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(21) International Application Number: PCT/US99/02710 (22) International Filing Date: 9 February 1999 (09.02.99) (30) Priority Data: 60/076,566 2 March 1998 (02.03.98) US (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Mid- land, MI 48674 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MOTTER, Gregg, A. [US/US]; 1401 Sylvan Lane, Midland, MI 48640 (US). BRENTIN, Robert, P. [US/US]; 5910 Woodcliff Drive, Midland, MI 48640 (US). (74) Agent: ZETTLER, Lynn, M.; Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: JP, KR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: SYNDIOTACTIC MONOVINYLDENE AROMATIC POLYMER FILM (57) Abstract <p>This invention utilizes syndiotactic styrene polymer to produce a thin film suitable for insulating electrically conductive metal support structures from current conducting magnet wire. The addition of impact modifiers enables the thin sheet to withstand the mechanical stress of fabrication in motor assembly operations. The resultant sheet exhibits good heat resistance, electrical dielectric strength and moisture insensitivity which provides greater dimensional stability and resistance to hydrolysis.</p>		

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SYNDIOTACTIC MONOVINYLIDENE AROMATIC POLYMER FILM

The present invention relates to impact modified syndiotactic monovinylidene aromatic polymers and film produced therefrom.

Electrical insulating film is used to provide insulation between an
5 electrically conductive metallic support structure and current conducting magnet wire. Such films have typically been produced from polymers such as polyester, polyethylene terephthalate, polypropylene, atactic polystyrene and polyimide. Polyesters are known to absorb moisture, resulting in poor dimensional stability. Additionally, polyester has a relatively low glass
10 transition temperature (~52 °C) which allows the film to soften under the load of tightly wound magnet wire. Polyester is also subject to hydrolysis which, over time in humid environments, will cause molecular weight degradation and insulation failure. Furthermore, polyester film requires the use of a secondary orientation step to achieve a sufficiently high level of crystallinity to increase
15 heat resistance. Polyethylene terephthalate, polypropylene and atactic polystyrene polymers do not offer sufficient heat resistance in such insulation applications. Polyimide film provides excellent electrical insulation and heat resistance performance. However, these materials are very costly, making their use impractical in most applications.

20 Other insulation substrates include kraft paper, rag paper, vulcanized fiber, and rag paper/PET. However, these materials can undergo considerable dimensional change due to moisture conditions.

US-A-5,093,758 by Funaki et al. discloses an electrical insulating film which comprises a styrene polymer having a syndiotactic configuration (SPS)
25 and containing not more than 1,000 ppm of residual aluminum derived from the catalyst used in the production of styrene polymer, and not more than 3,000 ppm residual styrene monomer. However, unmodified SPS film is inherently brittle which can cause film cracking during the slitting, cutting, and folding operations required in the fabrication of an electrical device.
30 Additionally, this application requires SPS having very low levels of impurities which requires further polymer treatment.

Therefore, there remains a need for an electrical insulating film which does not crack during fabrication, has good ductility, electrical insulation and

heat resistance properties, good dimensional stability and a high glass transition temperature.

The present invention is an electrical insulating film comprising an impact modified syndiotactic monovinylidene aromatic polymer. The electrical
5 insulating film can be used to provide electrical insulation between energized wires and a ground potential support structure.

The impact modified polymer used in the films of the present invention has high dielectric strength and is less affected by moisture than polyester, therefore, thinner film sheets can be used. Thinner insulation film sheets
10 provide an increase in volume in the motor slot which can be used to add additional windings, increasing motor efficiency.

The present invention is an electrical insulating film comprised of a rubber modified syndiotactic monovinylidene aromatic polymer.

As used herein, the term "syndiotactic" refers to polymers having a
15 stereoregular structure of greater than 90 percent syndiotactic, preferably greater than 95 percent syndiotactic, of a racemic triad as determined by ^{13}C nuclear magnetic resonance spectroscopy.

Syndiotactic monovinylidene aromatic polymers are homopolymers and copolymers of vinyl aromatic monomers, that is, monomers whose chemical
20 structure possess both an unsaturated moiety and an aromatic moiety. The preferred vinyl aromatic monomers have the formula



wherein R is hydrogen or an alkyl group having from 1 to 4 carbon atoms, and Ar is an aromatic radical of from 6 to 10 carbon atoms. Examples of such vinyl
25 aromatic monomers are styrene, alpha-methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, vinyl toluene, para-t-butylstyrene, vinyl naphthalene, and divinylbenzene. Syndiotactic polystyrene is the currently preferred syndiotactic vinyl aromatic polymer. Typical polymerization processes for producing syndiotactic vinyl aromatic polymers are well known
30 in the art and are described in US-A-4,680,353, US-A-5,066,741, US-A-5,206,197 and US-A-5,294,685.

