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(54) MANUFACTURING METHOD FOR FIBRE-REINFORCED COMPOSITE MATERIAL, HEAT RESISTANT MATERIAL USING SAID COMPOSITE MATERIAL, AND HEAT RESISTANT STRUCTURAL MATERIAL USING SAID COMPOSITE MATERIAL

VERFAHREN ZUR HERSTELLUNG EINES FASERVERSTÄRKTEN VERBUNDSTOFFES, HITZEBESTÄNDIGES MATERIAL MIT DIESEM VERBUNDSTOFF UND HITZEBESTÄNDIGES BAUMATERIAL MIT DIESEM VERBUNDSTOFF

PROCÉDÉ DE FABRICATION D'UN MATÉRIAU COMPOSITE RENFORCÉ PAR DES FIBRES, MATÉRIAU RÉSISTANT À LA CHALEUR UTILISANT LEDIT MATÉRIAU COMPOSITE ET MATÉRIAU STRUCTURAL RÉSISTANT À LA CHALEUR UTILISANT LEDIT MATÉRIAU COMPOSITE

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Description

Technical Field

[0001] The present invention relates to a method for producing a fiber-reinforced composite material. In particular, the invention relates to a method for producing a fiber-reinforced composite material that is suitable for use as a heat-resistant mold material or a heat-resistant structural material, as well as heat-resistant mold materials and heat-resistant structural materials obtained by the method.

Background Art

[0002] One molding method for fiber-reinforced composite materials is a method using a prepreg obtained by impregnating a matrix resin, composed mainly of a thermosetting resin, into reinforcing fibers, and it is employed in a wide range of uses from sports leisure applications to aircraft applications. Molding of a fiber-reinforced composite material using an intermediate base material comprising the aforementioned prepreg is carried out by laminating the prepreg, and then subjecting it to heating or to heating and pressing to cure the thermosetting resin as the matrix resin.

[0003] Prepregs can be classified into low temperature-curing (80-100°C), moderate temperature-curing (110-150°C) and high temperature-curing (160-200°C) types, depending on the curing temperature.

[0004] Low temperature-curing prepregs can be cured and molded near 90°C, while having a very wide range of selection of subsidiary materials to be used in molding and allowing use of resin dies for molding, thus permitting lower equipment investment. They are therefore advantageous for molding highly variable parts in small amounts. However, since the curing and molding are carried out near 90°C, it is not possible to obtain fiber-reinforced composite materials with excellent heat resistance.

[0005] Moderate temperature-curing prepregs serve primarily for molding of generic products for sports and leisure purposes, and allow curing and molding at temperatures near 130°C, and while they produce fiber-reinforced composite materials with excellent mechanical properties, it is not possible to obtain superior heat resistance.

[0006] High temperature-curing prepregs are subjected to curing and molding at temperatures near 180°C, and are used, for example, mainly for molding of fiber-reinforced composite materials to be supplied in fields that require excellent heat resistance, such as aircraft production, providing molded articles with extremely excellent heat resistance.

[0007] In order to obtain fiber-reinforced composite materials with high heat resistance, curing is accomplished at high temperature, thereby producing both high mechanical properties and high heat resistance. However, two major problems are associated with high temperature-curing systems.

[0008] One problem is resin flow. For fiber-reinforced composite material prepregs, the resin viscosity is usually set in consideration of manageability at room temperature. Because of the large difference between room temperature and the curing temperature in a high temperature-curing system, the viscosity of the impregnated resin tends to be reduced and resin flow readily occurs. This results in sections of resin deficiency or excess in the fiber-reinforced composite material. Variations in the matrix resin distribution not only affect the thickness and outer appearance of the molded article, but are also associated with reduced mechanical properties, and cracking. This is of particular concern for heat-resistant materials, which may suffer adverse effects to their long-term heat resistance.

[0009] Another problem is the heat resistance of mold materials and subsidiary materials. A fiber-reinforced composite material is usually molded using a molding die. Examples of molding methods include "hand lay-up" methods in which repetition of a procedure wherein a resin is impregnated into a reinforcing fiber material such as a cloth while applying it along a molding die, or wherein a prepreg having the resin already impregnated in a reinforcing fiber material is applied along a molding die, is followed by curing, and then removal from the die to obtain a molded article; resin transfer molding methods in which a reinforcing fiber material such as a cloth is set in a molding die, and then a resin is injected therein and cured and then removed from the die to obtain a molded article; molding compound methods in which a molding material comprising a mixture of a resin with a reinforcing fiber material cut into staple fibers is injected into a molding die and then cured, and then removed from the die to obtain a molded article; and methods in which rectangular columnar molding dies (mandrels) are used as inserts to hold and cure a prepreg in an I-beam or H-beam shape, and are then removed from the die to obtain a molded article.

[0010] The molding dies used in such molding methods are made of various types of materials including metal, resin, wooden and gypsum. Metal molding dies have excellent heat resistance and durability, but are expensive due to the effort and labor required for their formation, while their high specific gravity renders them problematically heavy. Resin molding dies and wooden molding dies, on the other hand, have inferior heat resistance and durability. At the current time, gypsum molding dies are in wide use because of their satisfactory balance between performance and cost.

[0011] In molding methods using such gypsum molding dies, the molding is preferably carried out at no higher than 130°C because of the heat resistance of the molding dies themselves or the subsidiary materials, and this generally hampers molding of highly heat-resistant materials using high temperature-curing prepregs that require molding temperatures of 180°C or higher. When it is attempted to cure and mold such high temperature-curing prepregs at low temperature or moderate temperature, molding is usually impossible to accomplish, or else an exceedingly long time is necessary and the molded article has vastly reduced heat resistance.

[0012] A widely employed solution is to carry out primary curing of the high temperature-curing prepreg at low temperature or moderate temperature, with addition of a curing agent and curing accelerator to the resin composition, and to subsequently carry out secondary curing at high temperature, but it is generally impossible to avoid reduction in mechanical properties and heat resistance, and even when mechanical properties are maintained, the heat resistance has been inevitably reduced due to addition of the curing agent and curing accelerator.

Prior Art Reference

Patent Document

[0013] Patent document 1: Japanese Unexamined Patent Publication No. 2003-96163

[0014] EP1275674 relates to an epoxy resin composition and a prepreg made with the epoxy resin composition.

Disclosure of the Invention

Problems to be Solved by the Invention

[0015] In light of the problems of the prior art described above, it is an object of the present invention to provide a method for producing a fiber-reinforced composite material with high mechanical properties and high heat resistance, which allows a gypsum die to be used in primary curing.

