(57) Cette invention concerne des polymères thermorégressables capables de supporter des températures élevées et destinés à des applications composites et adhésives. L’invention se rapporte en outre à des inhibiteurs permettant d’allonger le délai d’utilisation, le temps de gélification et d’augmenter la stabilité de conservation. Ces polymères conviennent parfaitement en tant qu’adhésifs et pour les moules par transfert de résine (RTM), pour le trempage de films de résine en milieu à température élevée, ainsi que pour des procédés de moulage de pré-imbriqués en vue de la fabrication de pièces composites renforcées par des fibres, à matrice de polymère.

(57) Thermosetting polymers with high temperature capability for composite and adhesive applications are disclosed. Inhibitors for improving pot life, gel time and storage stability are disclosed. These polymers are ideally suited for adhesives and RTM, resin film infusion, and prepreg methods to make polymer matrix, fiber reinforced composite parts.
(51) International Patent Classification : C08G 73/12

(11) International Publication Number: WO 97/18255

(43) International Publication Date: 22 May 1997 (22.05.97)

(21) International Application Number: PCT/US96/17501

(22) International Filing Date: 30 October 1996 (30.10.96)

(30) Priority Data: 60/006,447 13 November 1995 (13.11.95) US


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(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: THERMOSETTING POLYMERS FOR COMPOSITE AND ADHESIVE APPLICATIONS

(57) Abstract

Thermosetting polymers with high temperature capability for composite and adhesive applications are disclosed. Inhibitors for improving pot life, gel time and storage stability are disclosed. These polymers are ideally suited for adhesives and RTM, resin film infusion, and prepreg methods to make polymer matrix, fiber reinforced composite parts.
INHIBITORS FOR IMPROVING POT LIFE, GEL TIME AND
STORAGE STABILITY OF THERMOSETTING POLYMERS

This application claims priority from United States Provisional Application Serial No. 60/006,447 (filed November 13, 1995), which is incorporated by reference herein as if fully set forth.

Technical Field

This invention relates to the use of inhibitors for improving pot life, gel time and storage stability of bismaleimide resins. Such resins are suitable for resin transfer molding (RTM), adhesives, resin film infusion, and prepreg methods to make polymer matrix, and fiber reinforced composite parts for high temperature applications.

Background of the Invention

In a mixture in which solid bismaleimide reactants and liquid co-reactants are mixed, one problem often encountered by the application of heat is the imposition of thermal history on the subject resin and increasing viscosity, which is usually undesirable for composite and adhesive applications. Thermal history refers to the heat that is applied during processing to make the resin mixture. The resin mixture is the form of the product that contains all the reactants before the hardening that forms the final product. The resin mixture can then be applied to fibers to become prepreg which is then molded to form the final part. The resin mixture can also be used as an adhesive as is, or the resin mixture can be used as is for resin transfer molding and resin film infusion composite applications.

The effect of thermal history is usually undesirable, but inevitable during melt processing. The subject resin mixture can be melt processed by two methods, a completely homogeneous resin system or slurry mixing. The preparation of homogeneous resin requires higher temperature than slurry mixing, and therefore, more thermal history in the mixing to dissolve all the bismaleimide powder.

Another undesirable problem of the prepregs or the bismaleimide resin mixture is its instability during storage. During storage the resin mixture can continue to chemically change which manifests itself in continually shortening gel time, continually reducing pot life and reduced prepreg and adhesive tack. This is especially undesirable because the processing conditions to make the final product from the resin mixture will require adjustment to account for the changed reactivity.

As a result, there is a need in this technical area to control the advancement and chemical reactivity of the resin mixture during manufacturing, storage, and final part
processing such that the subject resin mixture can be inhibited from polymerization until the cure cycle.
Summary of the Invention

It has been surprisingly discovered that prepgs, adhesives and resin mixtures can be effectively inhibited in manufacturing and storage for the prevention of premature polymerization. In addition, since the cure cycle of the resin mixture is usually fixed, an adequate gel time is crucial and the inhibitors lengthen the gel time. In another example the resin mixture may contain solid bismaleimide resin components. Melting and dissolving must precede polymerization in these resin mixtures. An adequate gel time will ensure the subject resin mixture will attain optimized cured properties in accordance with its designed stoichiometry.

