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| <p>(21) International Application Number: PCT/US99/15095</p> <p>(22) International Filing Date: 2 July 1999 (02.07.99)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>60/092,347</td> <td>10 July 1998 (10.07.98)</td> <td>US</td> </tr> <tr> <td>09/342,746</td> <td>29 June 1999 (29.06.99)</td> <td>US</td> </tr> </table> <p>(71) Applicant: BP AMOCO CORPORATION [US/US]; Law Dept., 200 E. Randolph Drive, P.O. Box 87703, Mail Code 1907A, Chicago, IL 60680-0703 (US).</p> <p>(72) Inventor: KONING, Paul, A.; 1660 Berryhill Road, Cumming, GA 30041 (US).</p> <p>(74) Agent: MCDONALD, Scott, P.; BP Amoco Corporation, Law Dept., Mail Code 1907A, P.O. Box 87703, Chicago, IL 60680-0703 (US).</p> | 60/092,347 | 10 July 1998 (10.07.98) | US | 09/342,746 | 29 June 1999 (29.06.99) | US | <p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p> |
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| <p>(54) Title: LIQUID CRYSTAL POLYMER ENCAPSULANT</p> | | | | | | | |
| <p>(57) Abstract</p> <p>Molding compounds for encapsulating electronic components are disclosed. The molding compounds employ liquid crystal polymer resins and fillers coated with non-polar silane coupling agents to reduce the viscosity of the compounds.</p> | | | | | | | |

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LIQUID CRYSTAL POLYMER ENCAPSULANT

Related Applications

5 This application claims the benefit of U.S. Provisional Patent Application Serial No. 60/092,347, filed July 10, 1998.

Field of the Invention

10 The invention relates to molding compounds useful for encapsulating electrical and electronic components. More particularly, the invention relates to thermoplastic molding compounds capable of carrying relatively high fractions of filler material.

Background of the Invention

15 Materials used to encapsulated electrical and electronic components such as semiconductors typically have been thermosetting in nature. Typically these compounds are comprised of one or more epoxy thermosetting resins, a substantial weight fraction of an inert filler material such as silica, and a variety of additives such as catalysts, hardeners,
20 coupling agents, and release agents. Such compounds generally are well-suited for use as encapsulants as the compounds have relatively low melt viscosities that allow heated, uncured compound to flow around a device's connecting wires such as the 1 to 3 micron wires used in semiconductor leadframes prior to completion of the thermosetting process, and because the
25 relatively high weight fraction of inert filler provides for a low coefficient of thermal expansion of the molded device.

 Liquid crystalline polymers, or "LCPs" possess very low melt viscosities when compared to thermoplastics, and therefore are thought to be useful in molding compounds. LCP compounds are characterized by their ability to be
30 processed in an anisotropic melt phase. Unfortunately, LCP encapsulants require relatively high amounts of filler to provide acceptable moisture uptake

and thermal expansion performance. When inert filler materials are added to LCPs for use in encapsulation applications, the low viscosity of the LCP deteriorates with increasing filler loading. At loadings as low as about 30 weight percent, the viscosity of the compound increases to the point where
5 the compound shifts or displaces connecting wires for the device, resulting in the phenomena known as "wire sweep." Because LCP encapsulants generally are believed to require greater than 30 weight percent of filler to obtain adequate thermal and moisture uptake performance, and because such filler loadings result in viscosity increases and unacceptable wire sweep
10 performance, LCPs are not typically used in electronic molding compounds.

What is needed is a way to obtain the moisture uptake and thermal expansion performance of an LCP based encapsulant while minimizing viscosity increases that cause increased wire sweep.

15 Summary of the Invention

We have found that the wire sweep performance of certain LCP-based encapsulant compounds can be enhanced by coating fillers used in the compounds with certain silane coupling agents. In our preferred LCP-based compounds, the viscosity can be reduced by factors of 10 to 25 by using
20 appropriate non-polar silane coupling agents.

