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Dow Case No. 39,381-F

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Patents Act 1990

REQUEST FOR A STANDARD PATENT
and
NOTICE OF ENTITLEMENT

We, the Company identified below as the Applicant, request the grant of a patent to the Company identified below as the Nominated Person for an invention described in the accompanying Standard Complete Patent Specification.

We are not an opponent or eligible person described in Sections 33-36 of the Act.

[70,71] Applicant and Nominated Person:
THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road
Midland, Michigan 48640, U.S.A.

[54] Invention Title: **THERMOPLASTIC RESINS CONTAINING COATED ADDITIVES**

[72] Names of Actual Inventors: **Yi-Bin Huang, Bruce P. Thill.**

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(Note: The following applies only to Convention applications.)
Basic Convention Application Details:

[31] Application No.	[33] Country	Country Code	[32] Date of Application
660,461	United States of America	US	February 26, 1991

I, RICHARD G. WATERMAN, General Patent Counsel, The Dow Chemical Company, authorized to act for and on behalf of applicant Company state the following:

The basic application(s) referred to above is (are) the first application(s) made in a Convention country in respect of the invention the subject of the application.

The applicant Company is entitled to the grant of a patent and is entitled to claim priority from the basic convention application(s) as the assignee of the actual inventor(s).

Dated: January 9, 1992

SIGNATURE

THE DOW CHEMICAL COMPANY

By: R G Waterman

RICHARD G. WATERMAN
General Patent Counsel

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THERMOPLASTIC RESINS CONTAINING COATED ADDITIVES

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(56) Prior Art Documents
AU 446200 52237/69 47.7-47 19.62 47.7-52
AU 612152 17587/88 C08K 19/04 C08J 5/06 C08L 77/06
AU 614539 22289/88 C08J 5/06 C08K 19/04 C08L 23/04

(57)

The present invention relates to thermoplastic resins containing additives that have been surface coated with a modifying agent. The surface coating permits improved compatibility between the additive and thermoplastic resin.

Polar group functionalized polyarylene ethers are a known class of compounds prepared by contacting polar group containing reactants with polyarylene ethers.

CLAIM

1. A composition of matter including:

A) from 25 to 99 parts by weight of a non-functionalized thermoplastic resin, and

B) from 75 to 1 parts by weight of a reinforcing agent selected from the group consisting of glass fibers, glass roving, ceramic whiskers, polymeric fibers, polymeric fiber strands, carbon fiber strands, and boron nitride fibers,

.../2

wherein the compatibility of the non-functionalized thermoplastic resin and the reinforcing agent is enhanced by applying a surface coating of a polar group functionalized polyarylene ether to the reinforcing agent.

5. A composition according to claim 4 wherein the sizing composition includes a coupling agent selected from the group consisting of amine, aminosilane and aminophosphine functional coupling agents.

6. A composition according to any one of claims 1-5 wherein the polar group functionalized polyarylene ether is a dicarboxylic acid anhydride modified polyarylene ether.

7. A composition according to claim 6 wherein the dicarboxylic acid anhydride modified polyarylene ether is a maleic anhydride modified polyarylene ether.

8. A composition according to claim 7 wherein the maleic anhydride modified polyarylene ether is produced by melting a polyarylene ether, contacting from 0.5 to 15 weight percent maleic anhydride with the molten polyarylene ether, and recovering the resulting product.

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Patents Act

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COMPLETE SPECIFICATION
(ORIGINAL)

Class Int. Class

Application Number:
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Complete Specification Lodged:
Accepted:
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Priority

Related Art:

Name of Applicant:

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Invention Title:

THERMOPLASTIC RESINS CONTAINING COATED ADDITIVES

Our Ref : 241855
POF Code: 1037/1037

The following statement is a full description of this invention, including the best method of performing it known to appli ant(s):

6006

THERMOPLASTIC RESINS CONTAINING COATED ADDITIVES

The present invention relates to thermoplastic resins containing additives that have been surface coated with a modifying agent. The surface coating permits improved compatibility between the additive and thermoplastic resin.

