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(54) Title: CLAY FILLED POLYPHENYLENE ETHER COMPOSITIONS

(57) Abstract

Compositions comprising polyphenylene ether, an impact modifier such as an A-B-A^1 block copolymer a plasticizer and a particular clay filler in which the particles have a mean particle size of less than 0.6 micron, preferably between 0.1 and 0.6 micron, and a surface area of at least 15 m^2/g. The clay should be essentially free of large particles commonly known as 'grit', and should also be substantially non-agglomerated or clump-free. The compositions when molded possess unexpectedly high Gardner impact resistance.

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Description

Clay Filled Polyphenylene Ether Compositions

This invention relates to clay filled polyphenylene ether compositions, and more specifically, to compositions composed of polyphenylene ther, an impact modifier and a plasticizer which also contain clay particles characterized by a certain specified particle size and surface area.

Background of the Invention - The polyphenylene ether resins are well known in the art as comprising a family of thermoplastic materials which are suitable for various engineering purposes. These may be made by catalyzed and non-catalyzed processes described in the patent literature.

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such as in Hay, U.S. 3,306,874 and 3,306,875, and in Stamatoff, U.S. 3,257,357 and U.S. 3,257,358, all of which are incorporated herein by reference.

It is known that the polyphenylene ether resins may be admixed with polystyrene, either unmodified or modified, to produce compositions having properties better than those of either of the two polymers individually. Such compositions are disclosed in Cizek, U.S. 3,383,435, which is incorporated herein by reference.

To reduce the cost, it has been proposed to add mineral fillers such as aluminum silicate, calcium carbonate, magnesium silicate, calcium silicate, silica or others, to compositions containing a polyphenylene ether resin and polystyrene. Compositions comprising a polyphenylene ether resin, a rubber modified high impact polystyrene and aluminum silicate are disclosed in U.S. 4,166,812.

Copending application Serial No. 755,025, filed December 28, 1976, discloses compositions comprising a polyphenylene ether resin, alone, or in combination with an impact modifier which is not a high impact rubber modified polystyrene, a mineral filler and a plasticizer.

It is known that the addition of mineral fillers to polyphenylene ether resins can increase the rigidity and dimensional stability of the polymers. The toughness of the resulting composite is usually lower than that of the mineral filled-free polymer, however. It has been found that some

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mineral fillers increase the rigidity of the polymer and provide ductile composites having good impact resistance. Such benefits are more pronounced in falling weight-type impact tests, such as Gardner impact resistance. This type of impact resistance is much more important in actual practice than the impact resistance as measured by other means such as the Izod impact test.

It has now been discovered that as among mineral fillers in general, particulate clay and specifically clay having a mean particle size of less than 0.6 micrometer (micron) and a surface area of 15 square meters per gram (m^2/g) or more, dramatically improves the Gardner impact strength of certain polyphenylene ether compositions. These compositions are described below.

Description of the Invention. - According to this invention, there are provided thermoplastic compositions having improved impact strength when molded, comprising:

(a) a polyphenylene ether resin, alone, or together with an impact modifier;

(b) an effective amount of a plasticizer; and

(c) a particulate clay filler having a mean particle size of less than 0.6 micron and a surface area of at least 15 square meters per gram.

Preferably, the particulate clay filler is substantially free of large, gritty particles and has been well

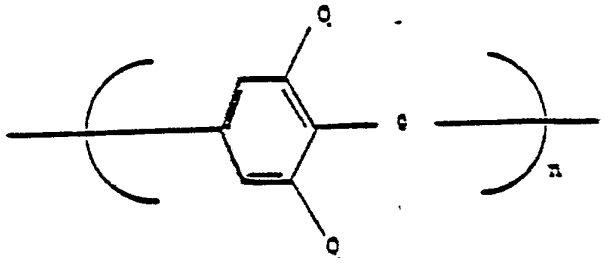
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dispersed to avoid the formation of lumps. The presence of grit and clumps may cause stress concentrations in the clay-resin composites which lower the impact resistance and also other physical properties.