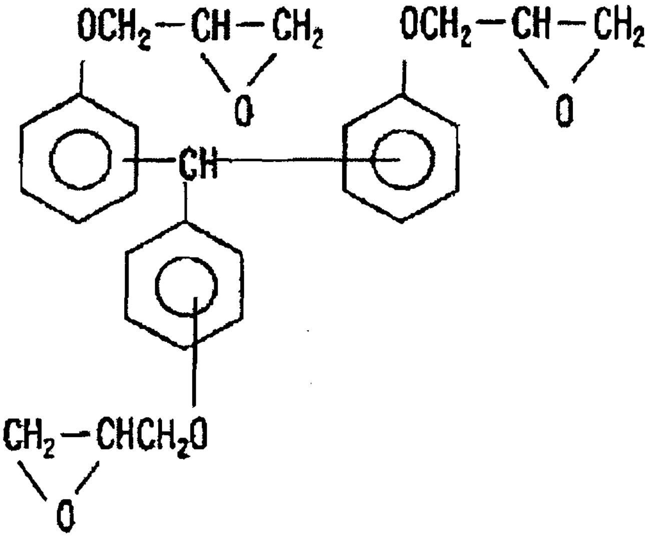
Means for Solving the Problems

[0016] The present inventors have completed this invention as a result of avid research conducted with the goal of solving the problems described above.

[0017] The invention provides the following (1) to (9).

(1) A method for producing a fiber-reinforced composite material, wherein a fiber-reinforced prepreg, obtained by impregnating reinforcing fibers with an epoxy resin composition comprising a triphenylmethane-type epoxy compound represented by the following formula 1 (A), N,N,N',N'-tetraglycidyldiaminodiphenylmethane (B) and diaminodiphenylsulfone (C), is subjected to primary curing at 110-130°C, and then to secondary curing at a temperature which is at least as high as the primary curing temperature.

[Chemical 1]



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(2) The method for producing a fiber-reinforced composite material according to (1) above, wherein the secondary curing temperature is 180°C or higher.
(3) The method for producing a fiber-reinforced composite material according to (1) above, wherein the fiber substrate of the fiber-reinforced composite material consists of carbon fibers.
(4) The method for producing a fiber-reinforced composite material according to (1) above, wherein the fiber substrate of the fiber-reinforced composite material is a woven fabric.
(5) The method for producing a fiber-reinforced composite material according to (1) above, wherein the fiber substrate of the fiber-reinforced composite material consists of a chopped material.
(6) The method for producing a fiber-reinforced composite material according to any one of (1) to (5) above, wherein a heat-resistant mold material is obtained as a fiber-reinforced composite material by primary removal from the mother die after primary curing, and secondary curing in a free standing state.
(7) The method for producing a fiber-reinforced composite material according to any one of (1) to (5) above, wherein a heat-resistant structural material is obtained as a fiber-reinforced composite material by primary removal from the mother die after primary curing, and secondary curing in a free standing state.
(8) A heat-resistant mold material obtained by the method according to (6) above.
(9) A heat-resistant structural material obtained by the method according to (7) above.

Effect of the Invention

[0018] According to the invention it is possible to provide a composite material exhibiting high mechanical properties and high heat resistance. A composite material obtained by the method of the invention is useful as a heat-resistant mold material or a heat-resistant structural material for which high mechanical properties and high heat resistance are required.

Brief Description of the Drawings

[0019]

Fig. 1 is a graph used to determine the G'-Tg of a cured product, from the intersection between a tangent on the graph of the cured product in the glassy state, and the tangent in the transition region.
Fig. 2 is a graph showing primary curing degrees with different temperatures and times.
Fig. 3 is a graph of log G' values for cured products. The ordinate represents G' and the abscissa represents temperature. The ordinate is offset. Modes for Carrying Out the Invention

[0020] Preferred modes of the invention will now be explained with the understanding that the invention is not limited only to these modes.

[0021] The epoxy resin composition to be used for the invention comprises a triphenylmethane-type epoxy compound represented by formula 1 above (A), N,N,N',N'-tetraglycidyldiaminodiphenylmethane (B) and diaminodiphenylsulfone (C). The mixing ratio of (A) and (B) in the epoxy resin composition is preferably 90:10 to 10:90 in terms of mass ratio, from the viewpoint of achieving both high resin properties and high heat resistance. It is more preferably 60:40 to 20:80. It is yet more preferably 50:50 to 20:80. From the viewpoint of the flexural modulus of the secondary cured product, the ratio is preferably 90:10 to 30:70. From the viewpoint of heat resistance, it is preferably 90:10 to 40:60. It is more preferably 90:10 to 60:40, and even more preferably 90:10 to 80:20. From the viewpoint of the primary curing degree, it is preferably 80:20 to 10:90.

[0022] The diaminodiphenylsulfone (C) to be used for the invention may be 4,4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfone, or the like. It is preferably 4,4'-diaminodiphenylsulfone. The content of the diaminodiphenylsulfone (C) is preferably an amount such that the ratio of amine equivalents to epoxy equivalents in the epoxy resin composition is 0.8 to 1.5. If the equivalent ratio is 0.8 to 1.5, the elastic modulus will not excessively increase, and there will be minimal adverse effect on the thermal crack resistance of the fiber-reinforced composite material. The amount is more preferably such that the equivalent ratio is 0.8 to 1.2.

[0023] The epoxy resin composition used for the invention preferably contains silica (D). The form may be amorphous or spherical, and the surface substrate may be hydrophobic or hydrophilic. Spherical hydrophilic silica is preferred. The content may be selected as appropriate. The preferred content is 1 to 20 parts by mass with respect to 100 parts by mass as the total of the triphenylmethane-type epoxy compound represented by formula 1 (A) and the N,N,N',N'-tetraglycidyldiaminodiphenylmethane (B). If the content is less than 1 part by mass the linear expansion coefficient of the composite material will tend to be higher, and the interlayer peel strength of the composite material will tend to be reduced. If the content is greater than 20 parts by mass the heat resistance of the composite material will tend to be lower and the viscosity of the resin composition will be too high, preventing formation of a prepreg. The content is more preferably 4 to 8 parts by mass.

[0024] The epoxy resin composition used for the invention preferably further contains a thermoplastic resin (E). Adding a thermoplastic resin (E) can minimize sticking of the resin composition and adjust the tack of the prepreg to a suitable level, or it can minimize changes in tack with time. Examples of such thermoplastic resins include phenoxy resins, polyvinyl formals and polyethersulfones. Phenoxy resins are preferred. The preferred content is 0.1 to 20 parts by mass with respect to 100 parts by mass as the total of the epoxy resin represented by formula 1 (A) and the N,N,N',N'-tetraglycidyldiaminodiphenylmethane (B). It is more preferably 3-7 parts by mass.