Specifically, this invention is directed to a thermosetable, curable, resin composition comprising one or more bismaleimide resins, a liquid olefinic co-reactant containing at least one aromatic ring, and inhibitors selected from the group consisting of free radical inhibitors that is useful for high temperature composite and adhesive applications.

This invention is further directed to a thermosetable, curable, resin composition comprising one or more bismaleimide resins, a liquid olefinic co-reactant containing at least one aromatic ring, and inhibitors selected from the group consisting of free radical inhibitors in which the composition after curing has a decreased weight loss upon thermal aging.

Description of the Preferred Embodiments

The process of the subject invention involves the combination of one or more solid bismaleimide monomers with the other resin system components. This invention is directed to the use of inhibitors as one such component.

In this application, "the solid bismaleimide monomers" may alternatively be described as a specific bismaleimide component, a solid reactant and/or solid aromatic diamine bismaleimide resin reactant.

The "liquid co-reactant" may be described to include a liquid olefinic species with at least one olefinic group and at least one aromatic ring.

The term "resin mixture" as used herein refers to a heat-curable resin composition in its final form. The composition may contain one or more reactive monomers and/or comonomers, inhibitors, curing agents, any necessary catalysts, and optionally filler, rheology control agents, tackifiers, tougheners, diluents, dyes, and pigments, but exclusive of fiber reinforcement.

The use of slurry mixing in the preparation of bismaleimide resin systems containing incompatible components is but one mode of practicing the subject invention.
See U.S. Patent No. 5,003,018. Slurry mixing is merely an aid in preparing the resin of the invention. Slurry mixing is important when large quantities of crystalline bismaleimides are contained in the resin formulation, as such formulations, when prepared by fully dissolving, are frequently very difficult to process. The slurry mixing process has been found to be useful whether or not the overall resin system components are compatible.

It should be noted that slurry mixing is not required for good resistance to oxidation. Good resistance to oxidation is a function of the monomers, not the process of preparation. However, for prepreg and adhesive applications, the invention will most likely be practiced using slurry mixing.

The resin system, upon cooling, will generally not show the presence of large or substantial amounts of crystals. In some cases, the resin system may have the appearance of a solid solution or glass. Yet despite the uniform appearance, these uncured resin systems frequently possess virtually no tack, and often are highly brittle. Surprisingly, when the same components are slurry mixed, the resulting resin system has excellent tack and drape.

The term "decreased weight loss" as used herein relates to a comparison of the weight loss of cured composites after the composites have been heat treated. Thermal aging is used to determine the effect of the resin and the composite materials after dormant treatment with heat over a period of time in air. It is expected that a certain component of the resin and composite will be oxidized during the aging process. Correlation can be made in the stability of a particular composite structure by comparing the weight loss from the composite structure after thermal aging. Generally, thermal aging takes place over a period of time at a particular temperature. For purposes of this invention, the time for such aging may range from one day to several years. For test purposes, the time of thermal aging used was from three weeks to nine weeks. For purposes of this invention, the temperature in which the thermal aging was evaluated ranges from about 200°C to 300°C, with a preferred temperature ranging from 220°C to 280°C. These times and temperatures are used for an accelerated evaluation of composite.

