RESIN COMPOSITIONS WITH HIGH THERMOPLASTIC LOADING

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Uncured thermosetting resins are loaded with relatively high amounts of solid thermoplastic resin particles to form a resin precursor. The resin precursor is heat treated so as to produce an uncured resin composition wherein the thermoplastic resin particles become substantially dissolved in the thermosetting resin without causing cure of the resin mixture. Heat treatment of highly loaded thermosetting resins in accordance with the present invention provides uncured resin compositions that are well suited for use in fabricating composite structures and particularly prepreg for use in lightning protection surface coatings.
RESIN COMPOSITIONS WITH HIGH THERMOPLASTIC LOADING

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

The present invention relates generally to thermosetting resin compositions that include varying amounts of one or more thermoplastic resins, which provide elastomeric toughening of the resin. More particularly, the present invention involves compositions and methods wherein the amount of thermoplastic resin in uncured thermosetting resin compositions is maximized to provide desired levels of resin toughening. These relatively high levels of thermoplastic loading are achieved without increasing the viscosity and/or tack of the uncured composition to levels that would render them unsuitable for handling and processing.

[0002] 2. Description of Related Art

Thermosetting resins are popular materials that are used in the fabrication of a wide variety of composite materials. Epoxy resins, bismaleimide resins and cyanate ester resins are examples of popular thermosetting resins. Composite materials typically include one or more resins that are combined with fibers or other support materials to form relatively lightweight structures that are relatively strong. In addition to their wide spread use as a matrix material in composites, thermosetting resins have also been used to provide a surface layer or finish coating on the exterior surface of composite materials. Composite materials and surface coatings or layers that utilize thermosetting resins have been widely used in the aerospace industry where their combination of lightweight and structural strength is particularly desirable.

[0005] In many situations it is desirable to modify thermosetting resins by adding one or more thermoplastic resins to the thermosetting resin mix. The use of thermoplastic resins provides an additional degree of flexibility or elasticity to the thermosetting resin which increases the toughness of the final cured resin product. Such thermoplastic toughened resins have been used both as resin matrix materials in combination with fibers and as coatings where a particularly tough resin is desired. Typical thermoplastic resins that have been used as toughening agents include polyethersulfone, polyetherimide and certain types of nylon and other thermoplastic polymers that can be dissolved in the thermosetting resin prior to ultimate cross-linking and cure.

[0006] In general, the degree of elastomeric toughening provided by the thermoplastic resin is related directly to the amount of thermoplastic resin that is incorporated into the thermosetting resin mixture. Accordingly, it is desirable in many situations to add as much thermoplastic resin as possible to achieve maximum toughening of the final cured resin. High thermoplastic loading is particularly desirable for thermosetting resins that are used as surface coatings on aircraft structures where extremely smooth and strong surfaces are desired in order to enhance the aerodynamics and appearance of the structure.

[0007] The amount of thermoplastic resins that can be added to thermosetting resin mixtures is limited by a number of practical considerations relating to processing of the uncured resin. For example, the viscosity of the uncured toughened resin must be kept low enough that the resin can be fabricated into thin films and/or used to impregnate or coat various materials. In addition, the tack of the resin must also be kept within certain limits that vary depending upon the particular fabrication process. For example, the resin cannot be fabricated into films or handled during fabrication of multi-component structures if the uncured resin is too tacky. High viscosity and high tack is a particular problem when uncured toughened resins are used in the fabrication of surface coatings. High viscosity and high tack cause handling problems that lead to surface imperfections that have a deleterious effect on appearance and may an adverse effect on aerodynamics. As a result, the amount of thermoplastic resin that is loaded into thermosetting resins for use in surface coatings is typically below 25 weight percent.

[0008] The thermosetting and thermoplastic resins that are used to make composite materials do not conduct electricity. The most common fibers used in composite materials (such as glass, ceramics and graphite) are not good conductors of electricity. This is a particular problem for aircraft because they operate in an environment where they may be exposed to lightning. It is well known that a lightning strike on an aircraft that includes substantial amounts of composite material may result in catastrophic failure of the aircraft. In order to protect against such catastrophic events, the composite material used in many aircraft are modified to include "lightning protection". Lightning protection typically involves adding one or more layers of conductive material to the composite materials used to make the aircraft. The conductive layers are generally located on or near the exterior surfaces of the composite portions of the aircraft. The conductive materials used for lightning protection are usually thin films of metal (or other conductive material) or metallic mesh or fabric that is relatively lightweight.

