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(71) Applicant: KAWASAKI CHEMICAL HOLDING CO., INC. [US/US]; Suite 1300, 1105 North Market Street, Wilmington, DE 19899 (US).

(72) Inventors: GLOGOVSKY, Joan; 4 Treetops Road, Landenberg, PA 19350 (US). BOLVARI, Anne, E.; 815 Brettingham Court, West Chester, PA 19382 (US).

(74) Agents: SCHWARZE, William, W. et al.; Panitch Schwarze Jacobs & Nadel, 1601 Market Street, 36th floor, Philadelphia, PA 19103 (US).

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(54) Title: TOUGHENED POLYPHENYLENE SULFIDE COMPOSITIONS AND METHOD OF MAKING THE SAME

(57) Abstract

Toughened polyphenylene sulfide compositions are provided having impact strength, weld line strength and tensile elongation, among other advantages. The compositions include a blend of polyphenylene sulfide and an olefin terpolymer for toughening the polyphenylene sulfide. The terpolymer has the formula E/X/Y (I), where E is an olefinic polymer, X is an acrylic ester and Y is a glycidyl ester. The compositions may also include reinforcing agents or fillers, preferably glass fibers or carbon fibers. The compositions are formed by blending polyphenylene sulfide and an olefin terpolymer of formula (I), with no acid, hot water or organic solvent wash pretreatment of the polyphenylene sulfide.

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TOUGHENED POLYPHENYLENE SULFIDE COMPOSITIONS AND METHOD OF MAKING THE SAME

Field of the Invention

The present invention relates to toughened polyphenylene sulfide compositions for mechanical and industrial applications and, more particularly, to toughening polyphenylene sulfide compositions to enhance impact strength, weld line strength and tensile elongation.

Background of the Invention

Polyphenylene sulfide (PPS) is a semicrystalline, high temperature resistant material which is used in many industrial and mechanical applications. Polyphenylene sulfide is often used for mechanical parts, such as gears, motor parts, furnace components, lighting sockets and electrical connectors. Automotive parts such as engine sensors and light reflectors can also be made from polyphenylene sulfide materials.

Polyphenylene sulfide suffers from low impact strength, poor weld line strength and a tendency to flash when injection molded. There have been numerous attempts in the prior art to toughen various thermoplastics, including polyphenylene sulfide.

For example, U.S. Patent No. 4,172,859 discloses a toughened multi-phase thermoplastic composition consisting essentially of 60 to 99 wt% of a polyester and polycarbonate matrix resin and 1 to 40 wt% of at least one random copolymer having a particle size of 0.01 to 3 microns adhered to the matrix resin. Suitable copolymers for toughening the polyester/polycarbonate matrix include ethylene/vinyl acetate/glycidyl methacrylate and ethylene/methyl acrylate/glycidyl methacrylate. The compositions may be modified by one or more conventional additives, such as fibrous and particulate fillers and reinforcements, etc. The compositions are useful for forming molded and extruded parts having greater ductility, toughness and less susceptibility to catastrophic failure.

Similarly, U.S. Patent No. 4,174,358 discloses a toughened thermoplastic composition consisting essentially of 60 to 99 wt% of a polyamide matrix resin and 1 to 40 wt% of at least one polymer having a particle size of 0.01 to 3 microns and being adhered to the polyamide. An example of a suitable toughening polymer is ethylene/vinyl acrylate/glycidyl methacrylate. Similar advantages were observed for the toughened polyamide compositions as those observed for the toughened polyester/polycarbonate compositions previously discussed.

U.S. Patent No. 4,753,980 discloses toughened thermoplastic polyester compositions comprising 60 to 97 wt% of a polyester matrix resin and 3 to 40 wt% of an ethylene copolymer, such as ethylene/methyl acrylate/glycidyl methacrylate. Molded articles formed from the toughened polyester compositions are characterized by extraordinary toughness, especially at low temperatures.

With regard to the prior art discussed above, it is believed that a terpolymer such as ethylene/methyl acrylate/glycidyl methacrylate reacts with the amine of the polyamide or carboxyl groups of the polyester. However, no similar reactivity is apparent with polyphenylene sulfide compositions.

