preferably less than about 2.0. In
25 another embodiment, suitable halogenated isobutylene elastomer components include copolymers (such as brominated isobutylene-paramethylstyrene copolymers) having a Mooney viscosity (1+4) at 125°C (as measured by ASTM D 1646-99) of 25 or more, preferably 30 or more,
30 more preferably 40 or more.

Preferred brominated copolymers of isobutylene and para-methylstyrene include those having 5 to 12 weight % para-methylstyrene, 0.3 to 1.8 mol % brominated para-
35 methylstyrene, and a Mooney viscosity of 30 to 65(1+4) at 125°C (as measured by ASTM D 1646-99).

The halogenated isobutylene elastomer component (A) according to the present invention can be prepared from isobutylene and about 0.5 to 25% by weight, preferably about 2 to 20% by weight, based upon the total amount of
5 the comonomers, of p-alkylstyrene, preferably p-methylstyrene, followed by the halogenation. The content of the halogen (e.g., Br and/or Cl, preferably Br) is preferably less than about 10% by weight, more preferably about 0.1 to about 7% by weight, based upon the total
10 amount of the copolymer.

The copolymerization can be carried out in a known manner as described in, for example, European Patent Publication No. EP-34402/A published November 29, 1989
15 and the halogenation can be carried out in a known method as described in, for example, U.S. Patent No. 4548995.

The halogenated isobutylene elastomer preferably has the number-average molecular weight ($\bar{M}_n$) of at least about 25,000, more preferably at least about 100,000 and
20 a ratio of the weight-average molecular weight ($\bar{M}_w$) to the number-average molecular weight ($\bar{M}_n$), i.e., $\bar{M}_w/\bar{M}_n$ of preferably less than about 10, more preferably less than about 8.

The polyamides usable in the present invention are
25 thermoplastic polyamides (nylons) comprise crystalline or resinous, high molecular weight solid polymers including copolymers and terpolymers having recurring amide units within the polymer chain. Polyamides may be prepared by polymerization of one or more epsilon lactams such as
30 caprolactam, pyrrolidione, lauryllactam and aminoundecanoic lactam, or amino acid, or by condensation of dibasic acids and diamines. Both fiber-forming and molding grade nylons are suitable. Examples of such polyamides are polycaprolactam (Nylon 6),
35 polylauryllactam (Nylon 12), polyhexamethyleneadipamide (Nylon 66), polyhexamethyleneazelamide (Nylon 69),

polyhexamethylenesebacamide (Nylon 610),
polyhexamethyleneisophthalamide (Nylon 6 IP), Nylon 612,
Nylon 46, Nylon MXD 6, Nylon 6/66 and the condensation
product of 11-amino-undecanoic acid (Nylon 11).

5 Additional examples of satisfactory polyamides
(especially those having a softening point below 275°C.)
are described in Kirk-Othmer, Encyclopedia of Chemical
Technology, v. 10, page 919, and Encyclopedia of Polymer
Science and Technology, Vol. 10, pages 392 - 414.

10 Commercially available thermoplastic polyamides may be
advantageously used in the practice of this invention,
with linear crystalline polyamides having a softening
point or melting point between 160°C - 230°C. being
preferred.

15 The amounts of the elastomer (A) and the polyamide
(B) usable in the present invention is preferably 95 to
25 parts by weight and 5 to 75 parts by weight, more
preferably 90 to 25 parts by weight and 10 to 75 parts by
weight, respectively, provided that the total amount of
20 the components (A) and (B) is 100 parts by weight.

The elastomer composition according to the present
invention may contain, in addition to the above-mentioned
essential ingredients, a vulcanization or cross-linking
agent, a vulcanization or cross-linking accelerator,
25 various types of oils, an antiaging agent, reinforcing
agent, plasticizer, softening agent, or other various
additives generally mixed into general rubbers. The
compounds are mixed and vulcanized by general methods to
make the composition which may then be used for
30 vulcanization or cross-linking. The amounts of these
additives added may be made the amounts generally added
in the past so long as they do not run counter to the
object of the present invention.

