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(54) Compositions of a polyphenylene ether resin and a rubber modified copolymer of styrene and bromostyrene

(57) Molding compositions comprise a polyphenylene ether resin and a rubber-modified styrene-bromostyrene copolymer, preferably having a styrene-bromostyrene weight ratio from 85:15 to 15:85. Preferred compositions comprise 20 to 90% by weight of polyphenylene ether and 80 to 10% by weight of the rubber-modified copolymer. Preferably the rubber modifying the copolymer is a diene rubber. Such compositions have better physical properties, e.g. heat deflection temperature, impact strength and stability towards UV light than polyphenylene ether compositions rendered flame-retardant by low molecular weight brominated additives.

SPECIFICATION

Compositions of a polyphenylene ether resin and a rubber modified copolymer of styrene and bromostyrene

This invention relates to compositions comprising a polyphenylene ether resin and a rubber-modified styrene/bromostyrene copolymer.

The term "polyphenylene ether resin" is descriptive of a well known group of polymers that may be made by a variety of catalytic and non-catalytic processes, as described in, for example, U.S. Patents No. 3,306,874, 3,306,875, 3,257,357, 3,257,258, 3,356,761, 3,337,499, 3,219,626, 3,384,619, 3,440,217, 3,442,885, 3,573,257,3,455,880 and 3,382,212.

U.S. Patent No. 3,383,435 describes compositions of polyphenylene ether resins and styrene resins, including halogenated styrene resins. In U.S. Patent No. 3,887,646, compositions that include a polyphenylene ether resin and a chlorostyrene resin are disclosed. U.S. Patent No. 3,639,506, describes compositions of a polyphenylene ether resin that include styrene resins, phosphates and halogenated flame retardants.

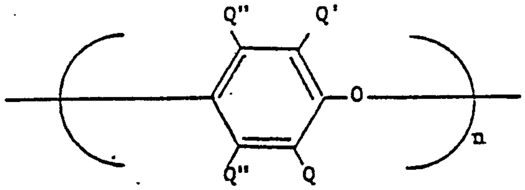
It has been found that the compositions of a polyphenylene ether resin and a rubber modified copolymer of styrene and bromostyrene have better physical properties, i.e. HDT and impact strength, better flammability and better ultraviolet light stability than compositions made with rubber modified polystyrene with the same concentration of bromine present in the form of typical low molecular weight brominated flame retardants.

The compositions of the invention comprise:

(a) a polyphenylene ether resin; and

(b) a rubber modified copolymer of styrene-bromostyrene

The polyphenylene ether resins comprise polymers of structural units of the formula:



wherein Q is selected from the group consisting of hydrogen, hydrocarbon radicals, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, Q′ and Q″ are the same as Q and in addition halogen with the proviso that Q and Q′ are both free of a tertiary carbon atom and n is an integer of at least 50.

The preferred polyphenylene ether resin is poly(2,6-dimethyl-1,4-phenylene) ether resin having an intrinsic viscosity of from about 0.40 dl/g to about 0.60 dl/g as measured in chloroform at 30°C.

The rubber modified copolymers of styrene and bromo- may be prepared from styrene and bromostyrene and a rubber. Alternatively, isomeric mixtures of bromostyrene may be employed which include para-, meta- and ortho-bromostyrene. Generally the weight ratio of styrene to bromostyrene in the copolymer may vary from 15:85 to 85:15 and more preferably from 30:70 to 85:15. The reason for specifying these ratios is because of phase separation that may occur when 100% bromostyrene is employed at 50:50 of polyphenylene ether:bromostyrene. An 85:15 bromostyrene copolymer is compatible as a 75:25 composition of polyphenylene ether; bromostyrene copolymer, while a composition of 50:50 polyphenylene ether:bromostyrene copolymer of either 85:15 or 100:0 bromostyrene:styrene copolymer is incompatible. A 70:30 bromostyrene: copolymer is compatible in all proportions with polyphenylene ether resins as are all bromostyrene:styrene copolymers having less than a 70:30 ratio of bromostyrene:styrene. The same degree of compatibility for the bromostyrene-styrene copolymers is expected at the lower end of the concentration range. From 80 to 10 parts by weight of the copolymer of styrene bromostyrene may be utilized in combination with from 20 to 90 parts by weight of the polyphenylene ether resin.