[0025] The epoxy resin composition used for the invention preferably further contains another epoxy resin (F). The other epoxy resin (F) is preferably bifunctional or greater, with no particular restrictions on bifunctional or greater epoxy resins, examples including epoxy resins such as bisphenol A-type epoxy resins, bisphenol F-type epoxy resins, bisphenol S-type epoxy resins, novolac-type epoxy resins, cresol-novolac-type epoxy resins, aminoglycidyl-type epoxy resins, aminophenol-type epoxy resins, aminocresol-type epoxy resins, naphthalene-type epoxy resins and cyclopentadiene-type epoxy resins. Preferred are bisphenol A-type epoxy resins and bisphenol F-type epoxy resins, with bisphenol A-type epoxy resins being even more preferred. The preferred content is 0.1 to 20 parts by mass with respect to 100 parts by mass as the total of the epoxy resin represented by formula 1 (A) and the N,N,N',N'-tetraglycidyldiaminodiphenylmethane (B). It is more preferably 5 to 15 parts by mass.

[0026] The method for producing the epoxy resin composition to be used for the invention is not particularly restricted, and a known technique such as a method using a mixing roll or kneader may be used for its production.

[0027] According to the method of the invention, primary curing of the epoxy resin composition is accomplished at a temperature of 110-130°C. A temperature of 110°C or higher will allow an industrially suitable curing time. If the temperature is no higher than 130°C, resin flow will not be excessive during the primary curing, and the molded article quality will not be impaired. Specific concerns are variation in the molded article thickness (especially reduced thickness on the outer periphery) and variation in the matrix resin distribution, resulting in reduced quality of the outer appearance of the molded article, and reduction in mechanical properties or increased cracking. This is of particular concern for heat-resistant materials, which may suffer adverse effects to their long-term heat resistance.

[0028] In consideration of heat resistance of the molding die material or subsidiary material, and of cost, the primary curing temperature is more preferably 110-120°C. Also the primary curing degree, described hereunder, is preferably 50-80% and more preferably 60-75%. Within these ranges, the molded article will be smoothly removable from the molding die after the primary curing.

[0029] According to the invention, the primary curing is followed by secondary curing at a temperature which is at least as high as the primary curing temperature. Secondary curing at a temperature which is at least as high as the primary curing temperature increases the mechanical properties and heat resistance of the matrix resin, and also increases the mechanical properties and heat resistance of the fiber-reinforced composite material.

[0030] Assuming that the obtained fiber-reinforced composite material will be used as a heat-resistant mold material or heat-resistant structural material, the secondary curing temperature is preferably 180°C or higher and more preferably 200°C or higher. There is no particular upper limit to the secondary curing temperature, but it is preferably no higher than 300°C considering the working temperatures of readily available heating furnaces.

[0031] For the fiber substrate of the fiber-reinforced composite material there may be used various inorganic fibers or organic fibers such as glass fibers, carbon fibers, metal fibers or aramid fibers, but glass fibers and/or carbon fibers are preferred in order to lower the linear expansion coefficient of the composite material. Carbon fibers are more preferred.

[0032] The fiber substrate can be used directly in the form of a fiber tow, in the form of a unidirectional material having the fiber tow aligned in one direction, in the form of a woven fabric, or in the form of a nonwoven fabric comprising short-cut reinforcing fibers, but considering use of the fiber-reinforced composite material as a heat-resistant mold material or heat-resistant structural material, the fiber substrate is preferably a woven fabric and especially a woven fabric with high shapeability. For a woven fabric, examples include sheets with fiber bundles aligned in one direction, such as plain weave, twill weave, satin weave or non-crimped fabric, or stitching sheets obtained by forming sheets with varied lamination angles, stitched together without looseness.

[0033] When the fiber-reinforced composite material is to be used as a cutting material, the fiber substrate preferably consists of a chopped material, such as chopped strands or chopped fibers.

[0034] The invention is a method for producing a fiber-reinforced composite material with high mechanical properties and high heat resistance, and it is preferably used for production of a heat-resistant mold material.

[0035] The invention is also a method for producing a fiber-reinforced composite material with high mechanical properties and high heat resistance, which is preferably used for production of a heat-resistant structural material.

[0036] In the production method of the invention, the secondary curing may be accomplished in a variety of forms, such as secondary curing on the mother die after primary curing, secondary curing reinforced with a support material after removal from the mother die, or free standing secondary curing after removal from the mother die, but in consideration of heat resistance and cost of the mother die and subsidiary materials, the secondary curing is preferably carried out in a free standing manner after removal from the mother die after primary curing.

[0037] A known method may be used to produce a prepreg comprising an intermediate material for the fiber-reinforced composite material. For example, there may be mentioned a method of producing a prepreg by supplying a resin to one or both sides of the fiber substrate and heating and pressing to impregnate the fiber substrate with the resin, a method of producing a prepreg by preparing the resin composition as a film and then laminating it with the fiber substrate, and heating and pressing it for impregnation into the fiber substrate, or a method of producing a prepreg by impregnating a fiber substrate with a solution of the resin composition dissolved in a solvent for impregnation of the resin, and then drying it.

[0038] Curing of the fiber-reinforced composite material may be accomplished by a known method. Examples of curing methods include autoclave molding methods, oven molding methods, vacuum bag molding methods and press molding methods, although there is no limitation to these. Autoclave molding methods are preferred. Examples

[0039] The construction of the invention will now be explained in detail based on examples in contrast to comparative examples.

Preparation of epoxy resin composition

[0040] The matrix resin composition to be used for production of the prepreg may be prepared in the following manner. The following abbreviations are used for the components used in the epoxy resin compositions of the examples and comparative examples.

Epoxy resin (A)

[0041] Tx742: Epoxy resin corresponding to formula 1, tris(hydroxyphenyl)methane triglycidyl ether, epoxy equivalents: 160 g/eq, Huntsman Advanced Materials Co.

Epoxy resin (B)

[0042] jER604: N,N,N',N'-Tetraglycidyldiaminodiphenylmethane, epoxy equivalents: 120 g/eq, Japan Epoxy Resins Co., Ltd.

Diaminodiphenylsulfone (C)

[0043] DDS: 4,4'-Diaminodiphenylsulfone, SEIKACURE S (ground product) by Wakayama Seika, amine active hydrogen equivalents: 62 g/eq

Silica (D)

[0044] A380: Silicon dioxide, AEROSIL380PE by Nippon Aerosil Co., Ltd.