EXAMPLES

35 The present invention will now be further
illustrated by, but is by no means limited to, the
following Examples.

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The following commercially available products were used for the components employed in the Examples.

1. Resin Component

Nylon 1: A blend of N11 (Rilsan BESN O TL) and
N6/66 (Ube 5033B)

Nylon 2: N6/66 (CM6001FS)

Additive 1: Plasticizer: N-
butylbenzenesulfonamide,
Compatibilizer: AR-201

Additive 2: Stabilizer: Irganox 1098, Tinuvin
622LD, and CuI

2. Rubber Component

BIMS: Brominated copolymer of isobutylene and
para-methylstyrene sold under the tradename EXXPRO 89-4
by ExxonMobil Chemical Company having a mooney viscosity
of about 45, approximately 5 weight % para-methylstyrene
and about 0.75 mol % bromine

DM16D: Hexadecyl dimethyl amine (Akzo Nobel)

6PPD: N-(1,3-dimethylbutyl)-N'-phenyl-p-
phenylenediamine

ZnO: Zinc oxide curative

St-acid: Stearic acid curative

ZnSt: Zinc stearate curative

MBTS: Benzyothiazyl disulfide

3. Anti-block Agent for Rubber Pelletization

Talc: hydrated magnesium silicate (Ciba)

ZnO: zinc oxide

Igafos: Igafos 168 antioxidant (Ciba)

The test methods used for evaluation of the Examples and
Comparative Examples were as follows:

A) Measuring volume average equivalent dispersion
diameter and number average equivalent dispersion
diameter

Tapping phase AFM was applied to evaluate dispersion
sizes and size distributions in these films. All film
samples were cryo-faced at -150°C using a Reichert
cryogenic microtome with diamond knives. Faced samples

were stored in a desiccator under flowing dry nitrogen to be warmed up to ambient temperatures without moisture. Samples were run within 24 hours after cryo-facing using an AFM (DI-3000, Digital Instrument) in tapping mode with a rectangular 225- μm silicon cantilever. All tapping phase AFM micrographs were converted to TIFF format and processed using PHOTOSHOP (Adobe Systems) for image enhancement. All image measurements were performed using a commercial image process tool kit (Reindeer Games) as an attachment to PHOTOSHOP. Results of image measurements were written into text files for subsequent data processing by EXCEL (Microsoft). The number average dispersion diameter D_n is calculated as:

$$D_n = \Sigma(n_i D_i) / \Sigma(n_i)$$

D_i is the equivalent diameter of individual dispersion and n_i is the number of the dispersion with an equivalent diameter of D_i . The volume average dispersion diameter D_v is expressed as:

$$D_v = \Sigma(n_i D_i^4) / \Sigma(n_i D_i^3)$$

with, n_i is the number of dispersion with equivalent diameter of D_i .

B) Tensile Fatigue Cycles

Film and a carcass compound were laminated together with an adhesive and cured at 190°C for 10 min. A JIS No. 2 dumbbell shape was then punched out and used for durability test at -20°C at 6.67 Hz and 40% strain.

C) Oxygen Permeability by Mocon

The oxygen permeation measurements were done using a Mocon OX-TRAN 2/61 permeability tester at 60°C.

D) Principal Refractive Indices by Metricon

Three principal refractive indices were measured using Metricon with an operating wavelength of 632.8 nm. Planar birefringence, PBR, and average refractive index,

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n, are calculated by

$$\text{PBR} = (n_1 + n_2)/2 - n_3 \quad (3)$$

$$n = (n_1 + n_2 + n_3)/3 \quad (4)$$

Here, n_1 , n_2 , and n_3 are refractive indices along the machine direction, the transverse direction, and the film normal direction, respectively.