The clay filler of the compositions of this invention can be prepared by conventional methods, using, e.g., sieving means to separate and collect clay particles having the appropriate size, preferably 0.1 to 3.6 micron and surface area, preferably 15 to 30 m^2/g, and to separate gritty particles and clumps.

The preferred polyphenylene ether resins are those having the formula:



wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, 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.

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The preparation of polyphenylene ether resins corresponding to the above formula is described in the above-mentioned patents of Hay and Stamatoff.

The most preferred polyphenylene ether resin for use in this invention is poly(2,6-dimethyl-1,4-phenylene)ether.

The particular impact modifier employed in the compositions is not critical and can be selected from a wide variety of elastomeric materials. By way of illustration, the term "impact modifier" employed herein includes copolymers of styrene and elastomeric materials such as acrylonitrile, EPDM rubber, maleic anhydride or diene rubber. Examples include copolymers of styrene and acrylonitrile, copolymers of styrene and butadiene, copolymers of styrene and maleic anhydride and copolymers of styrene and EPDM rubber. Other examples include terpolymers of styrene, acrylonitrile and butadiene, and terpolymers of styrene, butadiene and styrene of the A-B-A type or radial teleblock type, either hydrogenated or unhydrogenated.

Special mention is made of the A-B-A^1 block copolymers wherein terminal blocks A and A^1 are the same or different and are derived from a vinyl aromatic compound, e.g., styrene, α-methyl styrene, vinyl toluene, vinyl xylene, vinyl naphthalene, and the like, and center block B is derived from a conjugated diene, i.e., butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl butadiene, and the like. Hydrogenated derivatives of the foregoing are also preferred. Both the unhydrogenated and hydrogenated forms can be prepared by methods described

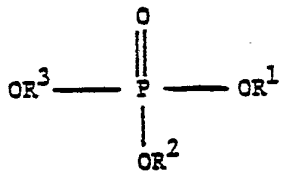
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in the patent literature, e.g., U.S. 3,251,905; U.S. 3,231,635; and U.S. 3,431,323, which are incorporated herein by reference.

The plasticizer can be selected from among any materials known to impart compatibility with polyphenylene ether resin. Preferably, the plasticizer is an aromatic phosphate, and especially a compound having the formula:



wherein R^1, R^2 and R^3 are the same or different and are alkyl, haloalkyl, cycloalkyl, halocycloalkyl, aryl, haloaryl, alkyl substituted aryl, haloalkyl substituted aryl, aryl substituted alkyl, haloaryl substituted alkyl, hydroxyalkyl, hydroxyaryl, hydroxyalkaryl, halogen and hydrogen.

Examples include cresyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, tricresyl phosphate, triisopropylphenyl phosphate, triphenyl phosphate, triethyl phosphate, dibutyl phenyl phosphate, diethyl phosphate, cresyl diphenyl phosphate, isooctyl diphenyl phosphate, tributyl phosphate, 2-ethylhexyl diphenyl phosphate, isodecyl diphenyl phosphate, isodecyl dicresyl phosphate, didecyl cresyl phosphate, tri-n-hexyl phosphate, di-n-octyl phenyl phosphate, di-2-ethyl-hexyl phenyl and tri-2-ethylhexyl phosphate or mixtures thereof. Especially preferred is triphenyl phosphate.

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The ingredients in the compositions of this invention can vary widely. In preferred embodiments, the compositions contain from 5 to 95 parts by weight of polyphenylene ether, from 95 to 5 parts by weight of impact modifier, from 5 to 50 parts by weight of plasticizer and from 5 to 50 parts by weight of clay.

Other ingredients, such as stabilizers, flame retardant agents, drip retardands, antioxidants, antistatic agents, coloring agents, pigments, mold release agents, and the like, can also be included for their conventionally employed purposes.

The compositions of this invention are prepared in any manner. Usually, however, the ingredients are formed into a preblend by tumbling in a mixer, the preblend is extruded at a temperature of from 550°F. to 620°F., the extrudate is cut into smaller pieces, and the pieces are injection molded at a temperature of from 530°F. to 640°F.