[0009] There are many different ways to add lightning protection to the surface of a composite structure. A common procedure involves preparing a "prepreg" that is lightning protected and incorporating the prepreg into the surface of the composite structure. "Prepreg" is a term used in the composite industry to describe a composite precursor wherein one or more layers of fabric have been impregnated with uncured resin. The resulting pre-impregnated structure is typically stored for later use in fabricating the final cured composite structure. The preparation and use of prepregs is particularly desirable in the fabrication of aircraft and other critical structures because it allows the manufacturer to carefully control the amount of resin that is combined with a given amount of fabric. As a result, the final properties of the cured composite structure can be carefully controlled. Prepreg that is suitable for use as a lightning protection surface coating will typically include an electrically conductive layer located between a layer of surface finish resin and a supporting layer of fabric that has been pre-impregnated with resin. Examples of lightning protection prepreg and composites are set forth in the following U.S. Pat. Nos. 5,225,265; 5,470,413; 5,370,921 and 5,397,618.

[0010] Prepregs that are intended for use in providing lightning protection for composite structures should have certain desirable characteristics. The prepreg should be as light as possible to avoid adding unnecessary weight to the aircraft. The prepreg should be compatible with the underlying prepregs or other pre-cure composite materials used to make the final composite structure. The prepreg should also
be relatively easily to handle and the surface finish provided by the cured prepreg should be relatively free of surface flaw or imperfections.

SUMMARY OF THE INVENTION

[0011] In accordance with the present invention, methods and compositions are provided wherein un cured thermosetting resins are initially loaded with relatively high amounts of solid thermoplastic resin particles to form resin precursors. These resin precursors are then heat treated so as to produce uncured resin compositions wherein the thermoplastic resin particles become substantially dissolved in the thermosetting resin without causing cure of the resin mixture. It was discovered that the heat treatment of highly loaded thermosetting resins in accordance with the present invention provides uncured resin compositions that are well suited for use in fabricating composite structures and particularly prepreg for use in lightning protection surface coatings.

[0012] The uncured resin compositions of the present invention include a thermosetting resin component that is made up of one or more thermosetting resins, a curing agent for the thermosetting resin(s) and a thermoplastic resin component that includes one or more thermoplastic resins. The thermoplastic resin component is combined with the thermosetting resin component by adding the thermoplastic resin(s) to the thermosetting resin(s) to form an uncured resin precursor. As a feature of the present invention, at least one of the thermoplastic resins is initially in the form of thermoplastic resin particles that are substantially dissolved in the thermosetting resin by heating the resin precursor for a sufficient time to dissolve the particles without causing curing of the resin precursor. The resulting uncured resin composition is highly loaded with thermoplastic resin while still retaining viscosity and tack properties that are appropriate for use in manufacturing prepreg and other composite materials.

[0013] The resin precursor may include thermoplastic resins that are only in particulate form or the precursor may include combinations of thermoplastic resin particles and thermoplastic resins that have been dissolved in the thermosetting resin. As a feature of the present invention, the viscosity and loading levels of the resin precursor can be controlled by varying the combinations of particulate and dissolved thermoplastic resins that are present in the resin precursor.

[0014] The uncured resin compositions in accordance with the present invention may be used in the fabrication of a wide variety of composite structures. The uncured resin compositions are well suited for use in fabricating surface finishes for composite structures where lightweight, high toughness and good surface finishes are required. The uncured compositions are particularly well suited for use in fabrication prepreg and other uncured composite structures that are used to form surface finishes that also provide lightning protection.

[0015] The above-described and many other features and attendant advantages of the present invention will become better understood by reference to the following detailed description when taken in conjunction with the accompanying drawings.
are added to the thermosetting resin and curing agent to form a resin precursor wherein at least one of the thermoplastic resins is in the form of thermoplastic resin particles. The resin precursor will have various initial properties, including viscosity, tack, and drape, heat of reaction and uncured glass transition temperature. The uncured resin composition is formed by heating the resin precursor to a dissolution temperature for a sufficient time to substantially dissolve all of the resin particles without curing the thermosetting resin(s). An important aspect of the present invention is that the heating times and dissolution temperatures be selected to provide an uncured resin composition where substantial dissolution of the thermoplastic resin particles has taken place without curing of the thermosetting resin(s).