Typically, the weight average molecular weight (Mw) of the syndiotactic monovinylidene aromatic polymer is sufficient such that the polymer obtains

good physical properties, yet low enough to have good melt processability, and is preferably between 150,000 and 400,000.

The impact modifier used in the films of the present invention can be any impact modifier which will impart sufficient strength and flexibility within
5 the syndiotactic polymer such that it can be used in an insulating film. Typically this means that the film can be folded back onto itself without cracking. Examples of impact modifiers include but are not limited to styrene-ethylene-butylene-styrene block copolymer (SEBS), styrene-ethylene-propylene-styrene block copolymers (SEPS), polyolefins such as ethylene-
10 octene and ethylene-hexene copolymers, polybutadiene, polyisoprene and copolymers of dienes with vinyl aromatic monomers such as butadiene-styrene and isoprene-styrene copolymers.

The impact modified syndiotactic monovinylidene aromatic polymer typically contains from 50, more preferably from 55, and most preferably from
15 60 to 95, preferably to 90 and most preferably to 85 percent by weight of the syndiotactic monovinylidene aromatic polymer, based on the total weight of the impact modified composition.

The impact modified syndiotactic monovinylidene aromatic polymer typically contains from 5, more preferably from 10 and most preferably from 15
20 to 50, preferably to 45 and most preferably to 40 weight percent of impact modifier, based on the total weight of the rubber modified composition.

In addition to the syndiotactic monovinylidene aromatic polymer and the impact modifier, other additives can also be used to produce the film of the present invention. Additives include as flame retardants, antioxidants,
25 including hindered phenols such as IRGANOX™ 1010, IRGANOX™ 555, SEENOX™ 412S, and IRGANOX™ 1076, AND ULTRANOX™ 626, ULTRANOX™ 815, STAB PEP™ 36, Ethanox™ 398, Hostanox™ PAR 24 and Hostanox™ 03, 2,6-di-t-butyl-4-methylphenol, stearyl-β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, and triethylene glycol-bis-3-(3-tert-butyl-4-hydroxy-
30 5-methylphenyl)propionate or phosphorus-based compounds such as tris(2,4-tert-butylphenyl)phosphite and 4,4'-butylidenebis(3-methyl-6-tert-butylphenyl-di-tridecyl)-phosphite; antiblock agents such as fine particles composed of

alumina, silica, aluminosilicate, calcium carbonate, calcium phosphate, and silicon resins; light stabilizers, such as hindered amine-based compounds or benzotriazole-based compounds; lubricants such as stearic acid, behenic acid, zinc stearate, calcium stearate, magnesium stearate, ethylene bis-steramide, pentaerythritol tetrastearate, organo phosphate, mineral oil, trimellitate, polyethylene glycol, silicone oil, epoxidized soy bean oil, tricresyl phosphate, polyethylene glycol dimethyl ether, dioctyl adipate, di-n-butyl phthalate, butylene glycol montanate (Wax OP), pentaerythritol tetramontanate (TPET 141), aluminum mono-stearate, aluminum di-stearate, montanic acid wax, montanic acid ester wax, polar polyethylene waxes, and non-polar polyethylene waxes; extrusion aids, stabilizers such as bis(2,4-di-tertbutylphenyl)pentaerythritol and tris nonyl phenyl phosphite. Additionally, other polymers can be combined with the impact modified syndiotactic monovinylidene aromatic polymer.

Nucleators may also be used in the present invention and are compounds capable of reducing the time required for onset of crystallization of the syndiotactic monovinylidene aromatic polymer upon cooling from the melt. Nucleators provide a greater degree of crystallinity in an extruded sheet and more consistent distribution of crystallinity under a variety of extrusion conditions. Higher levels of crystallinity are desired in order to achieve increased chemical resistance and improved heat performance. In addition, crystal morphology may be desirably altered. Examples of suitable nucleators for use herein are monolayer of magnesium aluminum hydroxide, calcium carbonate, mica, wollastonite, titanium dioxide, silica, sodium sulfate, lithium chloride, sodium benzoate, aluminum benzoate, talc, and metal salts, especially aluminum salts or sodium salts of organic acids or phosphonic acids. Especially preferred compounds are aluminum and sodium salts of benzoic acid and C₁₋₁₀ alkyl substituted benzoic acid derivatives. A most highly preferred nucleator is aluminum tris(p-tert-butyl)benzoate. The amount of nucleator used should be sufficient to cause nucleation and the onset of crystallization in the syndiotactic vinylaromatic polymer in a reduced time compared to compositions lacking in such nucleator. Preferred amounts are

from 0.5 to 5 parts by weight based on the total weight of the impact modified composition.