Detailed Description of the Invention

The following discussion of a preferred embodiment of our invention illustrates how a particular LCP and silane coupling agents can be selected to
25 produce an LCP based encapsulant having good thermal expansion, moisture resistance, adhesion and wire sweep properties.

A polyester-based liquid crystal polymer resin was used as the base resin for the encapsulants of the following Examples. The polymer used comprised approximately 7 mole percent hydroquinone, 10 mole percent
30 purified isophthalic acid, 10 mole percent purified terephthalic acid, 60 mole percent parahydroxybenzoic acid, and 13 mole percent 4, 4' biphenyldiol.

The polymer exhibited a melting point of approximately 300 degrees Centigrade.

Coupling agents used to coat fillers were pre-reacted to the fillers and dried prior to compounding at a loading of 0.5 weight percent coupling agent
5 calculated on the basis of filler weight. Molding formulations were then prepared by compounding on a 25 millimeter Berstorff co-rotating, meshing twin screw extruder. Compounded formulations were dried in a 100 degree Centigrade forced air drying prior to molding, and molding of samples was accomplished on a 55 ton Toyo injection molding machine using a three plate
10 mold having two fill gates, one located top dead center on the die, and the other located bottom dead center on the die.

In the following Examples 1-6, the effect of various coupling agents on melt viscosity was determined. The formulations were compounded as described above, and the viscosity of the melted compounds measured.
15 Viscosity measurements were made using a Rheometrics RDA II viscometer, using a 60 millimeter cone and plate at 330 degrees Centigrade and at a frequency of 100 rad/second.

Example 1

The formulation tested was unfilled LCP as described above. The
20 measured melt viscosity was 0.2 Pascal-seconds.

Example 2

The formulation tested was LCP filled with 50 weight percent of Denka FB-74 spherical silica filler having an average particle size of about 35 microns. The filler was uncoated. The measured melt viscosity was about 48
25 Pascal-seconds.

Example 3

The formulation tested was LCP filled with 50 weight percent of Denka FB-74 spherical silica filler having an average particle size of about 35 microns. The silica filler was coated and dried as described above using a
30 tri(2-methoxyethoxy) vinylsilane coupling agent available as Silquest A-172 from the Whitco Corporation of Tarrytown, New York. The measured melt viscosity was about 1 Pascal-second.

Example 4

The formulation tested was LCP filled with 50 weight percent of Denka FB-74 spherical silica filler having an average particle size of about 35 microns. The silica filler was coated and dried as described above using a 3-glycidyoxypropyltrimethoxysilane coupling agent available as Silquest A-187 from the Whitco Corporation of Tarrytown, New York. The measured melt viscosity was about 14 Pascal-second.

Example 5

The formulation tested was LCP filled with 50 weight percent of Denka FB-74 spherical silica filler having an average particle size of about 35 microns. The silica filler was coated and dried as described above using a 3-aminopropyltriethoxysilane coupling agent available as Silquest A-1100 from the Whitco Corporation of Tarrytown, New York. The measured melt viscosity was about 6 Pascal-second.

Example 6

The formulation tested was LCP filled with 50 weight percent of Denka FB-74 spherical silica filler having an average particle size of about 35 microns. The silica filler was coated and dried as described above using a trimethoxymethylsilane coupling agent available as Silquest A-1630 from the Whitco Corporation of Tarrytown, New York. The measured melt viscosity was about 2 Pascal-seconds.

As can be seen from Examples 2, 3, 4, 5 and 6, the use of silane coated silica coupling agents resulted in melt viscosities of up to almost 50 times when compared formulations using uncoated silica fillers.

Adhesion of any encapsulant to a substrate is of critical importance for any molding compound. The adhesion of liquid crystal polymers to metallic substrates of the type used in the fabrication of electronic components is generally considered to be problematic as LCPs tend to be non-wetting materials. The non-wetting nature of LCPs can result in weak knit lines where melt fronts flow together and poor molecular contact with substrate materials. In Example 7, below, the adhesion of an LCP formulation including in accordance with the present invention was demonstrated.