Thermoplastic resin (E)

[0045] YP50S: Phenoxy resin, Pheno-Tohto YP-50S by Tohto Kasei Co., Ltd.

Other epoxy resin (F)

[0046] jER828: Bisphenol A-type epoxy resin, epoxy equivalents: 189 g/eq, Japan Epoxy Resins Co., Ltd.

[0047] HP-4032: Naphthalene-type epoxy resin, epoxy equivalents: 151 g/eq, DIC

Curing accelerator (G)

[0048] DCMU: DCMU99, Hodogaya Chemical Co., Ltd.

Other curing agent (F)

[0049] DICY: DICY15, Japan Epoxy Resins Co., Ltd.

[0050] The components were mixed in the mixing ratios listed in Table 1, Table 2, Table 7 and Table 8, and the mixtures were uniformly dispersed at 60°C to obtain epoxy resin compositions.

[0051] After uniformly dissolving jER828 and YP50S at 160°C in the mixing ratios listed in Table 3, Table 4 and Table 6, each mixture were cooled to room temperature. Also, Tx742, jER604, A380 and DDS were mixed and uniformly dispersed at 60°C to obtain epoxy resin compositions.

Measurement of primary curing degree at different temperatures

[0052] The epoxy resin composition obtained in Example 2 described below was heated at different temperatures for different times, as shown in Table 7, using a DSC Q-1000 by TA Instruments, and then cooled to room temperature to obtain a primary cured resin. The residual heat value (E1) of the primary cured resin and the curing heat value (E0) of the uncured epoxy resin composition were measured using a DSC Q-1000 by TA Instruments, under conditions with a temperature-elevating rate of 10°C/min, at 30-300°C. The primary curing degree was determined by the following formula. The results are shown in Table 7 and Fig. 2.

$$\text{Primary curing degree (\%)} = \{(E0)-(E1)\}/(E0) \times 100$$

Measurement of bending properties of cured resin

[0053] After heating the obtained epoxy resin composition to 60°C for defoaming, it was cast onto a release-treated glass plate to a thickness of 2 mm and sandwiched with another similarly-treated glass plate, and subjected to primary curing from room temperature at a temperature-elevating rate of 1.7°C/min, and upon completion of the primary curing, the temperature was lowered to room temperature and the product was removed from the glass plate, or secondary curing was carried out on a different glass plate if necessary from room temperature at a temperature-elevating rate of 1.7°C/min, to obtain a 2 mm-thick molded sheet. The obtained molded sheet was cut to dimensions of 60 mm length × 8 mm width using a wet diamond cutter, to form a test piece. The obtained test piece was subjected to a 3-point bending test using an Instron5565 universal testing machine by Instron and Bluehill analysis software, under measuring conditions with an indenter of R = 3.2 mm, L/D = 16, and a cross head speed of 2 mm/min, and the flexural strength, flexural modulus and flexural elongation at break were calculated. The results are shown in Table 1, Table 2, Table 3 and Table 8.

Measurement of glass transition point temperature (Tg) of cured resin

[0054] In order to measure the bending properties of the cured resin, the molded sheet formation procedure was repeated to obtain a 2 mm-thick molded sheet. The obtained molded sheet was cut to dimensions of 55 mm length × 12.7 mm width using a wet diamond cutter, to form a test piece. A DMA ARES-RDA by TA Instruments was used to measure the Tg under conditions with a temperature-elevating rate of 5°C/min, a frequency of 1 Hz and a strain of 0.05%.

The logG' was plotted against temperature, and G'-Tg was recorded as the temperature determined from the intersection between an approximate straight line in the flat region before transition of logG', and an approximate straight line in the region of transition of G' (see Fig. 1). Also, tanδ was plotted against temperature, and the temperature showing maximum value for tanδ was recorded as tanδmax. The results are shown in Fig. 3 and Table 1, Table 2, Table 3 and Table 8.

Measurement of primary curing degree of primary cured molded sheet

[0055] After heating the epoxy resin composition obtained by preparation of the epoxy resin composition described above to 60°C for defoaming, it was cast onto a release-treated glass plate to a thickness of 2 mm and sandwiched between another similarly-treated glass plate, after which it was subjected to primary curing from room temperature at a temperature-elevating rate of 1.7°C/min (a temperature-elevating rate of 2.0°C/min only for Comparative Example 10), and removed from the glass plate to obtain a 2 mm-thick primary cured molded sheet. The residual heat value (E2) of the primary cured molded sheet and the curing heat value (E0) of the uncured epoxy resin composition were measured using a DSC Q-1000 by TA Instruments, under conditions with a temperature-elevating rate of 10°C/min, at 30-350°C. The primary curing degree was determined by the following formula. The results are shown in Table 1 and Table 8.

$$\text{Primary curing degree (\%)} = \{(E0)-(E2)\}/(E0) \times 100$$

Production of resin film of 3K cloth prepreg

[0056] The epoxy resin composition obtained by preparation of the epoxy resin composition described above was coated onto a release sheet using a film coater at 60°C to a resin basis weight of 133 g/m^2, to obtain a resin film.

Production of resin film of 12K cloth prepreg

[0057] The epoxy resin composition obtained by preparation of the epoxy resin composition described above was coated onto a release sheet using a film coater at 60°C to a resin basis weight of 194.4 to 216 g/m^2, to obtain a resin film.

Production of 3K cloth prepreg

[0058] Using a TR3110M carbon fiber woven fabric by Mitsubishi Rayon Co., Ltd. as the fiber substrate (using TR30S3L, plain weave, basis weight: 200 g/m^2), the resin film for a 3K cloth prepreg obtained as described above was attached to one side thereof, and heated, pressed and impregnated therein to obtain a prepreg with a resin content (RC) of 40%.

Production of 12K cloth prepreg

[0059] Using a TRK510M carbon fiber woven fabric by Mitsubishi Rayon Co., Ltd. as the fiber substrate (using TR50S12L, 2/2 twill weave, basis weight: 648 g/m^2), the resin film for a 12K cloth prepreg obtained as described above was attached to both sides thereof, and heated, pressed and impregnated therein to obtain a prepreg with a resin content (RC) of 37.5%-40%.

Production of composite panel

[0060] The obtained 12K cloth prepreg was cut into a pattern with dimensions of 300 mm length (warp yarn direction of carbon fiber woven fabric) × 300 mm width (weft yarn direction of carbon fiber woven fabric), or 200 mm length × 200 mm width. Four similarly patterned prepregs were laminated in alignment in the 0° direction (the warp yarn direction of the carbon fiber woven fabric) and bagged, and then an autoclave was used for primary curing under the curing conditions shown in Table 4 (pressure: 0.5 MPa, vacuum pressure: 0.1 MPa, temperature-elevating rate: 1.7°C/min), and where necessary, an oven was used for secondary curing under the curing conditions shown in Table 4 (temperature-elevating rate: 1.7°C/min), to obtain a composite panel.