Typically the impact modified syndiotactic monovinylidene aromatic polymer is prepared by blending the impact modifier with the syndiotactic monovinylidene polymer and other additives. Any means can be used to adequately reach uniform dispersion of the impact modifier and other additives in the syndiotactic monovinylidene aromatic polymer. This is generally accomplished by compounding the materials in an extruder and pelletizing. The compounded pellets are then melted and metered in an extruder to a sheet die to produce a sheet web which is cast onto a three roll stack to cool the web while maintaining uniform thickness and smooth surface quality. The extruded web is typically wound onto a roll for subsequent processing. The sheet is then slit to the proper width and cut to length. In preparing a motor assembly, small sections of plastic sheet are folded, cuffed and inserted into the slot liner of the motor to act as the electrical insulation.

The electrical insulating film can be produced on a conventional cast film/sheet extrusion line or on a cast tenter film/sheet line as disclosed in US-A-5,093,758. The extruded sheet/film can be uni- or bi-axially stretched. When using conventional cast film/sheet line, such as a single screw extruder feeding a coat-hanger type die which casts the molten web onto a three roll cooling stack, a faster production rate can be achieved while obtaining crystallinity in the sheet of 10 - 50 percent. Levels of less than 10 percent are achieved in compositions containing high levels of impact modifier. High levels of crystallinity are preferred to ensure dimensional stability in end use applications which involves elevated temperatures and/or thermal cycling. Syndiotactic monovinylidene aromatic polymers such as SPS, can be sufficiently crystallized in one step on a cast extrusion line by extending the path and increasing the temperature the molten web experiences before being cooled on the roll stack. Typically, the extrusion line path will be from 5 - 50 cm, preferably from 20 to 40 cm with the melt temperature ranging from 310 to 330°C. Preferably the crystallinity is from 15, preferably from 20 and most preferably from 25 to 50, preferably to 45, and most preferably to 40 percent.

The electrical insulating film is typically obtained in thicknesses of from 100 to 500 microns (μm), preferably from 150 to 400, more preferably from 150 to 300, and most preferably from 200 to 300 μm .

5 The electrical insulating film of the present invention is characterized by a glass transition temperature of 100°C. This allows the film to maintain a higher modulus at elevated temperatures compared to alternative materials such as polyester. Additionally, the film has good dead fold characteristics which is highly desirable for electrical ground insulation applications. Polymers used to make this film are non-hydroscopic, therefore dimensional
10 changes in the fabricated electrical insulation component are minimal. This allows for more predictable, tighter tolerance engineering of the electrical insulation system.

The electrical insulating film of the present invention has superior dielectric strength and breakdown voltage properties compared to commonly
15 used polyester films and vulcanized papers. This will enable the electrical designer to down gauge the film thickness to allow more space in the device for copper windings leading to a more electrically efficient machine.

An additional advantage of the electrical insulating film of the present invention is its inherently bright white color obtained without the addition of
20 pigments. Commonly used polyester films are tinted white with pigments such as titanium dioxide which incurs a loss in physical and electrical properties. The bright white color also provides a contrast background for the visual detection of flaws in the magnet wire coating.

The electrical insulating film of the present invention is useful for
25 electrical insulation in slot liners, wedges and phase insulation for motors and generators. This includes hermetic motor/compressor sealed units, fractional horsepower motors, diaphragms and industrial laminations.

The following examples are provided to illustrate the present invention. The examples are not intended to limit the scope of the present invention and
30 they should not be so interpreted. Amounts are in weight parts or weight percentages unless otherwise indicated.

EXAMPLE 1

The following materials are used in the following example as shown in Table I:

	Syndiotactic Polystyrene (SPS)	Mw 300,000
	Impact Modifier	styrene-ethylene-butylene-styrene block copolymer (SEBS) Kraton™ G1651 available from Shell Chemical
5	Nucleator	Aluminum tris (p-tert-butyl)benzoate

Table I

<u>Sample</u>	<u>SPS polymer</u>	<u>Impact Modifier</u>	<u>Nucleator</u>
T-1	85 percent	15 percent	-
T-2	80 percent	20 percent	-
T-3	79 percent	20 percent	1 percent
T-4	70 percent	30 percent	-
T-5	60 percent	40 percent	-
T-6	50 percent	50 percent	-
T-7	84 percent	15 percent	1 percent

SPS, impact modifier and nucleator are compounded on a twin screw extruder and pelletized. The pellets are then melted and extruded into thin
 5 (approximately 250 μm thick) sheet under the conditions listed in Table II.