[0025] Exemplary thermoplastic resins that are for dissolution in the initial resin precursor include thermoplastic polyetherimides such as ULTEM® 1000 P which is available from General Electric (Pittsfield, Mass.); microwaved polyethersulfone such as 5003 P, which is available from Sumitomo Chemical Co., Ltd. (Osaka, Japan); HRI-1, which is available from Hexcel Corp. (Dublin, Calif.); and polyimide MATRIMID® 9725 or 5218, which are available from Huntsman Inc. (Brewster, N.Y.). ULTEM® 1000 P and micronized PES are preferred. Micronized PES is especially preferred. Micronized PES refers to PES particles which have a rough surface configuration which is produced by grinding the particles or other abrasive techniques of manufacture which are known in the art. Micronized PES particles may also be made by spraying and drying procedures which are also known in the art. Micronized PES particles are preferably less than 120 microns in size. Specifically preferred are particles under 50 microns in size with a range of 10 to 25 microns being particularly preferred.

[0026] Densified polyethersulfone (PES) and densified polyetherimide resins may be used as suitable thermoplastic resins. Densified PES particles are preferred. The densified polyethersulfone (PES) particles are preferably made in accordance with the teachings of U.S. Pat. No. 4,945,154, the contents of which is hereby incorporated by reference. The average particle size of the PES particles range from 1 to 150 microns. Average particle sizes of 1 to 50 microns are preferred and average particle sizes of 10 to 25 microns are particularly preferred. It is preferred that the glass transition temperature (Tg) for the particles be above 200°C.

[0027] The amount and type of thermoplastic particles that are added to the epoxy resin mixture and the order in which they are added may be varied provided that the viscosity of the final resin precursor is between 20,000 and 100,000 poise when said viscosity is measured at 30°C. The preferred viscosity range is 30,000 to 90,000 poise. In a preferred embodiment, the micronized thermoplastic particles are added first and dissolved. Then, densified thermoplastic particles are added to form a resin precursor that includes both dissolved and particulate thermoplastic. As mentioned above, overall thermoplastic loading (dissolved and particulate) of the resin precursor should be between 20 and 60 weight percent. The viscosity of the heat-treated resin precursor increases substantially during the heat treatment process. The precise amount of increase in viscosity depends upon the particulars of the formulation.

[0028] In a preferred exemplary procedure, the uncured resin is made by first mixing the epoxy components together and then slowly adding the desired amount of micronized thermoplastic resin particles. Micronized polyetherimide or micronized PES particles are preferred. The resulting mixture is heated to around 130°C and mixed for a sufficient time to substantially dissolve the micronized thermoplastic particles. Once the micronized thermoplastic particles are dissolved, the mixture is cooled to around 75°C. A suitable aromatic amine curing agent and the desired amount of densified PES particles are then added to the mixture to form the resin precursor. The resin precursor should be kept at temperatures below about 70-75°C while the curative agent and densified PES particles are being mixed into the resin.

[0029] Once formed, the resin precursor may be impregnated into fabric/fibers to form prepreg, used to form films
or applied to any number of surfaces or structures. The resin precuror is then heated at the dissolution temperature for a sufficient time to dissolve the densified PES particles and form an uncured resin. Typical dissolution temperatures are from 110 to 140°C with dissolution temperatures of about 125°C being preferred. The heat treatment times will vary depending upon the dissolution temperature, particular thermoplastics and thermosets being used as well as the amount of particulate loading. The amount of time required to convert a specific resin precuror to the uncured resin can be determined by routine experimentation. In general, heat treatment times on the order of a few minutes up to 1 hour are sufficient. The final uncured resin, along with any fabric/fiber or other supporting component is then cooled to room temperature. The final uncured resin, whether it is in the form of a film or the resin matrix in a prepreg or as part of some other structure, can then be stored for later use. Alternatively, the uncured resin and associated components, if any, may be used immediately by applying the uncured resin to a desired structure, if necessary, and then curing the uncured resin in accordance with conventional curing procedures for thermosetting resins that are loaded with thermoplastic material.