Example 7

An LCP formulation was prepared from 47.5 weight percent of the resin used in Example 3, 50 weight percent of a 35 micron spherical silica filler equivalent to the filler used in Example 3, and 2.5 weight percent of a polysulfone adhesion promoter. The adhesion promoter was a polysulfone compound available from Amoco Chemical Company as Polysulfone P-1700 NT, CAS Number 25135-51-7. The adhesion of the molded formulation to a copper 194 alloy was measured by preparing lap shear strength test specimens. The test specimens with a one inch overlap. A 15 mil thick film of the LCP formulation was placed in the overlap within a metal fixture. The fixture was placed in a 330 degree Centigrade compression mold, allowed to heat, and pressurized to cause the melted formulation to flow slightly. The resulting 10 mil thick bond was allowed to cool to room temperature and tested in an Instron/MTS model 1122 tensile machine at a crosshead speed of 0.05 inches per minute. The lap shear strength measure in this manner was approximately 469 psi. The 469 psi value corresponds favorably to current low stress epoxy mold compounds which typically exhibit a lap shear strength to the same copper alloy of about 400 psi.

To demonstrate the effectiveness of LCP formulations in accordance with the present invention, an integrated circuit was molded, with wire sweep tested as described in Examples 8 and 9 below.

Example 8

A thin quad flat pack (TQFP) integrated circuit was prepared by molding an LCP formulation consisting of 45 weight percent of the resin used in Example 7, 50 weight percent of a 35 micron spherical silica filler equivalent to the filler used in Example 3, and 5 weight percent of the polysulfone adhesion promoter used in Example 7, around a TQFP die and leadframe assembly at about 300 degrees Centigrade. The TQFP wires connecting the die to the leadframe were 144, 100 mil long, 1.3 mil diameter gold lead wires. The molded device was examined by x-ray micrograph using a Nicolet NXR-300, and showed that the average wire sweep of the four worst wires was only about 5 percent.

Example 9

The experiment of Example 8 was repeated with a filler loading of approximately 70 weight percent. The x-ray micrograph showed severe wire sweep and in some cases, wire debonding from the die.

5 Example 8 demonstrates that complex devices such as a 144 lead TQFP can be successfully molded using LCP encapsulants in accordance with the present device at filler loadings of at least 50 weight percent. While the TQFP failed to mold successfully at 70 weight percent filler loading, it is believed that packages having fewer leads and or thicker wires, such as dual
10 in line packages (DIPs), can be successfully molded at filler loadings exceeding 50 weight percent.

The moisture resistance of the TQFP molded in Example 8 was measured in Example 10, below.

Example 10

15 The 144 lead TQFP of Example 8 was preconditioned at JEDEC Level 2 and exposed to 2 solder reflows at approximately 215 degrees Centigrade. Pre- and post reflow acoustic images were acquired using a Sonix scanning acoustic microscope. The acoustic images showed only slight evidence of increased delamination after solder reflow. This data suggests that at least
20 JEDEC Level 3 and most probably JEDEC Level 2 performance was possible from the TQFP package.

The physical robustness of the TQFP's of the type molded in Example 8 is demonstrated by Example 11, below.

Example 11

25 144 lead TQFP's of the type molded in Example 8 were decapped using nitric acid and microscopically examined at 400x magnification. The decapped devices showed no evidence of cracking in the passivation layer, no line/metalization shift, and no cracking of the wire bonds.

30 While the foregoing Examples demonstrate the excellent performance of a particular embodiment of my invention, the embodiments of the invention can utilize different LCP resins, coupling agents and fillers can be used. Other

electronic mold compound additives known to those skilled in the art can also be included.