Description of the Preferred Embodiments. - The compositions of this invention are illustrated in the following examples, which are not intended to be limiting.

EXAMPLES 1-14

Compositions according to this invention are prepared by tumbling the ingredients, extruding the resulting blend in a Werner Pfleiderer 28 mm twin screw machine, at a temperature of 590°F. and injection molding the extrudate in a Newbury

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injection molding machine at 600°F. (mold temperature 180°F.).

The molded compositions are evaluated for physical properties according to ASTM standards. The compositions and properties are reported in Tables I and II.

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TABLE I. Compositions Comprising a Polyphenylene Ether Resin, an A-B-A Block Copolymer, Triphenyl Phosphate and Clay Filler

Ingredients, parts by weight	1	2*	3*	4*	5*	6*	7*
Poly(2,6-dimethyl-1,4-phenylene)ether	95	95	95	95	95	95	95
Hydrogenated styrene-butadiene-styrene copolymer[a]	5	5	5	5	5	5	5
Triphenyl phosphate	10	10	10	10	10	10	10
ASP-100[b] (clay)	25	-	-	-	-	-	-
ASP-105[b] (clay)	-	25	-	-	-	-	-
ASP-170[b] (clay)	-	-	25	-	-	-	-
ASP-900[b] (clay)	-	-	-	25	-	-	-
ASP-400[b] (clay)	-	-	-	-	25	-	-
Satintone 4[b] (clay)	-	-	-	-	-	25	-
Satintone 1[b] (clay)	-	-	-	-	-	-	25

a Shell Chemical Company's KRATON G 1652

b Engelhard Minerals & Chemicals Corporation

* comparison experiment

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TABLE I. (cont'd)

Physical Properties	Sample Designations						
	1	2*	3*	4*	5*	6*	7*
Filler	ASP-100	ASP-105	ASP-170	ASP-900	ASP-400	Satintone No. 4	Satintone No. 1
Mean particle size of filler (microns)	0.55	0.55	0.55	1.5	4.8	1.0	20
Surface area of filler (m^2/g)	14.6-16.2	11.1-13.8	11.5-14.3	11	7.2	8.9-9.5	7.3-8.5
Gardner impact strength of composite (in-lbs)	235	63	27	9	2	12.5	6.5

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TABLE II. Compositions Comprising a Polyphenylene Ether Resin, an A-B-A Block Copolymer, Triphenyl Phosphate and Clay Filler

Ingredients, parts by weight	8	9	10	11	12*	13*	14*
Poly(2,6-dimethyl-1,4-phenylene)ether	95	95	95	95	95	95	95
Hydrogenated styrene-butadiene-styrene copolymer[a]	5	5	5	5	5	5	5
Triphenyl phosphate	10	10	10	10	10	10	10
HG-90[b] (clay)	25	-	-	-	-	-	-
Suprex[b] (clay)	-	25	-	-	-	-	-
Hulok 321[b] (clay)	-	-	25	-	-	-	-
Nucap 200[b] (clay)	-	-	-	25	-	-	-
Al-Sil-Ate NCF[c] (clay)	-	-	-	-	25	-	-
Al-Sil-Ate NC[c] (clay)	-	-	-	-	-	25	-
Al-Sil-Ate HO_2[c] (clay)	-	-	-	-	-	-	25

* comparison experiment

a Shell Chemical Company's KRATON G 1652

b J.M. Huber Corporation

c Freeport Kaolin Company

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TABLE II, (cont'd)

Physical Properties	Sample Designations 8	9	10	11	12*	13*	14*
Filler	HG-90	Suprex	Nulok No. 321	Nucap No. 200	Al-Sil-Ate NCF	Al-Sil-Ate NC	Al-Sil-Ate NO_2
Mean particle size of filler (microns)	0.3	0.3	0.3	0.3	97% below 2	82% below 2	82% below 2
Surface area of filler (m^2/g)	22	22	22	22	14-16	12-14	12-14
Gardner impact strength of composite (in-lbs)	225	225	190	210	95	15	15

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It can be seen that the compositions according to the invention, 1, 8, 9, 10 and 11, each containing clay having a mean particle size no greater than 0.6 micron and a surface area of at least 15 m^2/g, provide clearly better Gardner impact strength in comparison with the compositions containing a clay filler not in accordance with the invention, 2-7 inclusive and 12-14 inclusive.