Measurement of bending properties of composite

[0061] The obtained composite panel was cut to dimensions of 127 mm length × 12.7 mm width using a wet diamond cutter, to form a test piece. The obtained test piece was subjected to a 3-point bending test using an Instron5565 universal testing machine by Instron and Bluehill analysis software, according to ASTM D-790 (indenter R = 5.0, L/D = 40, cross head speed: 6.8-7.3 mm/min), and the flexural strength and flexural modulus were calculated. The results are shown in Table 4.

Measurement of glass transition point temperature (Tg) of composite

[0062] The obtained composite panel was cut to dimensions of 55 mm length × 12.7 mm width using a wet diamond cutter, to form a test piece. A DMA ARES-RDA by TA Instruments was used to measure the Tg under conditions with a temperature-elevating rate of 5°C/min, a frequency of 1 Hz and a strain of 0.05%. The logG' was plotted against temperature, and G'-Tg was recorded as the temperature determined from the intersection between an approximate straight line in the flat region before transition of logG', and an approximate straight line in the region of transition of G' (see Fig. 1). Also, tanδ was plotted against temperature, and the temperature showing maximum value for tanδ was recorded as tanδmax. The results are shown in Table 4.

Molding using stainless steel mother die

[0063] Three 3K cloth prepregs were laminated with alignment of their directions in the order 0°/45°/0°, where the warp yarn direction of the carbon fiber woven fabric was defined as 0°, and an additional eight 12K cloth prepregs were laminated with alignment of their directions in the order 0°/45°/90°/-45°/-45°/90°/45°/0°, where the warp yarn direction of the carbon fiber woven fabric was defined as 0°, in a SUS die with a convex cross-section, and were bagged, after which an autoclave was used for primary curing under the curing conditions shown in Table 5 (pressure: 0.5 MPa, vacuum pressure: 0.1 MPa, temperature-elevating rate: 1.7°C/min), and after removal, an oven was used for secondary curing in a free standing state under the curing conditions shown in Table 5 (temperature-elevating rate: 1.7°C/min), to obtain a concave composite.

Production of composite panel for thickness measurement

[0064] The obtained 12K cloth prepreg was cut into a pattern with dimensions of 800 mm length (warp yarn direction of carbon fiber woven fabric) × 1000 mm width (weft yarn direction of carbon fiber woven fabric), or 1000 mm length × 800 mm width. Six of these were laminated with their directions in the order 0°/90°/0°/0°/90°/0°, where the warp yarn direction of the carbon fiber woven fabric was defined as 0°, and bagged, and then an autoclave was used for primary curing under the curing conditions shown in Table 6 (pressure: 0.5 MPa, vacuum pressure: 0.1 MPa, temperature-elevating rate: 1.7°C/min), to obtain a composite panel with 1000 mm length × 800 mm width. The sides of the obtained composite panel were each trimmed to 10 mm, and then when necessary, an oven was used for secondary curing under the curing conditions shown in Table 6 (temperature-elevating rate: 1.7°C/min), and the thickness of each panel was measured at 24 points on the outer periphery section and 27 points on the inner wall section. The outer periphery section was defined as an arbitrary location on the inner side 20-25 mm from each side, and the inner wall section was defined as an arbitrary location on the inner side at least another 50 mm from the outer periphery section, and measurement was conducted at dispersed locations to avoid bias of the measuring locations.

Examples 1-12

[0065] The resin compositions of Examples 1 to 12 were cured by moderate temperature primary curing (120°C for 8 hours) and high-temperature secondary curing (200°C for 2 hours) to obtain cured resins with both high mechanical strength (resin bending properties) and high heat resistance (DMA-Tg) (Table 1, Table 2, Table 3). Upon measuring the curing degree at different temperatures in Example 2, the curing degree exceeded 50% with 6 hours at 110°C, 3 hours at 120°C and 2 hours at 130°C, whereas the curing degree did not exceed 50% at 100°C, even with heating for 12 hours (Fig. 2, Table 7). In Example 7, a composite was obtained having both high mechanical strength (12K cloth composite bending properties) and high heat resistance (12K cloth composite DMA-Tg) (Table 4). Also in Example 7, a satisfactory molded article was obtained with low resin flow and few resin excess areas (Table 5). In addition, the molded sheet obtained in Example 7 had a small thickness difference between the outer periphery and inner sections (Table 6).

Comparative Example 1

[0066] In Comparative Example 1 which did not use jER604 as the epoxy resin (B), the G'-Tg of the cured resin of the obtained resin composition was reduced (Table 1).

Comparative Example 2

[0067] In Comparative Example 2 which did not use Tx742 as the epoxy resin (A), the elastic modulus of the obtained resin composition was increased and the heat resistance was reduced (Table 1).

Comparative Example 3

[0068] The resin jER604 as the epoxy resin (B) was changed to jER828 as another epoxy resin (F). The cured resin of the obtained resin composition exhibited excellent flexural elongation at break, but the heat resistance was significantly reduced (Table 1).

Comparative Example 4

[0069] The resin jER604 as the epoxy resin (B) was changed to HP-4032 as another epoxy resin (F), which has a rigid backbone and was predicted to function advantageously for both the mechanical properties and heat resistance. The cured resin of the obtained resin composition exhibited excellent flexural elongation at break, but the heat resistance was significantly reduced (Table 1).

Comparative Example 5

[0070] Upon comparing Example 2 in which moderate temperature primary curing (120°C for 8 hours) and high-temperature secondary curing (200°C for 2 hours) were carried out, and Comparative Example 5 in which only high-temperature curing (200°C for 2 hours) was carried out, as a prior art method, for a resin with the same composition, Comparative Example 5 exhibited about the same resin bending properties and heat resistance as Example 2, but the molded sheet quality was slightly inferior to that of Example 2 (Table 2).

Comparative Example 6

[0071] Upon comparing Example 7 in which moderate temperature primary curing (120°C for 8 hours) and high-temperature secondary curing (200°C for 2 hours) were carried out, using a resin with the same composition, and Comparative Example 6 in which only low-temperature primary curing (120°C for 8 hours) was carried out, the resin bending properties and heat resistance of the resin of Comparative Example 6 were inferior to those obtained in Example 7 (Table 3). Also, the 12K cloth composite bending properties and the 12K cloth composite heat resistance in Comparative Example 6 were inferior to those obtained in Example 7 (Table 4).