Examples 1 - 8

BIMS was pre-compounded with curatives in a Banbury internal mixer and pelletized with the anti-block agent prior to its mixing with Nylon. Mixing and dynamic vulcanization of Nylon and BIMS were done in a twin-screw extruder at about 230°C. These mixes were then cast or blown into films. 2" diameter disks were punched out from these films and conditioned in a vacuum oven at 60°C overnight prior to the permeability measurements. Oxygen permeation values of these films at 60°C were measured using a Mocon OX-TRAN 2/61 permeability tester. Principal refractive indices along the three principal directions of these films were determined using a Metricon prism-coupling device. The operation wavelength was 632.8 nm generated by a low-power He-Ne laser. Using the three principal refractive indices, the average refractive index could be calculated as:

$$\langle n \rangle = (n_1 + n_2 + n_3)/3$$

wherein, $\langle n \rangle$ is the average refractive index. 1, 2, and 3 refer to machine, transverse, and normal (normal to the film plane) directions, respectively. The relative planar orientation could be expressed with the planar birefringence, or PBR, defined by (see US 5385704)

$$\text{PBR} = (n_1 + n_2)/2 - n_3$$

In Examples 1 - 8, Nylon 1 matrix with the addition of plasticizer and compatibilizer was used as shown in Table 1. Nylon 1 matrix with plasticizer has its viscosity closely match with that of BIMS. MBTS is a cure retarder and DM16D is a viscosity enhancer. Both can react with benzylic bromine of BIMS and affect its

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reactive compatibilization with Nylon. Because of the this interfacial bonding modification between BIMS and Nylon with MBTS and DM16D, Nylon orientation during film casting or blowing could be affected. As shown in

5 Table 1, reduction in cast film thickness through the increase in wind-up speed with the same cast die results in an increase in planar orientation and a corresponding reduction in permeability. Although the permeability of the blown films could not be measured due to film surface

10 adhesive, a reduction in film thickness through the increase in windup speed without changes in die or in blowup ratio, again, leads to an increase in planar orientation. The addition of MBTS and DM16D leads to a reduction in orientation. Overall, there is a strong

15 correlation between PBR and permeability. Since we are using the same Nylon matrix for all films listed in Table 1, the average refractive index, which represent the density or the crystallinity in Nylon, remains constant. The results are plotted in Fig. 1, wherein the

20 PBR in Example Nos. 4, 7 and 8 (see the plot # 4, # 7 and # 8) were not within the scope of the present invention.

Table 1

Example No.	1	2	3	4 ^{*3}	5	6	7 ^{*3}	8 ^{*3}
<u>Formulation</u> (parts by weight)								
BIMS	100	100	100	100	100	100	100	100
DM16D	0	0	0	0	0	0	0	0.5
MBTS	0	0	0	0	0	0	1	0
ZnO	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
St-acid	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
ZnSt	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Nylon 1	68	68	68	68	68	68	68	68
Additive 1	21	21	21	21	21	21	21	21
Additive 2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
<u>Process</u>								
Cast	Cast	Cast	Cast	Cast	-	-	Cast	Cast
Blown	-	-	-	-	Blown	Blown	-	-
<u>Properties</u>								
Thickness (μm)	130	180	230	280	130	180	150	150
<n>	1.5170	1.5165	1.5165	1.5167	1.5175	1.5184	1.5175	1.516
PBR (10 ⁻³)	4.91	3.95	3.02	1.25	2.24	2.11	1.85	1.4
Permeability ^{*1}	10.8	11.8	12.7	12.8	nm ^{*2}	nm ^{*2}	13.5	14.6

*1: in a unit of cc*mil/(m²-day-mmHg).

*2: did not measure due to the surface adhesive layer.

5 *3: Comparative Example

Examples 9 - 13

In Examples 9 to 13, Nylon 1 matrix was used but without the plasticizer and compatibilizer. 6PPD could be a curative at the mixing temperature of 230°C by crosslinking BIMS through benzylic bromines and, hence, removing them from reactive compatibilization. DM16D is a viscosity enhancer for BIMS that also react with benzylic bromine of BIMS. This modification of the interfacial bonding with the usage of DM16D and 6PPD could significantly lower the planar orientation and raise the film permeability as shown in Table 2. The results are shown in Fig. 1. Regardless, a good correlation could be found between PBR and permeability. The higher refractive index value in comparison with that in Table 1 reflects the fact that the Nylon matrix has no plasticizer. Hence, higher density or higher refractive

index is expected.