Table II

Zone	1	2	3	4	5
Extruder zone, °C	330	322	310	310	310
Transfer line, °C	310	310	310	310	
Feed throat, °C	38				

Front roll 46 °C
 Middle roll 62 °C
 10 Back roll 56 °C

Physical Property Characterization

Samples are injection molded and tested for physical properties.

Results are tabulated in Table III.

Table III

<u>Property</u>	<u>T-1</u>	<u>T-2</u>	<u>T-3</u>	<u>T-4</u>	<u>T-5</u>	<u>T-6</u>	<u>T-7</u>
DTUL@0.45 MPa, °C	103	97	101	94	92	91	103
Vicat, °C	239	222	229	184	126	118	235
Elongation@break, percent	17	47	34	101	73	79	23
Elongation@yield, percent	2.5	2.4	2.0	2.3	2.4	2.6	2.3
Tensile modulus, MPa	2500	2190	2270	1710	1280	1080	2470
Tensile strength@break, MPa	36	31	29	26	16	14	35
Tensile strength@yield, MPa	44	36	32	28	22	19	41
Flex modulus, MPa	2900	2550	2620	2000	1520	1310	2900
Flex strength, MPa	79	67	66	52	40	33	74
Specific gravity	1.020	1.015	1.014	0.998	0.984	0.973	1.021
Melt flow, g/10 min	5.5	4.5	4.0	3.2	2.3	1.9	4.6
Notch Izod impact, J/m	110	140	130	300	650	760	100

5

Thin Sheet Properties

Crystallinity in the thin sheet samples is determined using differential scanning calorimetry.

<u>Sample</u>	<u>T-1</u>	<u>T-2</u>	<u>T-3</u>	<u>T-4</u>	<u>T-5</u>	<u>T-6</u>	<u>T-7</u>
Heat Flow @ 145-160°C, J/g	12.66	6.83	13.47	7.21	6.94	10.35	8.21
Heat Flow @ 255-270°C, J/g	22.27	19.06	19.46	20.42	19.02	14.40	11.94
Crystallinity, percent	18.1	23.0	24.8	22.7	7.6	7.0	24.0

- 10 The need for a secondary operation to increase crystallinity is eliminated by selecting process conditions that keep the polymer melt above its glass transition temperature for a sufficient amount of time for crystallinity to develop before cooling. This includes having a melt temperature of 310°C and increasing the distance between the die lips and the first roll to
- 15 approximately 25 cm.

Once having produced the thin sheet, the film is slit and die stamped to the appropriate physical dimensions for insertion into a wire-wound electromechanical device.

CLAIMS:

1. An electrical insulating film produced from a composition comprising an impact modified syndiotactic monovinylidene aromatic polymer.
2. The film of Claim 1 wherein the polymer is syndiotactic polystyrene.
3. The film of Claim 1 wherein the impact modifier is selected from the group consisting of a styrene-ethylene-butylene-styrene copolymer, a styrene-ethylene-propylene-styrene copolymer, an ethylene-octene copolymer and an ethylene-hexene copolymer.
4. The film of Claim 3 wherein the impact modifier is a styrene-ethylene-butylene-styrene copolymer.
5. The film of Claim 1 wherein the composition further comprises a nucleator.
6. The film of Claim 5 wherein the nucleator is aluminum tris (p-tert-butyl)benzoate.
7. The film of Claim 1 wherein the syndiotactic monovinylidene polymer is a copolymer of para-methyl styrene.
8. The film of Claim 1 wherein the film is from 100 to 500 μm thick.
9. The film of Claim 8 wherein the film is from 200 to 300 μm thick.
10. The film of Claim 1 wherein syndiotactic monovinylidene aromatic polymer has a crystallinity of from 7 to 50 percent.
11. The film of Claim 10 wherein the crystallinity is from 30 to 40 percent.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/02710

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01B3/44 C08L25/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 757 064 A (IDEMITSU PETROCHEMICAL CO) 5 February 1997 see page 12, line 16 - line 21; example 2 ---	1-7
X	WO 97 32928 A (DOW CHEMICAL CO) 12 September 1997 see example 1; table 1 see example 1; table 2 ---	1-6
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

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