Other modifications and variations of this invention are possible in view of the description. It is to be understood, therefore, that changes may be made in the particular embodiments shown herein without departing from the principles or scope of the invention defined in the appended claims and without sacrificing the chief benefits.

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Claims

1. A thermoplastic composition comprising:

(a) a polyphenylene ether resin, alone, or together with an impact modifier;

(b) an effective amount of a plasticizer; and

(c) a particulate clay filler having a mean particle size of less than 0.6 micron and a surface area of at least 15 square meters per gram.

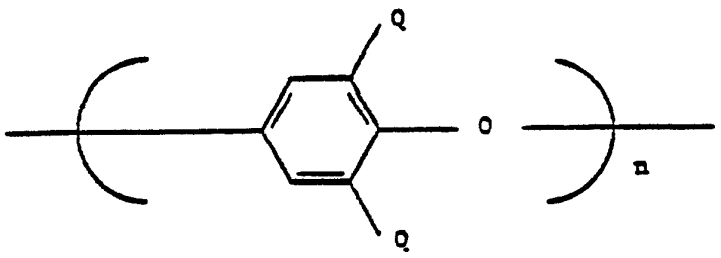
2. A composition as defined in Claim 1, in which the impact modifier is an A-B-A^1 block copolymer wherein terminal blocks A and A^1 are derived from a vinyl aromatic compound and center block B is derived from a conjugated diene.

3. A composition as defined in Claim 2, in which the terminal blocks are polystyrene and the center block is polybutadiene.

4. A composition as defined in Claim 2, in which the A-B-A^1 block copolymer has been hydrogenated.

5. A composition as defined in Claim 1, in which the polyphenylene ether resin has the formula

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wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, 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.

6. A composition as defined in Claim 1, in which the polyphenylene ether resin is poly(2,6-dimethyl-1,4-phenylene) ether.

7. A composition as defined in Claim 1, in which the plasticizer is triaryl phosphate.

8. A composition as defined in Claim 1, in which the plasticizer is triphenyl phosphate.

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9. A composition as defined in Claim 1, comprising from about 5 to about 95 parts by weight of said polyphenylene ether resin, from about 95 to 5 parts by weight of said impact modifier, from about 5 to about 50 parts by weight of said plasticizer and from about 5 to about 50 parts by weight of said clay.

10. A composition as defined in Claim 1, in which the particulate clay filler has a mean particle size of from to micron and a surface area of from to square meters per gram.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US81/01548

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.3 C08K 5/49

U.S. CL. 260/30.6

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	260/30.6R, 42.47, 37R

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 3,708,455, PUBLISHED 02 JANUARY 1973 NAKANISHI ET AL	1-9
A	US, A, 3,850,879, PUBLISHED 26 NOVEMBER 1974 ANDERSON	1-9
A	US, A, 3,923,929, PUBLISHED 02 DECEMBER 1975 WRIGHT ET AL	1-9
A	US, A, 4,166,812, PUBLISHED 04 SEPTEMBER 1979 LEE	1-9
A	US, A, 4,233,199, PUBLISHED 11 NOVEMBER 1980 ABOLINS ET AL	1-9
A	US, A, 4,239,673, PUBLISHED 16 DECEMBER 1980 LEE	1-9

* Special categories of cited documents: [15]

"A" document defining the general state of the art

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"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
20 JANUARY 1982	03 FEB 1982
International Searching Authority [1]	Signature of Authorized Officer [20]
ISA/US	L. JACOBS

Form PCT/ISA/210 (second sheet) (October 1977)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☒ Claim numbers 10, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

RANGES OF PARTICLE SIZE AND SURFACE AREA OF PARTICULATE CLAY FILLER HAVE BEEN OMITTED.

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.