In Japanese Kokai 1-135868, published May 29, 1989, there are disclosed certain resin compositions containing (a) inorganic fillers and (b) polyphenylene ether type resins including maleic anhydride modified poly(2,6-dimethyl-1,4-phenylene)ether. The resins are useful for electrical parts.

According to the present invention there is provided a composition of matter including A) from 25 to 99 parts by weight of a non-functionalized thermoplastic resin and B) from 75 to 1 parts by weight of a reinforcing agent selected from the group consisting of glass fibers, glass roving, ceramic whiskers, polymeric fibers, polymeric fiber strands, carbon fiber strands, and boron nitride fibers ~~and aramide fibers~~, the reinforcing agent having a surface coating of a polar group functionalized polyarylene ether.

Polar group functionalized polyarylene ethers are a known class of compounds prepared by contacting polar group containing reactants with polyarylene ethers. The reaction is normally conducted at an elevated temperature preferably in a melt of the polyarylene ether under conditions to obtain homogeneous incorporation of the functionalizing reagent. Suitable temperatures are from 150°C to 300°C. Polyarylene ethers are a known class of polymers having been previously described in United States Patents 3,306,874, 3,306,875, 3,257,357, 3,257,358, and elsewhere. A preferred polyarylene ether is poly(2,6-dimethyl-1,4-phenylene)ether. The polyphenylene ethers are normally prepared by an oxidative coupling reaction of the corresponding bisphenol compound.

Suitable polar groups include the acid anhydrides, acid halides, acid amides, sulfones, oxazolines, epoxies, isocyanates, and amino groups. Preferred polar group containing reactants are compounds having up to 20 carbons containing reactive unsaturation, such as ethylenic or aliphatic ring unsaturation, along with the desired polar group functionality. Particularly preferred polar group containing reactants are dicarboxylic acid anhydrides, most preferably maleic anhydride. Typically the amount of polar group functionalizing reagent employed is from 0.01 percent to 20 percent, preferably from 0.5 to 15 percent, most preferably from 1 to 10 percent by weight based on the weight of polyarylene ether. The reaction may be conducted in the presence of a free radical generator such as an organic peroxide or hydroperoxide agent if desired. Preparation of polar group

functionalized polyarylene ethers have been previously described in United States Patents 3,375,228, 4,771,096 and 4,654,405.

The general procedure for obtaining polar group functionalized polyarylene ethers is to contact a reagent containing both ethylenic unsaturation and the desired polar group as previously specified. Generally if less than 0.01 weight percent of the polar group containing reactant is employed, less than desired compatibility between the reinforcing agent and the thermoplastic resin is attained. If greater than 20 weight percent is employed no significant advantage in polymer properties is realized.

The ~~glass, ceramic, polymeric or carbon~~ reinforcing agent may be in the shape of fibers having a length to diameter ratio (L/D) of greater than 5 or in the shape of particulates having (L/D) less than 5. Preferred particle diameters are from 0.1 micrometers to 1 millimeter. Suitable reinforcing agents include ~~glass microspheres~~, glass fibers, ceramic whiskers, carbon fiber strands, boron nitride fibers, aramide fibers, etc. Preferred are glass fibers, aramide fibers, glass roving or chopped glass fibers having lengths from 0.1 to 10 millimeters and L/D from 5 to 100. One such suitable glass fiber is available from Owens Corning Fiberglas under the designation OCF 414™.

The reinforcing agent may include a sizing agent or similar coating which, among other functions, may promote adhesion between the reinforcing agent and the polar group functionalized polyarylene ethers. Suitable sizing agents may contain amine, aminosilane, and aminophosphine functional coupling agents.

Preferred are aminosilane coupling agents such as 3-aminopropyltrimethoxysilane.