The claimed heat-curable resin systems of the subject invention contain (excluding inorganic fillers, fibers and non-bismaleimide and co-reactant resin materials) from between about 20 to 90 percent by weight of one or more solid bismaleimide reactants. Preferably, the solid bismaleimide reactants are present from between about 40 to 80 percent by weight of the total resin composition. The claimed heat-
The curable system also contains from between about 10 to 80 percent by weight of one or more co-reactants (excluding inorganic fillers, fibers and bismaleimide and non-coreactant resin materials). Preferably, the liquid co-reactants are present from between about 20 to 60 percent by weight of the reactive components in the composition upon curing. The weight ratio of solid bismaleimide resin reactant to the liquid co-reactants ranges from about 80:20 to about 20:80. Also, the bismaleimide resin reactant and the olefinic co-reactant together comprise greater than 50 percent total weight of the reactive components in the composition. Preferably, the bismaleimide reactant and the liquid co-reactant have a high amount of aromatic groups. Bismaleimide of certain structures have unexpectedly been found to have significantly improved oxidative stability.

A number of suitable bismaleimide monomers exist. The common feature for this monomer is that it must be highly aromatic and preferably have more than one aromatic group. Groups connecting to the aromatic ring can be methylene, isopropylidene, oxygen, ketone sulfone or sulfide. Such bismaleimides when used in the invention have been found to have markedly improved oxidative stability as a result of thermal aging in air. Pendant aliphatic groups are detrimental, for example, methyl, ethyl, n-propyl, i-propyl and the like. However, the presence of methylene groups in the solid reactant tends to increase stability of the aromatic nucleus against oxidation. For the purpose of this invention, methylene dianiline bismaleimide (MDA-BMI) is preferred. Other preferred solid bismaleimide reactants of this invention include, but are not limited to, bis(aminophenoxypyphenyl)propane bismaleimides (BAPP-BMI), oxydianiline bismaleimide (ODA-BMI), bis(aminophenoxypybenzene bismaleimides (APB-BMI), diaminodiphenylsulfone bismaleimides (DADS-BMI), diaminodiphenylisopropylidine bismaleimides, diaminodiphenylketone bismaleimides, diaminodiphenyl sulfide bismaleimides, diaminodiphenylhexafluoroisopropylidine bismaleimides, bis(diaminodiphenylisopropylidine)benzene bismaleimides, and the like. Certain eutectic mixtures of BMI monomers containing methylene dianiline bismaleimide (MDA-BMI), toluene dianiline bismaleimide (TDA-BMI) and trimethylenehexamethylenediamine bismaleimide, and the like can also be used in the formulation of the present invention.

Wholly aliphatic bismaleimides, for example, hexamethylenediamine-bismaleimides can be used in small amounts to increase tack as long as the thermal aging properties are still acceptable.

Bismaleimide monomers are well known to those skilled in the art, and are generally prepared by the reaction of maleic anhydride, or substituted maleic anhydride, with a suitable diamine. Both aromatic and aliphatic diamines are suitable for the
preparation of the bismaleimide. Suitable diamines for the preparation of bismaleimides also include aromatic diamines such as phenylenediamine, dianinodiphenylsulfones, dianinodiphenylisopropylidenes, dianinodiphenylketones, dianinodiphenylooxides and dianinodiphenylsulfides and the like.

Bismaleimides derived from diamines containing heteroatoms and oligomers are also useful, for example those derived from amino terminated polyethersulfones, polyetherketones, polyetherketoneketones, polyetheretherketones and similar oligomers as prepared in accordance with U.S. Patent No. 4,175,175, as well as amino terminated polyoxyalkylene polyethers, amino terminated N,N-dialkyldiperidines, and the like.

Also useful are polyaminobismaleimide prepolymer which may be prepared through the reaction of a stoichiometric excess of one or more bismaleimides with a di- or polyamine. Such polyaminobismaleimides or related products may also be prepared in situ by including in the resin system one of the aforementioned diamines, preferably one of the dianinodiphenylsulfones.

The resin system of the subject inventions may contain one or more comonomers. These comonomers may be comonomers which react with the bismaleimide monomers, or which react with themselves or with other comonomers or may be the same or a different bismaleimide resin. Other comonomers include, for example, those discussed in U.S. Pat. Nos. 4,100,140 and 4,035,345, which are incorporated herein by reference.