Example 1

A resin precuror was made having the following formulation:

- 27.0 weight percent MY-0510 (N,N-Diglycidyl-4,4'-diglycidyloxyaniline)
- 24.9 weight percent GY285 (bis-F epoxy)
- 15.8 weight percent 3,3'-Diaminodiphenylsulfone
- 1.3 weight percent Dicyandiamide
- 13.5 weight percent micronized Polyethersulfone (PES)
- 17.5 weight percent densified Polyethersulfone (PES)

Precursor resin formulations in accordance with this example may also be made wherein the amounts of MY-510, GY281 and 3,3'-DDS are varied by up to ±15%. Also, the amounts of both types of PES may be varied by as much as ±40%. The amount of dicyandiamide may be varied by up to ±50%. The densified PES was made from PES 5003 P, which is available from Sumitomo Chemical Co. Ltd. (Osaka, Japan). The PES was densified in accordance with U.S. Pat. No. 4,945,154. Average particle size was 10-25 microns with no more than 13 weight percent smaller than 5 microns and no more than 4 weight percent greater than 40 microns.

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coater at about to form a film containing 245 gsm. The film was then heated for 3 minutes at 125° C. to form the uncured resin composition. During this time, the densified PES completely dissolved, resulting in an uncured resin film containing about 31 weight percent dissolved PES. This dissolution resulted in a color change from opaque white to translucent amber-brown. The tack was also substantially reduced to an essentially tack free state after the heat treatment and the viscosity increased substantially.

Example 2

[0043] The same combination of thermosetting resins and curing agents as set forth in Example 1 were used to make resin precursors that contained 25, 37.5 and 50 weight percent PES. The PES was added in the same manner as Example 1 except that the differences in overall PES loading was accounted for by varying the amount of densified PES that was added. The amount of micronized PES that was initially dissolved was kept constant at 13.5 weight percent. Films of resin precursor were made in the same manner as Example 1. The films were subjected to the same heat treatment step with the same dissolution process being observed. The resulting uncured resin films underwent the same color change from opaque white to translucent amber-brown. The tack of the uncured resin films was also substantially less than the resin precursor films and the final viscosity of the uncured resin films was substantially higher.

Example 3

[0044] A three layer uncured electrically conductive composite material as shown in the drawing was made as follows:

[0045] A resin precursor resin film 12 was prepared according to Example 1. The film 12 was combined with an expanded aluminum foil 14 and a prepreg 16 that was composed of 6080-glass fabric (48 gsm) and resin precursor (32 gsm) that was prepared as described in Example 1. The resulting lay-up 10 was heated for 5 minutes at 110° C. in order to substantially dissolve the PES particles without curing the 1-up. The resulting uncured electrically conductive composite structure 20 had substantially reduced tack.

[0046] The uncured composite structure 20 was applied as a surfacing layer to a number of composite structures that were each composed of 8 plies of unidirectional prepreg. The unidirectional prepreg contained unidirectional carbon fibers in an uncured epoxy resin matrix. The orientation of the unidirectional plies was -45, 90, 45 and 0. Upon final curing at 179° C. for 120 minutes, the uncured composite structure 20 was found to provide a good (i.e. smooth and defect free) surface finish. For comparison, lay-ups 10 that were not heat treated in accordance with the present invention were applied directly as a surfacing layer to the same composite structures and cured under the same conditions. The resulting surface finish was more pitted than the surface finish obtained using the heat-treated precursor resin film in accordance with the present invention.

[0047] Having thus described exemplary embodiments of the present invention, it should be noted that those skilled in the art that the within disclosures are exemplary only and that various other alternatives, adaptations and modifications may be made within the scope of the present invention. Accordingly, the present invention is not limited by the above-preferred embodiments, but is only limited by the following claims.

What is claimed is:

1. An uncured resin composition comprising:

   a thermosetting resin component comprising one or more thermosetting resins;

   a curing agent for said thermosetting resin component;

   and

   a thermoplastic resin component comprising one or more thermoplastic resins wherein said thermoplastic resin component is combined with said thermosetting resin component by adding said one or more thermoplastic resins to said one or more thermosetting resins to form a resin precursor wherein at least one of said thermoplastic resins is initially in the form of thermoplastic resin particles and wherein said resin precursor is heated to a sufficient temperature for a sufficient time to substantially dissolve said thermosetting resin particles without curing said thermosetting resin to thereby form said uncured resin composition.