Other resins useful in the invention include most polyester liquid crystal polymer resins having a number average molecular weight between about 5 1000 and 25,000 and melting points between about 230 and 500 degrees Centigrade. Those resins having number average molecular weights between about 1000 and 5000 and melting points between 250 and 350 degrees Centigrade are preferred. Most preferred are those resins containing three or more components selected from the group consisting of hydroquinone, 10 isophthalic acid, purified terephthalic acid, parahydroxybenzoic acid, and 4, 4' biphenyldiol. Preferred ranges for the foregoing components are 0-40 mole percent hydroquinone, 0-20 mole percent purified isophthalic acid, 0-40 mole percent purified terephthalic acid, 40-80 mole percent parahydroxybenzoic acid, and 0-40 mole percent 4, 4' biphenyldiol. Most preferred is a base 15 resin containing between 5 and 10 mole percent hydroquinone, 5 and 15 mole percent purified isophthalic acid, 5 and 15 mole percent purified terephthalic acid, 50 and 70 mole percent parahydroxybenzoic acid, and 8 and 18 mole percent 4, 4' biphenyldiol.

Alternatives silane coupling agents useful in the invention include any 20 non-polar silane coupling agent. As used in this application, the term "silane coupling agent" refers to a silicone molecule substituted with a plurality of (typically 3) alkoxy groups and an additional non-alkoxy group. Where the non-alkoxy group contains a heteroatom-substituted group such as an amine or a mercapto group, or contains a functional group such as a glycidal ether 25 group, that coupling agent is called a "polar" silane coupling agent, including for example 3-aminopropyltriethoxysilane and 3-glycidyloxypropyltrimethoxysilane, and where the non-alkoxy group is alkyl, alkenyl, aryl or combinations thereof, that coupling agent is called a "non-polar" silane coupling agent. Although the preferred coupling agent 30 concentration is 0.5 weight percent based on filler weight, the coupling agents can be used in any amount that can be carried successfully by the filler,

typically from 0.1 to 2.0 weight percent, based on filler weight, and most preferably 0.25 to 0.75 weight percent.

Fillers useful in the invention include any particulate inorganic material, and can be present in loadings of 10 to 80 weight percent, more preferably 5 30 to 70 weight percent, and most preferably 40 to 60 weight percent. While the fillers used typically will be angular or spherical silicon dioxide, other fillers may be used. For example, where improved filler heat transfer is desired, fillers such as boron nitride, silica coated aluminum nitride, or carbon fiber may be used. It should be noted that the use of spherical silica fillers is 10 preferred for use in LCP-based encapsulants according to the invention as the spherical shape maximizes the volume to surface area ratio of the filler and results in smaller increases in viscosity than result from similarly sized angular fillers at equivalent filler loadings.

Additives useful in the LCP formulations of the invention include any of 15 those known to those skilled in the art. These include, for example, silicon rubbers, dyes, mold release agents, pigments, antioxidants, adhesion promoters, flow promoters, impact modifiers and heat stabilizers. Where adhesion promoters such as those used in Example 7 are employed they may be added in an amount between about 0.05 and 10 weight percent of 20 the formulation, with the preferred range being from 0.25 to 5 weight percent. Other adhesion promoters thought to be particularly useful in the invention in addition to polysulfone materials include poly(bisphenol-A-co-epichlorohydrins) having average molecular weights between about 1000 and 70,000.

25 Additional details of LCP resins useful in the invention can be found in U.S. Patent No. 5,767,223, the disclosure of which is hereby incorporated by reference.

Other embodiments of my invention will be apparent to those skilled in the art. The scope of my invention, therefore, is intended to be limited only 30 by the following claims.