U.S. Patent No. 4,889,893 discloses a polyphenylene sulfide composition having enhanced impact properties comprising: (a) a polyphenylene sulfide resin which is treated with an acid, hot water or an organic solvent or combination thereof; and (b) an olefinic copolymer containing 60 to 99.5 wt% of an α-olefin and 0.5 to 40 wt% of a glycidyl ester of an α,β-unsaturated carboxylic acid. The polyphenylene sulfide must be treated with the acid, hot water and/or organic solvent to increase its affinity with the olefinic copolymer. Suitable olefinic copolymers include ethylene, propylene and butene-1. Suitable glycidyl esters of α,β-unsaturated acids include glycidyl acrylate, methacrylate and ethacrylate. The olefinic copolymer may further be copolymerized with 40 wt% or less of another copolymerizable unsaturated monomer, such as vinyl ether, vinyl acetate, vinyl propionate, methyl acrylate, methyl methacrylate, acrylonitrile or styrene.

Acid washing or otherwise pretreating of polyphenylene sulfide to enhance its affinity with an olefinic copolymer is expensive and unnecessarily complicates the production of polyphenylene sulfide compositions. It would be desirable to have a toughened polyphenylene sulfide composition having high impact strength, weld line strength and tensile elongation, among other attributes, without the necessity of an acid wash or other pretreatment of the polyphenylene sulfide.

Summary of the Invention

The present invention overcomes the drawbacks of prior art toughened polymeric compositions by providing a toughened polyphenylene sulfide composition which has high impact strength, weld line strength and tensile elongation, among other desirable benefits. The polyphenylene sulfide composition comprises a blend of (a) polyphenylene sulfide which has not been pretreated with an acid, hot water or organic solvent wash; and (b) an olefin terpolymer for toughening the polyphenylene sulfide, the terpolymer having the formula:

E/X/Y (I)

where E is an olefinic polymer, X is an acrylic ester and Y is a glycidyl ester. The composition may optionally include conventional additives such as fillers or reinforcing agents.

Another aspect of the present invention is a method for toughening a polyphenylene sulfide composition. The method comprises blending polyphenylene sulfide and an olefin terpolymer of the Formula I, with no acid, hot water or organic solvent wash pretreatment of the polyphenylene sulfide. The invention is particularly advantageous for toughening glass or carbon fiber reinforced polyphenylene sulfide compositions.

Description of the Preferred Embodiments

The toughened polyphenylene sulfide compositions of the present invention not only exhibit high impact strength, weld line strength and tensile elongation, but also have improved color stability during extrusion and molding operations and are believed to have improved wear resistance over polyphenylene sulfide alone. The need for an acid wash or other pretreatment of the polyphenylene

sulfide is eliminated in the present compositions, thereby providing a simple and inexpensive method for making toughened polyphenylene sulfide compositions.

The toughened polyphenylene sulfide composition of the present invention comprises polyphenylene sulfide which has not been pretreated with an acid wash, hot water and/or organic solvent to improve its affinity with the olefinic terpolymer. Although the polyphenylene sulfide may be of a branch configuration, a linear configuration is presently preferred. An example of a suitable linear polyphenylene sulfide resin is Fortron 214, which is commercially available from Hoechst Celanese Corp. of Chatham, New Jersey. A branched polyphenylene sulfide which is suitable for use in the present invention is Ryton P4, which is commercially available from Phillips 66 Co. of Pasadena, Texas.

Generally the percentage of polyphenylene sulfide in the unfilled or unreinforced composition is about 60 to about 97 wt%. However, it is presently preferred that the percentage of polyphenylene sulfide in the composition be about 70 to about 96 wt% and, more preferably, about 80 to about 93 wt%.

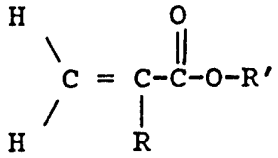
The toughening agent for the polyphenylene sulfide composition comprises an olefin terpolymer represented by the formula:

E/X/Y (I)

The component E is an olefinic polymer, such as ethylene, propylene, butene or pentene. Generally, the percentage of the olefinic polymer in the olefin terpolymer is about 40 to about 90 wt%. Presently, it is preferred that the percentage of

olefinic polymer is about 50 to about 80 wt% and, more preferably, about 60 to about 70 wt% of the total terpolymer.