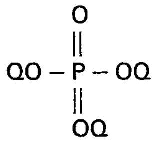
The copolymers of styrene-bromostyrene may be modified with rubbers such as a polybutadiene rubber by copolymerizing styrene monomer, bromostyrene monomer and the polybutadiene rubber to form a graft terpolymer that contains small, discrete particles of rubber partially cross-linked and grafted to the styrene-bromostyrene units. In addition, other rubber may be used such as EPDM rubbers, polysulfide rubbers, ethylene propylene copolymers, and the like. From 1 to 15 parts by weight of a thermoplastic rubber such as an ABA or AB block copolymer may also be utilized in the compositions of the invention. Suitable ABA block copolymers are the Kraton or Kraton-G polymers that are described in U.S. Patent 3,646,162 and U.S. Patent 3,595,942 respectively.

If desired, reinforcing amounts of reinforcing fillers may be added to the compositions in amount of from 5 to 40% by weight of total composition. Glass fibers or other reinforcing agents such as quartz, mica, wollastonite or carbon fibers may be used as the reinforcing fillers. Non-reinforcing fillers may also be employed.

If the amount of bromine in the composition of the invention is inadequate to attain the desired degree of flame retardance, a minor amount of a phosphorus compound, that is 0.1 to 7.5 parts by weight of phosphorus compound calculated as elemental phosphorus per 100 parts by weight of total composition, may be added.

In general, the preferred phosphate compounds may be selected from elemental phosphorus or organic phosphonic acids, phosphonates, phosphinates, phosphonites, phosphinites, phosphine oxides, phosphines, phospites and phosphates. Illustrative is triphenyl phosphine oxide. These can be used alone or with antimony oxide.

Typical of the preferred phosphorus compounds which may be employed in this invention would be those having the general formula:



$$\begin{array}{c} O \\ \| \\ QO - P - OQ \\ \| \\ OQ \end{array}$$

where each Q represents the same or different radicals including hydrocarbon radicals such as alkyl, cycloakyl, aryl, alkyl substituted aryl and aryl substituted alkyl; halogen; hydrogen and combinations thereof provided that at least one of said Q's is aryl. Typical examples of suitable phosphates include phenylbisdodecyl phosphate, phenylethyl hydrogen phosphate, ethyldiphenyl phosphate, 2-ethylhexyl di(p-tolyl) phosphate, diphenyl hydrogen phosphate, tricresyl phosphate, triphenyl phosphate, tri-i-propylphenyl phosphate, 2-chloroethyl-diphenyl phosphate, and diphenyl hydrogen phosphate. The preferred phosphates are those which are commerically available, such as Kronitex-50, which is a mixture of isomers of tri-i-propylphenyl phosphate.

The compositions may be prepared by tumble blending powders, beads or extruded pellets of the components with or without suitable reinforcing agents, stabilizers, pigments, non-reinforcing fillers, e.g. 5-50% by total weight of the composition of clays and talcs, added flame retardants, plasticizers or extrusion aids. The compositions may be prepared by extrusion of the ingredients into continuous strands, cutting the strands into pellets and molding the pellets into any desired shape.

Example 1

A rubber modified copolymer of styrene-bromostyrene was prepared by dissolving cis-trans poly(butadiene) rubber in a mixture of sytrene and bromostyrene and polymerizing the mixture of styrenes with stirring to yield a graft terpolymer of rubber, styrene and bromostyrene, containing discrete small particles of rubber, partially cross-linked and grafted to the styrene-bromostyrene copolymers. The rubber particles, measured by optical microscopy, had a median diameter of about 2.3 microns. The terpolymer contained 17.1% bromine (about 40% bromostyrene by weight) and 7.5% rubber. It contained 17% of toluene-insoluble rubbery gel, with a swelling index in toluene of 9.2. The styrene-bromostyrene copolymer, separated from the rubber phase by extraction with methyl ethyl ketone, had intrinsic viscosity of 0.77 dl/g in chloroform at 30°C.

