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(54) Title: FLAME-RETARDANT POLYOLEFIN / THERMOPLASTIC POLYURETHANE COMPOSITION

(57) Abstract: The present invention is a flame-retardant polyolefin / thermoplastic polyurethane formulation made from or containing a polyolefin, a thermoplastic polyurethane, and an intumescent, polyphosphate flame retardant composition. The invented system achieves elongations > 400% and tensile strengths > 1500 psi while the same polyolefin only achieved 100% elongation and <1000 psi tensile strength. Also, the present invention shows improved tape extrusion performance versus a comparable TPU only composition, indicating improved melt rheology / fabrication capability for extrusion applications.



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**FLAME-RETARDANT POLYOLEFIN /
THERMOPLASTIC POLYURETHANE COMPOSITION**

This invention relates to flame retardant formulations for wire and cable applications. Specifically, it relates to halogen-free, flame retardant polyolefin / thermoplastic polyurethane formulations for jacketing for wires, jacketing for cables, extruded sheeting, and extruded profiles.

Metal hydrate-based polyolefin compounds and intumescent-based polyolefin compounds do not achieve simultaneously industry-required flame and mechanical properties. Notably, the addition of flame retardant fillers at loadings of 40-50 weight percent to achieve good burn test performance will cause the resulting polyolefin compound to have poor mechanical properties. As such, it is desirable to provide a polyolefin composition with excellent mechanical properties, such as high elongation, high flexibility (low modulus), good tensile strength, and improved deformation temperature as well as excellent burn performance.

To that end, the presently invented composition is provided, comprising a polyolefin, a thermoplastic polyurethane, and an intumescent, polyphosphate flame retardant. Specifically, the present invention achieves elongations > 400% and tensile strengths > 1500 psi while the same polyolefin only achieved 100% elongation and <1000 psi tensile strength. Also, the present invention shows improved tape extrusion performance versus a comparable TPU only composition, indicating improved melt rheology / fabrication capability for extrusion applications. The present invention is particularly useful in the preparation of wire-and-cable jackets and other extruded articles, such as sheeting and profiles.

The composition of the present invention comprises a polyolefin, a thermoplastic polyurethane, and an intumescent, polyphosphate flame retardant composition. Preferably, the presently described composition is halogen-free.

The polyolefin may be polar, nonpolar, or a mixture thereof. The polyolefin is present in an amount of about 5 to about 90 weight percent.

Suitable polar polyolefins include (i) copolymers of ethylene and an unsaturated ester, (ii) copolymers of ethylene and an unsaturated acid such as acrylic or methacrylic acid, (iii) copolymers of ethylene and a vinyl silane (e.g., vinyltrimethoxysilane and vinyltriethoxysilane), and (iv) interpolymers of any of these comonomers. Preferably, the polyolefin is a polar, copolymer of ethylene and an unsaturated ester.

The portion of the copolymer attributed to the ester comonomer can be in the range of about 5 to about 50 percent by weight based on the weight of the copolymer, and is preferably in the range of about 15 to about 40 percent by weight. The melt index of the ethylene/unsaturated ester copolymers can be in the range of about 0.5 to about 50 grams per 10 minutes.

When the unsaturated ester is an alkyl acrylate or an alkyl methacrylate, the alkyl groups can have 1 to 8 carbon atoms and preferably have 1 to 4 carbon atoms. Examples of the acrylates and methacrylates are ethyl acrylate, methyl acrylate, methyl methacrylate, t-butyl acrylate, n-butyl acrylate, n-butyl methacrylate, and 2-ethylhexyl acrylate.

When the unsaturated ester is a vinyl carboxylate, the carboxylate group can have 2 to 8 carbon atoms and preferably have 2 to 5 carbon atoms. Examples of the vinyl carboxylates are vinyl acetate, vinyl propionate, and vinyl butanoate.

Suitable nonpolar polyolefins include (i) homopolymers of ethylene, (ii) copolymers of ethylene and one or more alpha-olefins, and, optionally, a diene, (iii) ethylene copolymers with carbon monoxide, propylene, and butene, (iv) homopolymers of propylene, (v) copolymers of propylene and other olefins, and (vi) terpolymers of propylene, ethylene, and dienes.