Comparative Example 7

[0072] Upon comparing Example 7 in which moderate temperature primary curing (120°C for 8 hours) and high-temperature secondary curing (200°C for 2 hours) were carried out, and Comparative Example 7 in which only high-temperature curing (180°C for 2 hours) was carried out, for a resin with the same composition, Comparative Example 7 exhibited about the same resin bending properties and heat resistance as Example 7 (Table 3). However, the 12K cloth composite bending properties and 12K cloth composite heat resistance in Comparative Example 7 were slightly inferior to those obtained in Example 7 (Table 4). Also, the difference in thickness between the outer periphery and inner sections of the molded sheet in Comparative Example 7 was greater than in Example 7 (Table 6).

Comparative Example 8

[0073] In Comparative Example 8, in which the same procedure was repeated as in Example 7 except for carrying out primary curing at 140°C for 6 hours, the resin flow was reduced compared to Comparative Example 7 in which only high-temperature curing was carried out, and compared to Comparative Example 9 described hereunder, but it was increased compared to Example 7 (Table 5).

Comparative Example 9

[0074] In Comparative Example 9, in which the same procedure was repeated as in Example 7 except for carrying out high-temperature curing for both the primary curing and secondary curing (primary curing at 160°C for 4 hours and secondary curing at 180°C for 2 hours), the resin flow was increased and more resin excess sections were observed (Table 5).

Comparative Example 10

[0075] The diaminodiphenylsulfone (C) was changed to DCMU as a curing accelerator (G) and DICY as another curing agent (H). The cured resin from the resin composition obtained by low-temperature primary curing (100°C for 4 hours) and high-temperature secondary curing (200°C for 2 hours) had an increased elastic modulus and lower elongation, as well as reduced heat resistance (Table 8).

Comparative Example 11

[0076] The cured resin from the resin composition obtained by moderate-temperature primary curing (120°C for 8 hours) and high-temperature secondary curing (200°C for 2 hours) of a resin with the composition shown in Table 8 had an increased elastic modulus and lower elongation, as well as reduced heat resistance (Table 8).

[Table 1]

[0077]

Table 1

			Example 1	Example 2	Example 3	Example 8	Example 4	Example 9	Example 5	Example 10	Example 11	Example 6	Example 12	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Composition	A	Tx742	40	40	40	90	80	70	60	50	30	20	10	100	-	40	40
	B	JER604	60	60	60	10	20	30	40	50	70	80	90	-	100	-	-
	C	DDS	37.2	46.5	55.8	40.0	41.3	42.6	42.9	45.2	47.7	49.1	50.4	38.6	51.7	35.2	40.1
	F	JER828	-	-	-	-	-	-	-	-	-	-	-	-	-	60	
		HP-4032	-	-	-	-	-		-	-	-	-	-	-	-	-	60
Active hydrogen equivalents of DDS (C)			0.8	1.0	1.2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Flexural strength of secondary curing product (MPa)			158	171	171	168	153	166	151	160	166	172	162	155	172	152	181
Flexural modulus of secondary curing product (GPa)			3.4	3.4	3.4	3.3	3.2	3.4	3.3	3.2	3.4	3.6	3.6	3.2	3.7	3.0	3.5
Flexural elongation at break, for secondary curing product (%)			6.4	7.3	7.4	8.4	6.3	7.4	6	7.1	7.1	7	6.9	8.8	7.3	9.6	8.2
Glass transition temp. of secondary curing product (°C) DMA G'-Tg			269	266	259	315	301	287	278	268	258	257	253	234	251	223	222
Glass transition temp. of secondary curing product (°C) DMA tanδmax			286	281	273	328	316	303	293	285	274	271	268	337	266	238	241
Primary curing degree (%)			59	67	72	77	73	70	69	68	70	66	65	78	65	84	77
All curing conditions: Primary curing (120°C × 8 hrs), secondary curing: (200°C × 2 hrs)																	

[Table 2]

[0078]

Table 2

			Example 2	Comp. Ex. 5
Composition	A	Tx742	40	40
	B	jER604	60	60
	C	DDS	46.5	46.5
Primary curing conditions		Temp. (°C)	120	200
		Time (h)	8	2
Secondary curing conditions		Temp. (°C)	200	-
		Time (h)	2	-
Active hydrogen equivalents of DDS (C)			1.0	1.0
Flexural strength of secondary curing product (MPa)			1.71	157
Flexural modulus of secondary curing product (GPa)			3.36	3.41
Flexural elongation at break, for secondary curing product (%)			7.3	7
Glass transition temp. of secondary curing product (°C) DMA G'-Tg			266	263
Glass transition temp. of secondary curing product (°C) DMA tanδmax			281	278

[Table 3]

[0079]

Table 3

			Example 7	Comp. Ex.	Comp. Ex.
Composition	A	Tx742	40	40	40
	B	jER604	60	60	60
	C	DDS	48.4	48.4	48.4
	D	A380	5.75	5.75	5.75
	E	YP50S	5	5	5
	F	jER828	10	10	10
Primary curing conditions		Temp. (°C)	120	120	180
		Time (h)	8	8	2
Secondary curing conditions		Temp. (°C)	200	-	-
		Time (h)	2	-	-
Active hydrogen equivalents of DDS (C)			1.0	1.0	1.0
Flexural strength of secondary curing product (MPa)			170	151	170
Flexural modulus of secondary curing product (GPa)			3.5	3.8	3.4
Flexural elongation at break, for secondary curing product (%)			8	4.6	6.8
Glass transition temp. of secondary curing product (°C) DMA G'-Tg			250	130	206
Glass transition temp. of secondary curing product (°C) DMA tanδmax			270	153	229

[Table 4]

[0080]

Table 4

			Example 7	Comp. Ex. 6	Comp. Ex. 7
Composition	A	Tx742	40	40	40
	B	jER604	60	60	60
	C	DDS	48.4	48.4	48.4
	D	A380	5.75	5.75	5.75
	E	YP50S	5	5	5
	F	jER828	10	10	10
Primary curing conditions		Temp. (°C)	120	120	180
		Time (h)	8	8	2
Secondary curing conditions		Temp. (°C)	200	-	-
		Time (h)	2	-	-
Active hydrogen equivalents of DDS (C)			1.0	1.0	1.0
Flexural strength of 12K cloth composite (MPa)			825	623	667
Flexural modulus of 12K cloth composite (GPa)			54.6	53.1	54
Glass transition temp. of 12K cloth composite (°C) DMA G'-Tg			225	137	206
Glass transition temp. of 12K cloth composite (°C) DMA tanδ max			252	166	249
Vf of 12K cloth composite			52.6	52.6	53.2