A mixture of 80 parts of poly(2,6-dimethyl-1,4-phenylene ether (PPO, General Electric Company having a IV of about 0.5 in $CHCl_3$ at 30°C.), 20 parts of the rubber modified copolymer of styrene-butadiene (Composition A) was extruded in a single screw extruder and then molded into standard test pieces with a screw injection molding machine.

For comparison a mixture (Composition B) was also extruded and molded, with the bromostyrene terpolymer replaced by an equal weight of a rubber modified polystyrene (Monsanto HT-91), a graft copolymer of cis-trans poly(butadiene) with polystyrene that contains 20% of toluene-insoluble gel, with a swelling index of 7.7. Another blend (Composition C) was prepared from poly(2,6-dimethyl-1,4-phenylene) ether and a mixture of a copolymer of styrene and bromostyrene containing 27% bromine, polystyrene homopolymer (Dylene 8G) and a styrene butadiene block copolymer (Kraton 1101), with the proportions adjusted to make the bromine concentration, the rubber concentration and the poly(2,6-dimethyl-1,4-phenylene) ether-polystyrene ratio the same as the Composition A. Properties are summarized in Table 1. The composition containing the styrene-bromostyrene-rubber graft terpolymer has a higher heat distortion temperature and Izod impact strength than either of the other two. It has V-0 flammability rating, while the composition containing the same amount of bromine in the form of a styrene-bromostyrene copolymer was V-1, with significantly higher average burning time.

TABLE 1

Composition No.*	Izod Impact (J/m.of notch)	HDT (°C)	UL 94 rating	UL 94 Avg Burn Time
A	96.1	153	V-0	4.9 sec.
B**	80.1	145	V-1	15.0 sec.
C**	58.7	147	V-1	6.5 sec.

* each composition also contains 3 phr of triphenylphosphate, 1 phr or diphenyl decyl phosphite, 1.5 phr of polyethylene, 0.15 phr of zinc sulfide and zinc oxide.

** Control

A blend of 60 parts of poly(2,6-dimethyl-1,4,phenylene) ether, 40 parts of the bromostyrene terpolymer described in Example 1, 1 part diphenyldecylphosphite, 1.5 parts of polyethylene, 0.15 parts of zinc sulfide and 0.15 parts of zinc oxide was extruded and molded as described in Example 1. Another blend was prepared from 60 parts of poly(2,6-dimethyl-1,4, phenylene ether), 40 parts of rubber modified polystyrene (Monsanto HT-91), with the other additives noted above and with the addition of 8.9 parts of decarbromodiphenyl ether (DBDPE) to make the bromine concentration equal in the two blends. Two other blends were prepared in the same way, but with 3 parts of triphenyl phosphate (TPP) added to each blend. Properties of the molded material are summarized in Table 2. The compositions made with styrene-bromostyrene-rubber terpolymer have higher Izod impact strength and heat distortion temperature than the corresponding compositions having the same amount of bromine as decabromodiphenyl ether. Also, bromine added as the bromostyrene terpolymer was more effective as a flame retardant than in the form of the low molecular weight brominated additive. Both formulations with the terpolymer had V-0 flammability rating, while the formulations containing decabromodiphenyl ether were V-1, with longer average burning times, as determined by the flammability test in Bulletin 94 of the Underwriters' Laboratory.