Thermoplastic resins suitably utilized in the present invention include homopolymers and copolymers of vinylaromatic monomers, particularly homopolymers and copolymers of styrene. Suitable comonomers include acrylonitrile, methyl methacrylate, N-phenylmaleimide, etc. Preferred copolymers are those containing from 5 to 50 percent by weight of one or more such comonomers. Also included are rubber modified homopolymers and copolymers of vinylaromatic monomers such as high impact polystyrene-containing butadiene or styrene butadiene based elastomers; specifically high impact polystyrene and ABS resins. Preferred vinylaromatic polymers are those having a stereoregular structure that is highly syndiotactic. Additional suitable thermoplastic resins include polycarbonates, polyamides, polyvinylchloride, polyesters, polyimides, and polyarylene ethers. In addition, mixtures of all of the foregoing thermoplastic resins may additionally be employed.

A most preferred thermoplastic resin is syndiotactic polystyrene prepared by coordination polymerization of styrene monomer under conditions to provide a high degree of syndiotacticity. Most highly preferred are those polymers containing greater than 50 percent syndiotacticity at a racemic triad. Such polymers are known in the art having been previously disclosed in United States Patents 4,680,353, 4,959,435, 4,950,724, 4,774,301, and elsewhere.

The compositions of the present invention are prepared by combining the respective components under conditions to provide uniform dispersal of the

reinforcing agent. The surface coating is suitably applied to the reinforcing agent by contacting the same with a solution of the polar group functionalized polyarylene ether. Suitable solvents for dissolving the polar group functionalized polyarylene ether include methylene chloride, trichloromethane, trichloroethylene, trichloroethane, etc. Preferably the concentration of polar group functionalized polyarylene ether in the solution is from 0.1 weight percent to 20 weight percent, preferably 0.5 to 2 percent by weight. After coating of the reinforcing agent the solution is removed such as by evaporation, devolatilization, vacuum drying, etc.

The resulting surface coating is desirably from 0.001 to 10 weight percent of the uncoated reinforcing agent weight. Homogeneous incorporation of the thermoplastic resin and coated reinforcing agent is obtained by mechanical mixing devices such as extruders, ribbon blenders, solution blending or any other suitable technique. Preferred compositions are those containing from 5 to 95 parts thermoplastic resin and 49 to 5 parts reinforcing agent.

Additional additives such as fillers, elastomers, blowing agents, extrusion aids, antioxidants, pigments, plasticizers, stabilizers, lubricants, etc. may also be included in the composition in amounts up to 50 percent, preferably up to 25 percent, by weight.

Having described the invention the following example is provided as further illustrative and is not

to be construed as limiting. Unless stated to the contrary parts and percentages are based on weight.

Example 1

A maleic anhydride modified polyphenylene oxide resin containing 3 weight percent maleic anhydride (MAPPO) is prepared by injecting maleic anhydride at an appropriate rate to provide the desired maleic anhydride content into a 0.8" (2.0 cm) Welding Engineers Twin Screw extruder which is charged with poly(2,6-dimethyl-1,4-phenylene)ether and operated under conditions to melt plastify the resin. The resulting product is extruded and chopped into granules. A 1 weight percent solution of the resulting MAPPO in trichloroethylene solvent was prepared. Glass fibers (Owens Corning Fiberglas 414™ fiber, desized by treatment with methylene chloride) are contacted with the solution in the following manner. Individual fibers are glued to aluminum tabs using epoxy resin on one end of the fiber. The free fiber end is then dipped into the solution for approximately 1 second, removed and dried in a vacuum oven overnight at approximately 50°C. A molten droplet of the desired thermoplastic resin is picked up on the end of a single fiber applicator and is then transferred, while still molten, to the heated test fiber, by drawing the applicator fiber across the test fiber. Individual adhesive strength measurements on the fibers are then used to quantify the degree of the adhesive strength attained between the resin and the fiber. This technique is referred to as the microbond pullout technique and is disclosed in B. Miller, et al., "A Microbond Method for Determination of the Shear

Strength of a Fiber/Resin Interface", Composites Science and Technology, 28, 17-32 (1987).