Allylnadicimide resins, epoxy resins, di- and polyamines, cyanate resins, acrylis, unsaturated polyester resins, and alkenylphenol-terminated oligomeric tougheners similar to those disclosed in European published application 230,741 are useful. Silicone rubbers may also be utilized as comonomers, particularly those terminated with maleimide, epoxy, vinyl and amino groups.

In addition to such comonomers, the resin systems of the subject invention may also include engineering thermoplastic tougheners, particularly polyimides, polyetherimides, polyetherketones, polyarylenesulfides, polyarylenesulfones, polyethersulfones, and the like. Such thermoplastic tougheners should have glass transition temperatures, Tg, in excess of about 100°C.

Suitable epoxy comonomer resins are disclosed in the treatise Handbook of Epoxy Resins, McGraw-Hill, Inc., 1967. Examples of such resins are the bisglycidyl ethers of the bisphenols, particularly bisphenol A, bisphenol F and bisphenol S. Also suitable are the various phenolic and cresolic novolac-type resins, as well as the various glycidoxy amines.
and aminophenols, particularly N,N,N',N'-tetraakis(glycidyl)-4,4'-diaminodiphenylmethane and N,N,O-tris(glycidyl)-4-aminophenol. Epoxy resin based on
the glycidyl ethers of the various dihydroxynaphthalenes and phenolated dicyclopentadienes are also suitable.

Cyanate functional comonomers are also useful. Such monomers are prepared by the reaction of cyanogen chloride or bromide with a diol or polyol. Examples of suitable diols include the bisphenols, the tetramethylbisphenols, other cyanates commercially available and in the literature, resorcinol, the hydroxyalkcyanurates and isocyanurates and the like. Such cyanate systems are well known to those skilled in the art, and are commercially available from a number of sources. Their preparation is also well known, and may be accomplished by the methods proposed in U.S. Pat. No. 4,546,131. Cyanate resins might need a catalyst.

The resin systems of this invention may also include other components, some of which may also affect the compatibility of the bismaleimide monomers. Catalysts are generally present, for example, in amounts of from 0.01 percent to about 5.0 percent by weight. Preferred catalysts include triphenylphosphine, the various tertiary amines, imidazoles, or diamines. The comonomers may require a catalyst for their polymerization when cured at lower temperatures. The system may also contain various dyes, pigments, fillers and rheology control agents. These additional components are well known to those skilled in the art.

Most of the resin mixtures described herein can be made by solution methods, and solution processing of these resin mixtures would not add thermal history to the resin mixtures. Also, this invention is also useful to stabilize the resin system as well during storage.

This invention offers an effective method for controlling gel time, pot life and storage stability of the bismaleimide resin for high temperature use. One or more free radical inhibitors are used in this invention. The term "free radical inhibitors" as used herein refers to compounds that retard or stop an undesired chemical reaction, such as oxidation or polymerization. Examples are substituted quinones, hindered phenols, phenothiazines, substituted catechols, copper naphthenate, zinc-dimethyldithiocarbamate. Preferably, free radical inhibitors in this invention are provided as 1 ppm to 5% w/w concentration of hydroquinone (HQ), 1 ppm to 5% w/w 1,4-naphthoquinone (NQ), copper naphthenate (8% w/w Cu Nap All), and tert-butyl hydroquinone (MTBHQ) at 0.05% (w/w) or more.

The liquid co-reactant of this invention is an olefinic species containing at least one olefinic group and at least one aromatic ring. Generally, for high temperature use, it
is preferred to have a high ratio of aromatic moieties to other groups. The liquid co-
reactant can be monofunctional or bi-functional. Examples of preferable bi-functional
liquid co-reactants include, but are not limited to 4,4'-bis[O-(1-propenyl)-
phenoxy]benzophenone ("PPB") and 2,6-bis[O-(1-propenyl)phenoxy]pyridine ("PPP")

Monofunctional co-reactants having only one alkenyl group are also a part of the preferred
embodiment. Such substances in general, have lower molecular weight compared to
substances with two alkenyl groups, and hence, lower viscosity which will impart prepreg
tack. The monofunctional co-reactants can also have a high ratio of aromatic to aliphatic
groups, thus do not reduce oxidative stability. It is generally preferable to have primarily a
bi-functional curing agent because monofunctional curing agents tend to reduce the
bonding in the molecular network and can reduce Tg. An example of a monofunctional
modifier is (3-allyl-2-hydroxyphenyl)benzene.