I claim:

1. A molding compound comprising a liquid crystal polymer resin and between 10 and 80 weight percent of a particulate inorganic filler coated with a non-polar silane coupling agent.
- 5 2. The molding compound of Claim 1 wherein the liquid crystal polymer has a number average molecular weight between about 1000 and 5000 and a melting point between about 250 and 350 degrees Centigrade.
3. The molding compound of Claim 1 where in the liquid crystal polymer resin three or more components selected from the group consisting
10 of hydroquinone, isophthalic acid, purified terephthalic acid, parahydroxybenzoic acid, and 4, 4' biphenyldiol.
4. The molding compound of Claim 1 wherein the liquid crystal polymer comprises between 5 and 10 mole percent hydroquinone, 5 and 15 mole percent purified isophthalic acid, 5 and 15 mole percent purified
15 terephthalic acid, 50 and 70 mole percent parahydroxybenzoic acid, and 8 and 18 mole percent 4, 4' biphenyldiol.
5. The molding compound of Claim 1 wherein the filler is selected from the group consisting of spherical or angular silica filler.
6. The molding compound of Claim 5 wherein the filler comprises
20 between 30 and 70 weight percent of the molding compound.
7. The molding compound of Claim 1 wherein the non-polar silane coupling agent is selected from the group consisting of trimethoxymethylsilanes and tri(2-methoxyethoxy) vinylsilane.
8. The molding compound of Claim 1 wherein the non-polar silane
25 coupling agent is tri(2-methoxyethoxy) vinylsilane.
9. The molding compound of Claim 1 wherein the liquid crystal polymer comprises between about 7 mole percent hydroquinone, about 10 mole percent purified isophthalic acid, about 10 mole percent purified terephthalic acid, about 60 mole percent parahydroxybenzoic acid, and about
30 13 mole percent 4, 4' biphenyldiol.

10. The molding compound of Claim 9 wherein the filler comprises between 45 and 55 weight percent of the molding compound.

11. The molding compound of Claim 4 wherein the filler comprises between 40 and 60 weight percent of the molding compound.

5 12. The molding compound of Claim 11 wherein the non-polar silane coupling agent is selected from the group consisting of trimethoxymethylsilanes and tri(2-methoxyethoxy) vinylsilane.

13. The molding compound of Claim 12 wherein the non-polar silane coupling agent is tri(2-methoxyethoxy) vinylsilane.

10 14. The molding compound of Claim 9 wherein the non-polar silane coupling agent is tri(2-methoxyethoxy) vinylsilane.

15. The molding compound of Claim 9 wherein the filler comprises between about 40 and 60 weight percent of the molding compound.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/15095

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09K19/00 C08K9/06

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)
 IPC 7 C09K C08K

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | DATABASE WPI Section Ch, Week 199348 Derwent Publications Ltd., London, GB; Class A23, AN 1993-383233 XP002119965 & JP 05 287177 A (POLYPLASTICS KK), 2 November 1993 (1993-11-02) abstract --- | 1,5,6 |
| A | EP 0 273 646 A (POLYPLASTICS CO) 6 July 1988 (1988-07-06) claims 1-4 --- | 1-15 |
| A | EP 0 353 933 A (POLYPLASTICS CO) 7 February 1990 (1990-02-07) examples 1-3 page 8, line 25 - line 36 --- -/-- | 1-15 |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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 Fax: (+31-70) 340-3016

Authorized officer

Siemens, T

INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|---|-----------------------|
| A | EP 0 779 338 A (TORAY INDUSTRIES) 18 June 1997 (1997-06-18) page 6, line 39 - line 48 claim 1 ----- | 1-15 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/15095

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|------------------|--|--|
| JP 5287177 A | 02-11-1993 | NONE | |
| EP 0273646 A | 06-07-1988 | JP 7025996 B JP 63162753 A DE 3780435 A US 4861515 A | 22-03-1995 06-07-1988 20-08-1992 29-08-1989 |
| EP 0353933 A | 07-02-1990 | AT 127269 T DE 68924019 D DE 68924019 T HK 179195 A JP 2167362 A US 5110861 A | 15-09-1995 05-10-1995 18-04-1996 01-12-1995 27-06-1990 05-05-1992 |
| EP 0779338 A | 18-06-1997 | CA 2192921 A JP 9221582 A JP 9302203 A JP 10030052 A US 5804634 A | 16-06-1997 26-08-1997 25-11-1997 03-02-1998 08-09-1998 |