Comparative runs are performed on individual fibers that are not treated with the maleic anhydride modified polyarylene ether. The identities of the various thermoplastic resins tested and the results of the testing are contained in Table 1. Results are the average of 15 individual fiber tests.

Table 1

Surface Coating	Thermoplastic Resin	Interfacial Sheer Strength psi (kPa x 10^3)
-	SPS[1]	1700 (12)
MAPPO	SPS	2300 (16)
-	SPS/MAPPO[2]	3500 (24)
MAPPO	SPS/MAPPO	5000 (34)

[1] Syndiotactic polystyrene, Mw 360,000, >95% syndiotactic
[2] Blend of SPS and MAPPO, 2.5 weight percent MAPPO

The above results indicate that improved compatibility between the reinforcing agent and thermoplastic resin is attained by use of the surface coated reinforcing agent of the present invention. This result indicates that resinous blends incorporating the coated reinforcing agents would possess improved compatibility and accordingly improved strength properties, such as tensile and flexural strength.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A composition of matter including:

A) from 25 to 99 parts by weight of a non-functionalized thermoplastic resin, and

B) from 75 to 1 parts by weight of a reinforcing agent selected from the group consisting of glass fibers, glass roving, ceramic whiskers, polymeric fibers, polymeric fiber strands, carbon fiber strands, and boron nitride fibers,

wherein the compatibility of the non-functionalized thermoplastic resin and the reinforcing agent is enhanced by applying a surface coating of a polar group functionalized polyarylene ether to the reinforcing agent.

2. A composition according to claim 1 wherein the reinforcing agent includes chopped glass fibers.

3. A composition according to claim 1 wherein the reinforcing agent includes aramide fibers.

4. A composition according to any one of claims 1-3 wherein the reinforcing agent additionally includes a sizing composition on the surface thereof.

5. A composition according to claim 4 wherein the sizing composition includes a coupling agent selected from the group consisting of amine, aminosilane and aminophosphine functional coupling agents.

6. A composition according to any one of claims 1-5 wherein the polar group functionalized polyarylene ether is a dicarboxylic acid anhydride modified polyarylene ether.

7. A composition according to claim 6 wherein the dicarboxylic acid anhydride modified polyarylene ether is a maleic anhydride modified polyarylene ether.

8. A composition according to claim 7 wherein the maleic anhydride modified polyarylene ether is produced by melting a polyarylene ether, contacting from 0.5 to 15 weight percent maleic anhydride with the molten polyarylene ether, and recovering the resulting product.

9. A composition according to any one of claims 1-8 prepared by coating the reinforcing agent with a solution of the polar group functionalized polyarylene ether in a solvent and thereafter removing the solvent.

10. A composition according to claim 1 wherein the polyarylene ether is poly(2,6-dimethyl-1,4-phenylene)ether.

11. A composition according to any one of claims 1-10 wherein the non-functionalized thermoplastic resin is selected from the group consisting of homopolymers and copolymers of vinylaromatic monomers, polycarbonates, polyamides, polyarylene ethers and mixtures thereof.

12. A composition according to claim 11 wherein the non-functionalized thermoplastic resin is syndiotactic polystyrene or a mixture of syndiotactic polystyrene and a polyarylene ether.

13. A composition according to claim 1 substantially as hereinbefore described with reference to the Example.

DATED : 27 OCTOBER, 1994

PHILLIPS ORMONDE & FITZPATRICK
ATTORNEYS FOR:
THE DOW CHEMICAL COMPANY

ABSTRACT

A composition of matter comprising 25 to 99 parts by weight thermoplastic resin and 75 to 1 part by weight solid reinforcing agent having a surface coating of a polar group functionalized polyarylene ether.