The component X of the olefin terpolymer is an acrylic ester. The acrylic ester is preferably one having the general formula:

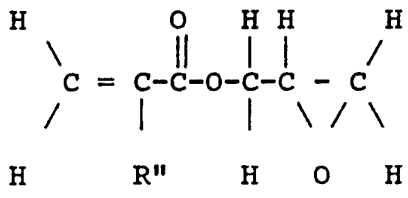


(II)

where R is selected from the group consisting of H and a lower alkyl group and R′ is a hydrocarbon group having 1 to 8 and preferably 1 to 4 carbons. The lower alkyl group has 1 to 6, and preferably 1 to 3 carbons. Examples of suitable acrylic esters include ethyl acrylate and butyl acrylate.

The percentage of the component X in the olefin terpolymer is generally about 15 to about 40 wt%. However, it is presently preferred that the percentage of X is about 20 to about 35 wt% and, more preferably, about 25 to about 32 wt% of the total terpolymer.

The component Y of the olefin terpolymer is a glycidyl ester. Preferably, the glycidyl ester is one having the general formula:



(III)

where R" is selected from the group consisting of hydrogen and a lower alkyl group, wherein lower alkyl is as defined above. Examples of suitable glycidyl esters include glycidyl acrylate, glycidyl methacrylate and glycidyl ethacrylate.

Generally the component Y comprises about 1 to about 20 wt% of the olefin terpolymer. Preferably, the component Y comprises about 3 to about 16 wt% and, more preferably, about 5 to about 9 wt% of the olefin terpolymer.

Suitable olefin terpolymers are commercially available or may be polymerized according to methods well known to those of ordinary skill in the art. Among the olefin terpolymers suitable for use in the present invention is an ethylene/ethyl acrylate/glycidyl methacrylate terpolymer which is commercially available from Elf Atochem North America, Inc. of Philadelphia, Pennsylvania under the trademark Lotader. Preferably, the terpolymer to be blended with the polyphenylene sulfide is in powdered or pelletized form.

The polyphenylene sulfide and olefin terpolymer may be blended by dry tumbling and mixing in a single screw extruder having a mixing screw design, for example. A suitable single screw extruder for use in the present invention is commercially available from Welex of Blue Bell, Pennsylvania. Other methods for blending the polyphenylene sulfide and olefin terpolymer will be evident to those of ordinary skill in the art.

The toughened polyphenylene sulfide composition may also include additives such as reinforcing agents, fillers, lubricants, static dissipating materials, and/or processing aids. Suitable additives include polytetrafluoroethylene; silicone; molybdenum disulfide; polyethylene; carbon fiber or powder; glass fiber, powder or beads; silicon carbide fibers; aramid fibers; ceramic fibers; graphite fibers or powder; metal fibers; and fillers, such as silicates, mica, talc, wollastonite,

clay, carbonates, such as calcium and magnesium carbonates, and sulfates, such as barium and calcium sulfates.

The additive(s) in the polyphenylene sulfide composition may be present in an amount up to about 80 wt% of the total composition. Preferably the percentage of additive is about 30 to about 60 wt% of the composition.

Particularly preferred is the addition of glass fibers to the present polyphenylene sulfide composition, which increases the strength, stiffness, creep resistance, thermoconductivity and heat distortion temperature of the composition. Carbon fibers may be added to the polyphenylene sulfide composition to increase the strength, thermoconductivity, electrical conductivity, and creep and fatigue endurance of the composition.

Preferably, the additive is mixed with the composition after the polyphenylene sulfide and olefin terpolymer have been blended, but each of the components may be blended together and extruded as discussed above, as desired.

The toughened polyphenylene sulfide compositions of the present invention may be used in the same types of applications as polyphenylene sulfide alone, and are especially advantageous where enhanced toughness, high impact strength, weld line strength and tensile elongation are desired.

The present invention will now be illustrated by the following specific, non-limiting examples.

EXAMPLE 1

Polyphenylene sulfide and olefin terpolymer composites were prepared by dry tumbling varying percentages of linear polyphenylene sulfide (Hoechst Celanese) and ethylene/ethyl acrylate/glycidyl

methacrylate (E/EA/GMA) (Atochem) to form compositions according to the present invention. No acid, hot water, organic solvent or other pretreatment of the PPS was used. Glass fibers (GF) (1/8" x 10 um, which are commercially available from PPG Industries, Inc. of Pittsburgh, Pennsylvania) were blended together with the polyphenylene sulfide and olefin terpolymer at different percentages. The compositions were extruded in a 2 1/2" single screw extruder having a mixing screw design. Percentages of toughening agent and glass fiber reinforcement present in each test sample are set forth in Table I.