Composition No.	TPP (phr)	DBDPE (phr)	Izod Impact (J/m)	HDT (°C)	UL-94 Rating	UL-94 Avg. Burn Time(sec)
D	None	None	128.1	148	V-0	4.4
E*	None	8.9	85.4	131	V-1	6.2
F	3	None	112.1	130	V-0	3.8
G*	3	8.9	80.1	124	V-1	5.7

* Control

Example 3

Mixtures of 40 parts poly(2,6-dimethyl-1,4-phenylene) ether and 60 parts of rubber modified polystyrene (Monsanto HT-91) or the styrene-bromostyrene-rubber graft terpolymer described in Example 1 were extruded and molded as described in Example I. To some of the blends containing rubber modified polystyrene was added enough of several typical brominated flame-retardant additives to make the overall bromine concentration the same as in the blend with the bromostyrene terpolymer. Each composition also contained 3 parts of triphenylphosphate, 0.5 parts of zinc sulfide, 0.5 parts of zinc oxide and 3 parts of titanium dioxide. Properties of the molded compositions are listed in Table 3. The composition made with the bromostyrene terpolymer had higher impact strength and heat distortion temperature than those containing the brominated flame-retardant additive, as well as better color and improved flammability.

TABLE 3

					UL-94		
Composition No.	Polystyrene	Additive	Izod Impact (J/m.)	HDT (°C)	Rating	Avg. burn time	Yellowness Index.
H	bromostyrene terpolymer	None	117.4	118	V-1	5.5 sec**	21.7
I*	HT-91	None	85.4	109	Fail	36 sec.	21.0
J*	"	decabromodiphenyl ether	69.4	107	Fail	11.2	26.4
K*	"	1,2-bis (penta bromophenoxy) ethane	64.1	98	V-1	6.3 sec.	29.0
L*	"	Hexabromobiphenyl	64.1	100	Fail	13.6 sec.	24.8
M*		Pentabromophenyl carbonate	53.4	102	Fail	16.7 sec.	***

* Control

** Rating and average burn time greatly affected by a single specimen with long burning time. Repetition with a second group of specimens showed V-0 flammability rating, with average burn time of 2.1 seconds.

*** Badly discolored, dark grey.

Example 4

A solution of 10 g of a butadiene-styrene di-block copolymer (Solprene 308) and 143 g. of polybutadiene (Taktene 1202) in 620.5 g. of bromostyrene monomer (27% ortho; 70% para; 3% meta by I.R. analysis) and 926.5 g. of styrene monomer was transferred to a one gallon reactor along with 0.9 g. of azo-bis-(isobutyronitrile) and 0.9 g. of dicumyl peroxide. The mixture was stirred (750 rpm) for six hours at 82°C, to a styrena conversion of 32%, and suspended with 1500 ml of water containing 4.5 g. of poly(vinyl alcohol) and 3.3 g of gelatin. The mixture was stirred for five hours at 100°C, 5 hours at 120°C and finally for six hours at 140°C. The product, in the form of large beads, was filtered off, washed with hot water, and dried. It was found to contain 22.1% of toluene-insoluble gel, with a swelling index of 8.9.

A composition of 50 parts of rubber modified styrene-bromostyrene copolymer; 50 parts of poly(2,6-dimethyl-1,4- phenylene) ether resin; 1 part of diphenyldecyl phosphite; 1.5 parts of polyethlene; 3 parts of triphenyl phosphate; 0.15 parts of zinc sulfide; and 0.15 parts of zinc oxide was extruded in a 28 mm twin-screw extruder and moulded into test pieces on a screw injection molding machine. For composition, a composition was made that except for the substitution of rubber modified high impact polystyrene (Foster Grant 834) for the rubber modified copolymer of bromostyrene, was the same. Properties of the molded parts were as follows:

Property	Rubber Modified High Impact Polystyrene*	rubber Modified High Impact Polybromostyrene Styrene Copolymer
Tensile Elongation (%)	66	48
Tensile Yield Strength (kg/m^2)	6749760	7171620
Tensile Strength (psi)	5835730	6327900
Izod Impact Strength (J/m. of notch)	224.2	202.8
Gardner Impact Strength (m.-kg)	1.15	1.15
Gloss (7°C)	44.1	48.3
Heat Deflection Temperature (°C)	114	124
UL94 (rating)	Fail	V-0
UL94 (avg. burn time, seconds)	35	3.6

*Control

Example 5

A solution of 100 g. of EPDM rubber (Epcar 387) in 400 g. of styrene and 600 g. of bromostyrene (27% ortho, 70% para and 3% meta) was placed in a stirred stainless steel reactor along with 1.0 g of *tert*-butyl peracetate. The reactor was purged with nitrogen and the mixture was heated for fourteen hours at 120°C. The product contained 17% of toluene-insoluble gel with a swelling index of 9.9. The bromine was 25.7%.