2. An uncured resin composition according to claim 1 wherein said thermosetting resin component comprises one or more resins selected from the group consisting of epoxy, bismaleimide and cyanoate ester resins.

3. An uncured resin composition according to claim 1 wherein said resin particles comprise micronized or densified thermoplastic resins that have a glass transition temperature that is above 200° C.

4. An uncured resin composition according to claim 3 wherein said resin particles comprise thermoplastic resins selected from the group consisting of micronized polether-sulfone, densified polyether sulfone, micronized polyetherimide and densified polyetherimide.

5. An uncured resin composition according to claim 1 wherein said thermoplastic resin component comprises one or more of said thermoplastic resins that is substantially dissolved in said thermosetting resin prior to heating of said resin precursor.

6. An uncured resin composition according to claim 5 wherein said one or more thermoplastic resins that is substantially dissolved in said thermosetting resin prior to heating of said resin precursor comprises a thermoplastic resin selected from the group consisting of polyethersulfone, polyetherimide and polyimide.

7. A prepreg designed for application to a surface of a body to provide a surface finish for said body, said prepreg comprising:

   a) an outer finish layer consisting essentially of an uncured resin comprising a thermosetting resin component, a curing agent for said thermosetting resin component and a thermoplastic resin component comprising one or more thermoplastic resins wherein said thermoplastic resin component is combined with said thermosetting resin component by adding said one or more thermoplastic resins to said one or more thermosetting resins to form a resin precursor wherein at least one of said thermoplastic resins is initially in the form of thermoplastic resin particles and wherein said resin precursor is heated to a sufficient temperature for a sufficient time to substantially dissolve said thermo-
plastic resin particles without curing said thermosetting resin to thereby form said uncured resin composition; and

b) a fiber layer comprising a plurality of fibers that are impregnated with a matrix resin.

8. A prepreg according to claim 7 wherein a layer of electrically conducting material is located between said outer finish layer and said fiber layer.

9. A prepreg according to claim 8 wherein said electrically conducting material is in the form of a mesh.

10. A composite material comprising a prepreg according to claim 7 that has been heated at a sufficient temperature for a sufficient time to cure said uncured resin composition to form said composite material.

11. A method for forming a surface finish on a body comprising the steps of applying an uncured resin composition to the surface of said body and curing said uncured resin composition to form a surface finish on said body; said uncured resin composition comprising:

a thermosetting resin component comprising one or more thermosetting resins;

a curing agent for said thermosetting resin component; and

a thermoplastic resin component that comprises one or more thermoplastic resins wherein said thermoplastic resin component is combined with said thermosetting resin component by adding said one or more thermoplastic resins to said one or more thermosetting resins to form a resin precursor wherein at least one of said thermoplastic resins is initially in the form of thermoplastic resin particles and wherein said resin precursor is heated to a sufficient temperature for a sufficient time to substantially dissolve said thermoplastic resin particles without curing said thermosetting resin to thereby form said uncured resin composition.

12. A method for forming a surface finish on a body according to claim 11 wherein said thermosetting resin component comprises one or more resins selected from the group consisting of epoxy, bismaleimide and cyanate ester resins.

13. A method for forming a surface finish on a body according to claim 11 wherein said resin particles comprise micronized or densified thermoplastic resins that have a glass transition temperature that is above 200° C.

14. A method for forming a surface finish on a body according to claim 11 wherein said thermoplastic resin component comprises one or more of said thermoplastic resins that is substantially dissolved in said thermosetting resin prior to heating of said resin precursor.

15. A method for forming a surface finish on a body according to claim 11 which includes the additional step of making said surface finish electrically conductive by combining an electrically conducting material with said uncured resin composition.

16. A method for forming a surface finish on a body according to claim 12 wherein said electrically conducting material is a metal.

17. A method for forming a surface finish on a body according to claim 12 wherein said electrically conducting material is in the form of a mesh.

18. A method for forming a surface finish on a body according to claim 11 wherein said uncured resin composition is in the form of a prepreg.

19. A method for forming a surface finish on a body according to claim 18 wherein said prepreg comprises a layer of electrically conducting mesh that is located between an outer finish layer and a fiber layer wherein said electrically conducting mesh is impregnated with said uncured resin.

20. A method for forming a surface finish on a body according to claim 11 wherein said body is located on an aircraft.

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