Each extrudate was pelletized and injection molded into 5" x 0.5" x 0.125" thick samples (according to ASTM standard D-256) for notched Izod testing. Testing was conducted at room temperature (73°F). Test specimens of 2 1/2" length were cut from the center of each molded test bar. A notch with a radius of 0.25 $\pm$ 0.12 mm was milled into each bar using a TMI Notching Cutter, Model No. 22-05-02. A two-pound hammer was used in the TMI impact tester, which is of cantilever beam design. The results of the notched Izod testing are set forth in Table I.

TABLE I

	Notched Izod Results (ft lb/in)		
Weight Percentage of E/EA/GMA	Weight Percentage of Glass Fiber		
	30	40	50
0	1.9	2.1	2.0
5	2.7	3.1	3.1
7.5	3.3	3.5	3.3
10	3.5	3.5	3.4
20	5.3	4.6	3.8

The results indicate that the incorporation of the terpolymer greatly increases the notched Izod impact values when compared to samples without the terpolymer. As shown in Table I, as the weight

percentage of ethylene/ethyl acrylate/glycidyl methacrylate is progressively increased in samples having the same percentage of glass fiber, the notched Izod values also increase. For example, for 30 wt% glass fiber samples, the notched Izod value almost tripled when 20 wt% ethylene/ethyl acrylate/glycidyl methacrylate was included in the polyphenylene sulfide composition. Similar increases in notched Izod strength values were observed for samples containing 40 and 50 wt% glass fiber, respectively.

EXAMPLE 2

Polyphenylene sulfide and olefin terpolymer composites were prepared in the same manner using the same components as Example 1, except 40 wt% glass fiber and 8.5 wt% carbon fiber were included in each sample. No acid, hot water, organic solvent or other pretreatment of the PPS was used. Test samples of each composite were prepared and tested in the same manner as that set forth in Example 1. The test results are set forth in Table II.

TABLE II

Weight Percentage of E/EA/GMA	Notched Izod Results (ft lb/in)
0	0.7
5	1.0
8	1.26

The results set forth in Table II indicate that the presence of the terpolymer enhances notched Izod impact values of PPS samples having both glass fiber and carbon fiber incorporated therein. As the weight percentage of E/EA/GMA is increased, the notched Izod values of the corresponding samples also increase.

EXAMPLE 3

To compare the desirability of linear versus branched polyphenylene sulfide in the present compositions, polyphenylene sulfide and ethylene/ethyl acrylate/glycidyl methacrylate compositions were prepared according to the method set forth above. However, linear polyphenylene sulfide (Fortron 214) was used in one run and branched polyphenylene sulfide (Ryton P4) was used in a second run. As in Example 1, no acid, hot water, organic solvent or other pretreatment of the PPS was used. Ten percent of the terpolymer and 30% of glass fibers of the types used in Example 1 were used to prepare the compositions. Notched and unnotched Izod tests were performed on each of the compositions according to ASTM D-256 at the test conditions set forth in Example 1.

As shown in Table III, both the notched and unnotched values for the linear polyphenylene sulfide-containing compositions were superior to those for the compositions containing branched polyphenylene sulfide. Therefore, it can generally be concluded that the effect of at least the terpolymer used in the example is enhanced when used in linear as opposed to branched polyphenylene sulfide compositions. It is believed that similar olefin terpolymers will also have a superior strengthening effect on linear as opposed to branched polyphenylene sulfide.

TABLE III

PPS	Notched Izod (ft lb/in)	Unnotched Izod (ft lb/in)
branched	1.8	11.8
linear	3.5	15.6

The test results show that the olefin terpolymers of the present invention enhance the toughness and strength of polyphenylene sulfide compositions without acid, hot water or organic solvent treatment of the polyphenylene sulfide prior to compounding. The use of an olefin terpolymer according to the present invention not only increases the impact strength of polyphenylene sulfide, but also the weld line strength and tensile elongation. It is also believed that the olefin terpolymer improves the color stability of polyphenylene sulfide compositions of the present invention during extrusion and molding and the wear resistance of articles formed from the compositions.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the invention as defined by the appended claims.

CLAIMS

1. A toughened polyphenylene sulfide composition having high impact strength, weld line strength and tensile elongation, comprising a blend of:

(a) polyphenylene sulfide which has not been pretreated with an acid, hot water or organic solvent wash; and

(b) an olefin terpolymer for toughening said polyphenylene sulfide, the terpolymer having the formula:

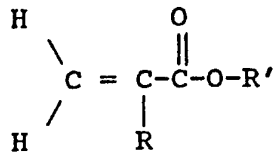
E/X/Y (I)

where E is an olefinic polymer, X is an acrylic ester and Y is a glycidyl ester.