A composition was prepared using 50 parts of a rubber modified copolymer of bromostyrene/styrene whose preparation is described above; 50 parts of poly(2,6-dimethyl-1,4-phenylene) ether resin; 1 part of diphenyl decyl phosphite; 1.5 parts polyethylene; 3 parts triphenyl phosphate; 0.16 parts zinc sulfide and 0.16 parts zinc oxide by extrusion with a twin screw extruder. The extrudate was chopped into pellets which were molded into test pieces in a screw injection molding machine. The product had a notched Izod impact strength of 186.8 J/m. of notch, heat deflection temperature of 128°C and was V-0 in section by UL–94 with an average burning time of 2.0 seconds.

Example 6

A solution of 90 g. of polybutadiene rubber (Taktene 1202) in 607 g. of bromostyrene monomer and 303 g. of styrene monomer was placed in a stainless steel reactor with 0.5 g. dicumyl peroxide; 0.5 g. of benzoyl peroxide; and 0.5 g. *tert*-dodecyl mercaptan. The mixture was heated, under nitrogen, with vigorous agitation for seven hours at 135°C. The beads of rubber-modified copolymer were filtered off, washed and dried; the bromine content was 26.8%.

A composition of 50 parts of this copolymer; 50 parts of poly(2,6-dimethyl-1,4-phenylene) ether resin and 3 parts of triphenyl phosphate was extruded and molded as described in Example 4. The molded part had good surface appearance with a 7°C gloss number of 59.4; Izod impact strength of 144.1 J/m. of notch; Gardner impact strength of 2.66 m-kg. heat distortion temperature, 134°C; and V-0 flammability rating by UL-94, with an average burning time of 1.5 seconds.

Example 7

A solution of 7 g. of butadiene-styrene diblock copolymer (Solprene 308) and 95 g. of polybutadiene rubber (Taktene 1202) in 906 g. of bromostyrene and 227 g. of styrene was transferred to a stirred reactor with 0.6 g. of azo-bis (isobutyrontrile) and was stirred for five hours at 82°C and suspended in 2000 ml of water containing 4.5 g. of gelatin and 8 g of poly(vinylalcohol). The suspension was heated for five hours at 100°C, 5 hours at 120°C, then for 8 1/2 hours at 140°C. The polymer beads were filtered off, washed with water and dried.

Example 8

A solution of 162 g. of polybutadiene rubber (Taktene 1202) in 545 g. of styrene and 1093 g. of bromostyrene (mixed isomers) was transferred to a stirred stainless steel reactor with 0.9 g. dicumyl peroxide, 0.9 g. of benzoyl peroxide and 0.9 g. of *tert*-dodecyl mercaptan. The reactor was purged with nitrogen and heated for seven hours at 90°C. The product was suspended in 2000 ml of hot water containing 4.5 g. of gelatin and 6.0 g of poly(vinyl alcohol) and heated for fourteen hours at 135°C. The mixture was cooled and the polymer beads were filtered off, washed with hot water and dried. The product contained 29.8% of toluene-isoluble gel, with a swelling index of 4.7. The bromine content was 26.7%.