Thermoplastic polyurethane polymers are known in the art and are typically obtained by the reaction of a linear hydroxyl-terminated polyol, an organic diisocyanate, and a chain extender. Thermoplastic polyurethanes (TPUs) useful in the present invention include polyester TPUs and polyether TPUs.

Notably, the polyesters TPUs can be made with di-acids like adipic acid and diols like ethylene glycol, propane diol, and butane diol while the polyether TPUs can be made with polyols of polyethylene oxide, propylene oxide, and butylene oxide. The TPU is present in an amount of about 0.1 to 95 weight percent.

The intumescent, polyphosphate flame retardant composition is a blend of (i) an intumescent, nitrogen-containing polyphosphate and (ii) a melamine or a melamine-derivative co-additive. Preferably, the intumescent, nitrogen-containing polyphosphate is an ammonium polyphosphate, a piperazine polyphosphate, or derivatives thereof. More preferably, the intumescent, nitrogen-containing polyphosphate is piperazine polyphosphate. As an intumescent flame retardant, the nitrogen-containing polyphosphate has the character of swelling and charring when

exposed to flame. The intumescent, polyphosphate flame retardant composition is present in an amount of about 0.1 to about 70 weight percent.

The composition of the present invention may further comprise other non-halogen flame retardants, such as metal oxides, metal oxide hydrates, metal carbonates, a carbonate plus an acid or acid-generating material, cement, urea, and polyalcohols.

The composition may further comprise other polymers such as non-olefin polymers, polyvinyl chloride, ester-ether block copolymers, ester/amide block copolymers, olefin block copolymers, and engineering plastics such as polycarbonates, polysulfones, and polyimides. The composition may also further comprise other additives such as minerals and peroxides.

In another embodiment, the present invention is a cable comprising one or more electrical conductors or a core of one or more electrical conductors, each conductor or core being surrounded by a flame retardant layer comprising the flame-retardant polyolefin / thermoplastic polyurethane composition described herein.

In yet another embodiment, the present invention is an extruded article comprising the flame-retardant polyolefin / thermoplastic polyurethane composition described herein.

EXAMPLES

The following non-limiting examples illustrate the invention.

Testing

- (1) Yield Strength (psi);
- (2) Tensile Strength @ Peak (psi);
- (3) Tensile Strength @ Break (psi);
- (4) Elongation @ Break (%);
- (5) 1% Secant Modulus (psi);
- (6) 2% Secant Modulus (psi);
- (7) 5% Secant Modulus (psi); and
- (8) Burn property of Not Burn Flag;
- (9) Time to Flag (sec);
- (10) Burn property of Total Time (sec);
- (11) Not Fully Burned;
- (12) Uncharred (mm below flag);
- (13) No Flaming Drip;

- (14) High Melt Flow, wherein 1 no flow (best), 5 high flow; and
- (15) Overall Rating**; Best(1)>>Worst(5), wherein #1 No Flaming Drip; #2 Char Length; #3a No melt flow; #3b not burn to flag; #3c time to flag.

Burn Test

The burn tests were performed by a vertical strip test for a 45-sec perpendicular UL94 ignition @ bottom. The test specimens were prepared to be a 100-mil strip of 75-mil plaque with embedded wire and 8" long.

Exemplified Compositions

The test specimens were prepared using the following components:

- (1) PELLETHANE™ 2102-75A caprolactone polyester thermoplastic polyurethane, having a Shore A Hardness of 77A, a specific gravity of 1.17, and available from The Dow Chemical Company;
- (2) PELLETHANE™ 2103-80AE polyether thermoplastic polyurethane, having a Shore A Hardness of 82A, a specific gravity of 1.13, and available from The Dow Chemical Company;
- (3) ELVAX™ 40L-03 ethylene/vinyl acetate copolymer having a vinyl acetate content of 40 percent and a melt index of 3 dg/m measured at 190 degrees Celsius and 2.16 kg, available from E. I. du Pont de Nemours and Company; and
- (4) FP-2100™ intumescent, nitrogen-containing polyphosphate-based flame retardant, which is a blend of piperazine polyphosphate and a phosphoric acid compound and available Amfine Chemical Corporation or Adeka Corporation.