2. The composition according to claim 1, wherein the polyphenylene sulfide is linear.

3. The composition according to claim 1, wherein the olefin is selected from the group consisting of ethylene, propylene, butene and pentene.

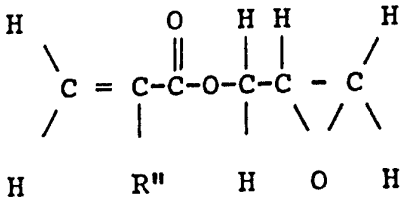
4. The composition according to claim 1, wherein the acrylic ester is of the formula:



(II)

where R is selected from the group consisting of H and a lower alkyl group and R′ is a hydrocarbon group having 1 to 8 carbons.

5. The composition according to claim 1, wherein the glycidyl ester is of the formula:



(III)

where R" is selected from the group consisting of hydrogen and a lower alkyl group.

6. The composition according to claim 5, wherein the glycidyl ester is selected from the group consisting of glycidyl acrylate, glycidyl methacrylate and glycidyl ethacrylate.

7. The composition according to claim 1, wherein the polyphenylene sulfide comprises about 60 to about 97 weight percent of the polymeric composition.

8. The composition according to claim 1, wherein E comprises about 40 to about 90 weight percent of the olefin terpolymer.

9. The composition according to claim 1, wherein X comprises about 15 to about 40 weight percent of the olefin terpolymer.

10. The composition according to claim 1, wherein Y comprises about 1 to about 20 weight percent of the olefin terpolymer.

11. The composition according to claim 1, further comprising an additive selected from the group consisting of a reinforcing agent and a filler.

12. The composition according to claim 11, wherein said additive comprises up to about 80 weight percent of the composition.

13. The composition according to claim 11, wherein said additive is selected from the group consisting of glass fibers, mineral powders, glass beads, carbon fibers, aramid fibers, ceramic fibers,

metal fillers, silicates, carbonates, sulfates, polytetrafluoroethylene, silicone, molybdenum disulfide and graphite.

14. An article of manufacture molded from the composition of claim 1.

15. A toughened polyphenylene sulfide composition having high impact strength, weld line strength and tensile elongation, comprising a blend of:

(a) linear polyphenylene sulfide which has not been pretreated with an acid, hot water or organic solvent wash;

(b) an olefin terpolymer for toughening said polyphenylene sulfide, the terpolymer having the formula:

E/X/Y (I)

where E is ethylene, X is ethyl acrylate and Y is glycidyl methacrylate; and

(c) a reinforcing agent selected from the group consisting of glass fibers, carbon fibers and mixtures thereof.

16. An article of manufacture molded from the composition of claim 15.

17. A method for toughening a polyphenylene sulfide composition, comprising blending polyphenylene sulfide, with no acid, hot water or organic solvent wash pretreatment of the polyphenylene sulfide, and an olefin terpolymer having the formula:

E/X/Y (I)

where E is an olefinic polymer, X is an acrylic ester, and Y is a glycidyl ester.

18. The method according to claim 17, further comprising the step of blending the polyphenylene sulfide and olefin terpolymer with an

additive selected from the group consisting of reinforcing agents, fillers, lubricants, static dissipating materials and processing aids.

INTERNATIONAL SEARCH REPORT

Ir ational application No.
PCT/US94/00103

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : CO8L 81/02, 51/06; CO8G 63/91
US CL : 525/189, 64

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)

U.S. : 525/189, 64

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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP, A, 0 327 300 (POLYPLASTICS CO. LTD.) 09 AUGUST 1989, see page 2, lines 42-63, page 5, lines 21-46 and 65.	1-18
Y,P	US, A, 5,204,405 (ORIKASA, ET AL.) 20 APRIL 1993, see column 3, line 68; column 4, lines 34-56; column 5, lines 25-36.	1-18
A	US, A, 4,889,893 (KOBAYASHI, ET AL.) 26 DECEMBER 1989, see column 5, lines 42-68.	2-16, 18
A	EP, A, 0 345 094 (TORAY INDUSTRIES, INC.) 06 DECEMBER 1989, see page 4, lines 18-39.	2-16, 18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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