A mixture of 50 parts of the product, 50 parts of poly(2,6-dimethyl-1,4-phenylene) ether, 3 parts of triphenyl phosphate, 1 part of diphenyl decyl phosphite, 1.5 parts of polyethylene, 0.15 parts of zinc sulfide and 0.15 parts of zinc oxide was extruded and molded as described in Example 4. The molded composition had satisfactory physical properties and excellent flame resistance:

Tensile Yield Strength	7382550 kg./m^2
Elongation at Break	48%
Izod Impact Strength	144.1 J/m of notch
Heat Deflection Temperature	134°C
Gloss (7°C)	59.4
Gardner Impact Strength	2.66 m.-kg.
Flammability (UL94)	V-0
Average Burn Time	1.5

Example 9

The following compositions were prepared from poly(2,6-dimethyl-1,4-phenylene) ether and 9% polybutadiene rubber (Taktene 1202) modified copolymers of styrene and bromostyrene[2] according to the procedure of Example 4 and were found to have the reported properties:

Bromostyrene In copolymer (wt. %)	poly (2,6-dimethyl-1,4-phenylene) ether & copolymer of styrene-bromostyrene	Izod Impact J/m of notch	Gardner (m.-kg.)	HDT °C	UL-94
0[1]	50:50	165.5	1.15	119	V-0 (33.0)*
40	50:50	181.5	2.66	126	V-0 (3.6)*
67	50:50	181.5	1.15	133	V-0 (1.4)*
80	50:50	37.3	0.08	131	V-0 (0.6)*
100	50:50	26.7	0.08	126	V-0 (0.9)*
0[1]	75:25	122.8	1.15	144	V-1 (12.6)*
40	75:25	149.5	4.56	153	V-0 (3.1)*
67	75:25	186.8	3.80	154	V-0 (1.3)*
80	75:25	224.2	2.66	157	V-0 (1.3)*
100	75:25	101.4	0.08	159	V-0 (1.0)*

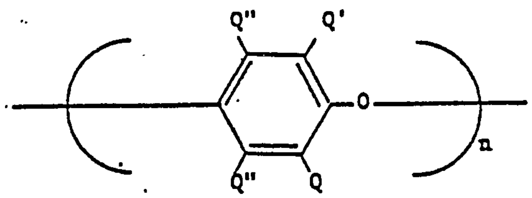
1. rubber modified high impact polystryene
2. each composition also included 3 phr (parts per hundred by weight) of resin triphenyl phosphate, 1 phr diphenyl decyl phosphite, 1.5 phr polyethylene, 0.15 phr zinc sulfide and 0.15 phr zinc oxide.

* average burning time in seconds.

CLAIMS

1. A flame retardant thermoplastic molding composition which consists essentially of:
(a) a polyphenylene ether resin; and
(b) a rubber modified graft copolymer of styrene-bromostyrene.

2. A composition as claimed in Claim 1 wherein the polyphenylene ether resin includes structural units of the formula:



where Q, Q′ and Q″, which can be the same or different, are each hydrogen, halogen, hydrocarbon, halohydrocarbon having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy and halohydrocarbonoxy having at least two carbon atoms between the halogen atom and the phenyl nucleus, with the proviso that Q and Q′ are both free of a tertiary carbon atom, Q is not halogen, and n is at least 50.

3. A composition as claimed in Claim 2 wherein each Q″ is hydrogen.

4. A composition as claimed in Claim 2 wherein the polyphenylene ether resin is poly(2,6-dimethyl-1,4-

phenylene) ether resin.

5. A composition as claimed in any preceding Claim wherein the copolymer contains styrene and bromostyrene in the weight ratio of 85:15 to 15:85.

6. A composition as claimed in any preceding Claim which further includes a reinforcing filler.

7. A composition as claimed in any preceding Claim which comprises, by weight, from 20 parts to 90 parts of the polyphenylene ether and from 80 parts to 10 parts of the copolymer.

8. A composition as claimed in any preceding Claim wherein the rubber in the copolymer is a diene rubber.

9. A composition as claimed in any preceding Claim which further includes a phosphate flame retardant.

10. A composition as claimed in any preceding Claim which further includes a thermoplastic rubber.

11. A composition as claimed in Claim 10 wherein the thermoplastic rubber is an ABA block copolymer.

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