Other co-reactant are the alkenylphenols and alkenyloxyphenyls. Suitable are, for
example, o,o'-diallyl- and o,o'-dipropenylbisphenols such as o,o'-diallyl- and o,o'-
dipropenylbisphenol A, bisphenol F and/or bisphenol S. Also suitable are the
alkenyloxyphenol- and alkenyloxyphenyl terminated dicyclopentadienes. The latter are
prepared by first forming the phenolated dicyclopentadiene precursor as taught in U.S.
Pat. No. 3,536,734. The precursor is then reacted with the requisite alkenylhalide such as
allyl chloride or propenyl chloride in the presence of base to form the allyl or propenyl
ether. These ethers may be used as such or may be isomerized through Claisen
rearrangement to the ortho substituted phenol. Various other comonomers are described
in U.S. Pat. No. 5,003,018, which are incorporated herein by reference.

Prepregs were made from fibers at 145 g/m² AFW at 115°C for 2.1 m/min. The
cure cycle for all test panels was 45 min at 143°C followed by 4 hours at 191°C. Post
cure was performed for 6 hours at 227°C.

Gel time is a standard measure of resin reactivity and is well known to those skilled
in the art. The time required to gel up the liquid resin is defined a gel-time. The
measurement takes place at the temperatures and for the times that mimic the conditions
of actual use. The gel-time is measured in a test tube containing 10 grams of the subject
bismaleimide resin by a stirring rod at 149°C and 163 °C. An oil bath is prepared at the
temperature of the gel test. The test tube is immersed in the bath and the resin is probed
with a glass rod. The gel time is taken at the point where the resin has become a solid
mass, and no longer flows. Generally, for resin transfer molding applications, the longer
the gel time, or the longer the pot life, the better the system is for the application.
WHAT IS CLAIMED IS:

1. A thermosettable resin composition comprising:
   A. one or more bismaleimide resins;
   B. a liquid olefinic co-reactant containing at least one olefinic group and at least one aromatic ring; and
   C. one or more free radical inhibitors,
   wherein the mixture before curing has improved room temperature storage stability.

2. The composition of claim 1, wherein said bismaleimide resin is selected from the group consisting of methylenedianiline bismaleimides, 1,1-bis(aminophenyl)ethane bismaleimides, bis(aminophenoxyphenyl)isopropylidene bismaleimides, oxydianiline bismaleimides, bis(aminophenoxy)benzene bismaleimides, diaminodiphenylsulfone bismaleimides, diaminodiphenylsulfoxide bismaleimides, bis(aminophenyl)isopropylidine bismaleimides, diaminodiphenylketone bismaleimides, diaminodiphenyl sulfide bismaleimides, bis(aminophenyl)hexafluoroisopropylidine bismaleimides and bis(2-[aminophenyl]isopropyl)benzene bismaleimides.

3. The composition of claim 2, wherein said bismaleimide resin is a methylenedianiline bismaleimide.

4. The composition of claim 1, wherein said liquid alkenylphenyl resin is selected from the group consisting of bis(alkenylphenoxy)benzophenones, bis(alkenylphenoxy)pyridines, and alkenylphenylphenols.

5. The composition of claim 4, wherein said liquid alkenylphenyl resin is selected from the group consisting of 4, 4'-bis [O-(1-propenyl)-phenoxy]benzophenone ("PPB"), 2,6-bis[O-(1-propenyl)phenoxy]pyridine ("PPP") and 3-allyl-2-hydroxyphenylbenzene.

6. The composition of claim 5, wherein said liquid alkenylphenyl resin is 4, 4'-bis [O-(1-propenyl)-phenoxy]benzophenone ("PPB").