Table 1 shows two comparative examples (Comp. Ex. 1 and 2) and three examples of the present invention (Example 3-5). Each amount is shown in weight percent.

Desired mechanical properties include a tensile strength > 1500 psi and elongation > 200 percent. For flame retardancy performance, an overall flame rating of 2 or less is acceptable.

TABLE 1

Components	Comp. Ex. 1	Comp. Ex. 2	Ex. 3	Ex. 4	Ex. 5
PELLETHANE™ 2102-75A	60.00		45.00	30.00	15.00
PELLETHANE™ 2103-80AE		60.00			
ELVAX™ 40L-03			15.00	30.00	45.00
FP-2100™ flame retardant	40.00	40.00	40.00	40.00	40.00
volume filler (cc/gram)	0.24	0.24	0.24	0.24	0.24
volume intumescent (cc/g)	0.24	0.24	0.24	0.24	0.24
volume resin (cc/gram)	0.51	0.51	0.54	0.56	0.59
Volume Fraction Resin	0.684	0.684	0.695	0.706	0.716
Calculated specific gravity	1.34	1.34	1.30	1.25	1.21
resin to polyphosphate additive ratio	1.50	1.50	1.50	1.50	1.50
Physical Properties					
Yield Strength (psi)	666	974	1073	370	280
Tensile Strength @ Peak (psi)	3807	1518	2959	1168	456
Tensile Strength @ Break (psi)	3807	1518	2959	1168	456
Elongation @ Break (%)	515	485	513	518	883
1% Secant Modulus (psi)	6228	14204	3697	2321	3159
2% Secant Modulus (psi)	6093	13119	3875	2459	2236
5% Secant Modulus (psi)	5350	10921	3583	2478	1798
Burn Results					
Not Burn Flag	2/3	2/3	2/3	2/3	3/3
Time to Flag (sec)	10	0	1	8	NA
Total Time (sec)	11	7.667	7	29	1
Not Fully Burned	2/3	2/3	2/3	2/3	3/3
Uncharred (mm below flag)	45	50	30	38	57
No Flaming Drip	2/3	0/3	3/3	3/3	3/3
High Melt Flow	3.5	5	2	1.5	3
Overall Rating	3	4	2	2	2

What is claimed is:

1. A flame-retardant polyolefin / thermoplastic polyurethane composition comprising:
 - (a) a polyolefin;
 - (b) a thermoplastic polyurethane; and
 - (c) an intumescent, polyphosphate flame retardant composition.
2. The flame-retardant polyolefin / thermoplastic polyurethane composition of Claim 1 wherein the composition is halogen-free.
3. The flame-retardant polyolefin / thermoplastic polyurethane composition of Claim 1 or Claim 2 wherein the polyolefin is polar.
4. The flame-retardant polyolefin / thermoplastic polyurethane composition of Claim 3 wherein the polar polyolefin is a copolymer of ethylene and an unsaturated ester.
5. The flame-retardant polyolefin / thermoplastic polyurethane composition of Claim 1 or Claim 2 wherein the intumescent, polyphosphate flame retardant composition comprises:
 - (i) an intumescent, nitrogen-containing polyphosphate and
 - (ii) a melamine or a melamine-derivative co-additive.
6. The flame-retardant polyolefin / thermoplastic polyurethane composition of Claim 5 wherein the intumescent, nitrogen-containing polyphosphate is selected from the group consisting of ammonium polyphosphate and piperazine polyphosphate.
7. The flame-retardant polyolefin / thermoplastic polyurethane composition of Claim 6 wherein the intumescent, nitrogen-containing polyphosphate is piperazine polyphosphate.
8. A cable comprising one or more electrical conductors or a core of one or more electrical conductors, each conductor or core being surrounded by a flame retardant layer comprising the flame-retardant polyolefin / thermoplastic polyurethane composition according to any of Claims 1 to 7.
9. An extruded article comprising the flame-retardant polyolefin / thermoplastic polyurethane composition according to any of Claims 1 to 7.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/033236

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08L75/04 C08L75/06 C08L23/08 H01B7/295 H01B3/30
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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)

C08L H01B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	abstract claim 1 page 4, table 1, example 5 page 4, paragraphs 18,20,21	8
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Y	claim 1	8,9
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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- *&* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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