[Table 5]

[0081]

Table 5

		Example 7	Comp. Ex. 8	Comp. Ex. 9
Primary curing conditions	Temp.	120°C	140°C	160°C
	Time	8 hr	6 hr	4 hr
Resin flow[a)]		1	2	3
Resin-rich sections[b)]		1	2	3
Restrictions on die/secondary materials[c)]		1	2	3
Secondary curing conditions	Temp.	200°C	200°C	380°C
	Time	2 hr	2 hr	2 hr
Warping in secondary curing		None	None	None
a) Few 1↔3 Numerous b) Few 1↔3 Numerous c) Low 1↔3 High				

[Table 6]

[0082]

Table 6

			Example 7	Comp. Ex. 7
Composition	A	Tx742	40	40
	B	jER604	60	60
	C	DDS	48.4	48.4
	D	A380	5.75	5.75
	E	YP50S	5	5
	F	jER828	10	10
Primary curing conditions		Temp. (°C)	1.20	180
		Time (h)	8	2
Secondary curing conditions		Temp. (°C)	200	-
		Time (h)	2	-
Active hydrogen equivalents of DDS (C)			1.0	1.0
Thickness (mm)	Inner wall section	Mean	3.967	3.953
		Max.	4.000	4.010
		Min.	3.915	3.905
	Outer periphery section	Mean	3.938	3.867
		Max.	3.985	3.918
		Min.	3.867	3.798

[Table 7]

[0083]

Table 7

<table>
<tr><td colspan="4"></td><td>Example 2</td></tr>
<tr><td rowspan="5">Composition</td><td colspan="2">A</td><td>Tx742</td><td>40</td></tr>
<tr><td colspan="2">B</td><td>jER604</td><td>60</td></tr>
<tr><td colspan="2">C</td><td>DDS</td><td>46.5</td></tr>
<tr><td colspan="2" rowspan="2">F</td><td>jER828</td><td>-</td></tr>
<tr><td>HP-4032</td><td>-</td></tr>
<tr><td colspan="4">Active hydrogen equivalents of DDS (C)</td><td>1.0</td></tr>
<tr><td colspan="5"></td></tr>
<tr><td colspan="2">Curing temperature</td><td colspan="2">Curing time (h)</td><td>Primary curing degree</td></tr>
<tr><td colspan="2" rowspan="3">100°C</td><td colspan="2">8</td><td>26%</td></tr>
<tr><td colspan="2">12</td><td>46%</td></tr>
<tr><td colspan="2">24</td><td>61%</td></tr>
</table>

(continued)

Curing temperature	Curing time (h)	Primary curing degree
110°C	2	13%
	4	28%
	6	47%
	8	59%
	12	64%
	24	67%
120°C	2	27%
	4	56%
	6	65%
	8	68%
	12	69%
130°C	2	49%
	4	69%
	6	73%
	8	73%
	12	74%

[Table 8]

[0084]

Table 8

			Comp. Ex. 10	Comp. Ex. 11
Composition	A	Tx742	40	50
	B	jER604	60	60
	G	DCMU	3	3
	H	DICY	9.45	9.45
Primary curing conditions		Temp. (°C)	100	120
		Time (h)	4	8
Secondary curing conditions		Temp. (°C)	200	200
		Time (h)	2	2
Flexural strength or secondary curing product (MPa)			135	132
Flexural modulus of secondary curing product (GPa)			3.8	3.9
Flexural elongation at break, for secondary curing product (%)			4.0	3.7
Glass transition temp. of secondary curing product (°C) DMA G'-Tg			218	216
Glass transition temp. of secondary curing product (°C) DMA tan δ max			237	234
Primary curing degree (%)			60	73

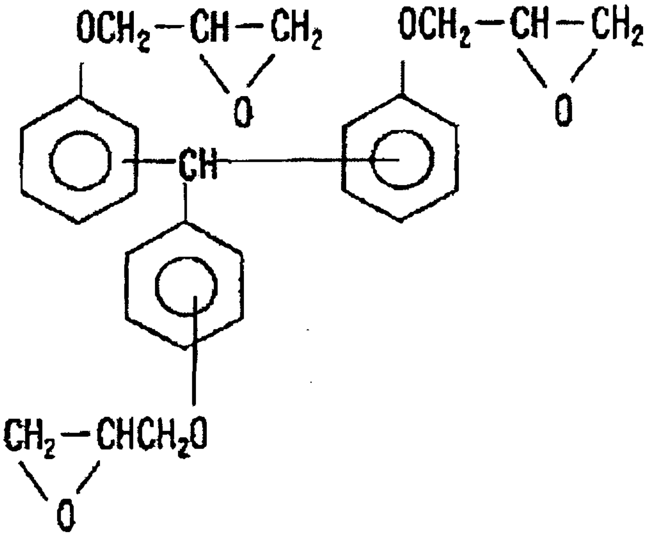
Industrial Applicability

[0085] According to the invention it is possible to provide a fiber-reinforced composite material with excellent mechanical strength, heat resistance, moldability and outer appearance. This minimizes restrictions on the mold material and subsidiary materials, and allows a wide variety of molding operations to be performed. The invention is therefore very useful for industry.

Claims

1. A method for producing a fiber-reinforced composite material, wherein a fiber-reinforced prepreg, obtained by impregnating reinforcing fibers with an epoxy resin composition comprising a triphenylmethane-type epoxy compound represented by the following formula 1 (A), N,N,N',N'-tetraglycidyldiaminodiphenylmethane (B) and diaminodiphenylsulfone (C), is subjected to primary curing at 110-130°C, and then to secondary curing at a temperature which is at least as high as the primary curing temperature.

   [Chemical 1]



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2. The method for producing a fiber-reinforced composite material according to claim 1, wherein the secondary curing temperature is 180°C or higher.

3. The method for producing a fiber-reinforced composite material according to claim 1, wherein the fiber substrate of the fiber-reinforced composite material consists of carbon fibers.

4. The method for producing a fiber-reinforced composite material according to claim 1, wherein the fiber substrate of the fiber-reinforced composite material is a woven fabric.

5. The method for producing a fiber-reinforced composite material according to claim 1, wherein the fiber substrate of the fiber-reinforced composite material consists of a chopped material.

6. The method for producing a fiber-reinforced composite material according to any one of claims 1 to 5, wherein a heat-resistant mold material is obtained as a fiber-reinforced composite material by primary removal from the mother die after primary curing, and secondary curing in a free standing state.