Table 2

Example No.	9	10	11 ^{*1}	12 ^{*1}	13 ^{*1}
<u>Formulation</u> (parts by weight)					
BIMS	100	100	100	100	100
DM16D	0	0	1.0	2.0	3.0
6PPD	0	0.6	0	0	0
ZnO	0.15	0.15	0.15	0.15	0.15
St-acid	0.60	0.60	0.60	0.60	0.60
ZnSt	0.30	0.30	0.30	0.30	0.30
Nylon 1	95	95	95	95	95
Additive 1	0	0	0	0	0
Additive 2	0.7	0.7	0.7	0.7	0.7
<u>Process</u>					
Cast	Yes	Yes	Yes	Yes	Yes
<u>Properties</u>					
<n>	1.5184	1.5174	1.5175	1.5170	1.5171
PBR (10 ⁻³)	3.2	2.25	1.1	0.98	1.1
Permeability	5.31	6.43	7.05	7.69	7.47

*1: Comparative Example
Examples 14 - 19

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In Examples 14 - 19, Nylon 2 matrix, without N11 and without plasticizer, was used. In blending with Nylon 2, viscosity modifier, such as DM16D and 6PPD, is required to provide good viscosity matching and fine BIMS rubber dispersions. The concentration used for the anti-blocking agents listed in Table 3 is 0.5 to 1 phr. As indicated in Table 3, using ZnO as the anti-blocking agent could significantly affect the orientation. This anti-blocking agent may act as curative and, hence, remove benzylic bromines from BIMS for its reactive compatibilization with Nylon. A large removal of benzylic bromines from BIMS could lower the interfacial bonding between the Nylon and BIMS dispersions and reduce the ability of the film manufacturing process to orient Nylon. However, overall correlation between PBR and permeability holds. The even higher refractive index value as compared with that in Table 2 is the result of the N6/66 matrix used. The results are also shown in

Fig. 1.

Table 3

Example No.	14	15	16 ^{*1}	17	18	19
<u>Formulation</u> (parts by weight)						
BIMS	100	100	100	100	100	100
DM16D	0	0	0	1.0	1.0	0
6PPD	0.5	0.5	0.5	0	0	0.5
Pelletization	Talc	Irgafos	ZnO	Talc	Irgafos	Talc
ZnO	0.15	0.15	0.15	0.15	0.15	0.15
St-acid	0.60	0.60	0.60	0.60	0.60	0.60
ZnSt	0.30	0.30	0.30	0.30	0.30	0.30
Nylon 2	98	98	98	98	98	98
Additive 1	0	0	0	0	0	0
Additive 2	0.75	0.75	0.75	0.75	0.75	0.75
<u>Process</u>						
Cast/blown	Cast	Cast	Cast	Cast	Cast	Blown
<u>Properties</u>						
<n>	1.5215	1.5216	1.5215	1.5222	1.5217	1.5219
PBR (10 ⁻³)	6.1	5.15	1.4	4.55	3.25	5.4
Permeability	1.38	1.51	1.92	1.27	1.37	1.42

*1: Comparative Example

CLAIMS

1. An oriented thermoplastic elastomer film having reduced permeability and improved fatigue resistance comprising a dynamically vulcanized polymer blend of (A) a halogenated isobutylene elastomer and (B) polyamide, the film is produced by casting or blowing the above polymer blend under the condition such that a shear rate at a die lip for casting or blowing is regulated to control the molecular arrangement in the film, whereby the planar birefringence (PBR) of the resultant film becomes greater or equal to 0.002.

2. An oriented thermoplastic elastomer film as claimed in claim 1, wherein the amount of the halogenated isobutylene elastomer is 95 to 25 parts by weight and the amount of the polyamide is 5 to 75 parts by weight.

3. An oriented thermoplastic elastomer film as claimed in claim 1 wherein the halogenated isobutylene elastomer is brominated poly(isobutylene-co-p-methylstyrene).

4. An oriented thermoplastic elastomer film as claimed in claim 1, wherein the polyamide is at least one member selected from the group consisting of Nylon 6, Nylon 66 Nylon 11, Nylon 69, Nylon 12, Nylon 610, Nylon 612, Nylon 46, Nylon MXD6, Nylon 6/66 and the copolymers thereof, and the blends thereof.