7. The composition of claim 1, wherein the inhibitor is selected from the group consisting of substituted quinones, napthoquinone hindered phenols, phenothiazines, substituted catechols, copper naphthenate, and zinc-dimethylthiocarbamate.

8. The composition of claim 7, wherein the inhibitor is selected from the group
consisting of hydroquinone, 1,4-naphthoquinone, copper naphthenate, and tert-butyl hydroquinone.

9. The composition of claim 8, wherein the inhibitor is selected from the group consisting of 1,4-naphthoquinone and copper naphthenate.

10. The composition of claim 9, wherein the inhibitor is 1,4-naphthoquinone.

11. The composition of claim 1, wherein
   A. said bismaleimide resin is selected from the group consisting of methylenedianiline bismaleimides, 1,1-bis(aminophenyl)ethane bismaleimides, bis(aminophenoxyphenyl)isopropylidene bismaleimides, oxydianiline bismaleimides, bis(aminophenoxy)benzene bismaleimides, dianimidophenylsulfone bismaleimides, dianimidophenylsulfoxide bismaleimides, bis(aminophenyl)isopropylidine bismaleimides, dianimdophenylketone bismaleimides, dianimidophenyl sulfide bismaleimides, bis(aminophenyl)hexafluoroisopropylidine bismaleimides and bis(2-[aminophenyl]isopropyl)benzene bismaleimides;
   B. said liquid alkenylphenyl resin is selected from the group consisting of bis(alkenylphenoxy)benzophenones, bis(alkenylphenoxy)pyridines, and alkenylphenylphenols; and
   C. said inhibitor is selected from the group consisting of substituted quinones, hindered phenols, naphthoquinone phenothiazines, substituted catechols, copper naphthenate, and zinc-dimethylidithiocarbamate.

12. The composition of claim 11, wherein said liquid alkenylphenyl resins is selected from the group consisting of 4,4'-bis(O-(1-propenyl)-phenoxy)benzophenone ("PPB"), 2,6-bis[O-(1-propenyl)phenoxy]pyridine ("PPP") and 3-allyl-2-hydroxyphenylbenzene.

13. The composition of claim 11, wherein said inhibitor is selected from the group consisting of hydroquinone, 1,4-naphthoquinone, copper naphthenate, and tert-butyl hydroquinone.

14. The composition of claim 11, wherein
   A. said bismaleimide resin is a methylenedianiline bismaleimide;
   B. said liquid alkenylphenyl resin is 4,4'-bis[O-(1-propenyl)-phenoxy]benzophenone ("PPB");
   C. said inhibitor is selected from the group consisting of hydroquinone, 1,
4-naphthoquinone, copper naphthenate, and tert-butyl hydroquinone.

15. The composition of claim 14, wherein said inhibitor is selected from the group consisting of 1, 4-naphthoquinone and copper naphthenate.

16. The composition of any of claims 1 to 15, further comprising one or more of the following:
   A. one or more comonomers;
   B. one or more catalysts;
   C. one or more silicone rubbers; and
   D. one or more engineering thermoplastics.

17. The composition of any of claims 1 to 15, wherein said improved room temperature storage stability is characterized by gel time measured in minutes at 163 °C immediately upon preparation of the composition, and again at 163 °C at 35 days post-preparation; wherein the gel time at 35 days post-preparation is no more than about 6 minutes less than the initial gel time.

18. A prepreg made from impregnating fibrous material with the thermosettable resin composition of any of claims 1 to 15.

19. The use of the thermosettable resin composition of any of claims 1 to 15 as an adhesive.

20. The use of the thermosettable resin composition of any of claims 1 to 15 in resin transfer molding.

21. The use of the thermosettable resin composition of any of claims 1 to 15 in resin film infusion.

22. The use of the thermosettable resin composition of any of claims 1 to 15 in composite parts.

23. The use of the thermosettable resin composition of any of claims 1 to 15 in adhesive bonded structures.