7. The method for producing a fiber-reinforced composite material according to any one of claims 1 to 5, wherein a

heat-resistant structural material is obtained as a fiber-reinforced composite material by primary removal from the mother die after primary curing, and secondary curing in a free standing state.

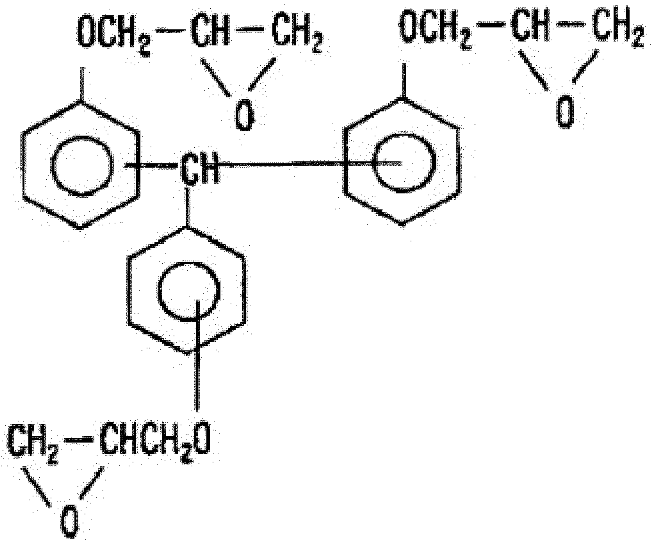
8. A heat-resistant mold material obtained by the method according to claim 6.

9. A heat-resistant structural material obtained by the method according to claim 7.

Patentansprüche

1. Verfahren zur Herstellung eines faserverstärkten Kompositmaterials, worin ein faserverstärktes Prepreg, erhalten durch Imprägnieren von verstärkenden Fasern mit einer Epoxyharzzusammensetzung, umfassend eine Epoxyverbindung vom Triphenylmethantyp, dargestellt durch die folgende Formel 1, (A), N,N,N',N'-Tetraglycidyldiaminodiphenylmethan (B) und Diaminodiphenylsulfon (C), einem primären Härten bei 110 bis 130°C unterzogen wird und dann einem sekundären Härten bei einer Temperatur unterzogen wird, die zumindest so hoch ist wie die primäre Härtungstemperatur.

[Chemische Formel 1]



· · · 1

2. Verfahren zur Herstellung eines faserverstärkten Kompositmaterials gemäß Anspruch 1, worin die sekundäre Härtungstemperatur 180°C oder höher ist.

3. Verfahren zur Herstellung eines faserverstärkten Kompositmaterials gemäß Anspruch 1, worin das Fasersubstrat des faserverstärkten Kompositmaterials aus Carbonfasern besteht.

4. Verfahren zur Herstellung eines faserverstärkten Kompositmaterials gemäß Anspruch 1, worin das Fasersubstrat des faserverstärkten Kompositmaterials ein Gewebe ist.

5. Verfahren zur Herstellung eines faserverstärkten Kompositmaterials gemäß Anspruch 1, worin das Fasersubstrat des faserverstärkten Kompositmaterials aus einem gehäckselten Material besteht.

6. Verfahren zur Herstellung eines faserverstärkten Kompositmaterials gemäß irgendeinem der Ansprüche 1 bis 5, worin ein wärmebeständiges Formmaterial als ein faserverstärktes Kompositmaterial durch primäre Entfernung aus der Mutterform nach dem primären Härten und sekundäres Härten in einem freistehenden Zustand erhalten wird.

7. Verfahren zur Herstellung eines faserverstärkten Kompositmaterials gemäß irgendeinem der Ansprüche 1 bis 5, worin ein wärmebeständiges strukturelles Material als ein faserverstärktes Kompositmaterial durch primäres Entfernen aus der Mutterform nach dem primären Härten und sekundäres Härten in einem freistehenden Zustand erhalten wird.

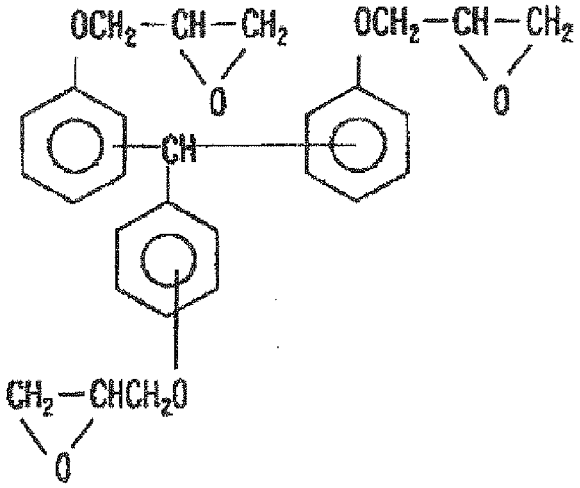
8. Wärmebeständiges Formmaterial, erhalten durch das Verfahren gemäß Anspruch 6.

9. Wärmebeständiges strukturelles Material, erhalten durch das Verfahren gemäß Anspruch 7.

Revendications

1. Procédé pour produire un matériau composite renforcé par des fibres, dans lequel un préimprégné renforcé par des fibres, obtenu par imprégnation de fibres de renforcement avec une composition de résine époxy comprenant un composé époxy de type triphénylméthane représenté par la formule 1 (A), du N,N,N',N'-tétraglycidyldiaminodiphénylméthane (B) et de la diaminodiphénylsulfone (C), est soumis à un durcissement primaire à 110-130°C, et ensuite à un durcissement secondaire à une température qui est au moins aussi élevée que la température de durcissement primaire.

[Formule chimique 1]



1

2. Procédé pour produire un matériau composite renforcé par des fibres selon la revendication 1, dans lequel la température de durcissement secondaire est de 180°C ou plus.

3. Procédé pour produire un matériau composite renforcé par des fibres selon la revendication 1, dans lequel le substrat fibreux du matériau composite renforcé par des fibres est constitué de fibres de carbone.

4. Procédé pour produire un matériau composite renforcé par des fibres selon la revendication 1, dans lequel le substrat fibreux du matériau composite renforcé par des fibres est une étoffe tissée.

5. Procédé pour produire un matériau composite renforcé par des fibres selon la revendication 1, dans lequel le substrat fibreux du matériau composite renforcé par des fibres est constitué d'un matériau haché.

6. Procédé pour produire un matériau composite renforcé par des fibres selon l'une quelconque des revendications 1 à 5, dans lequel un matériau de moule résistant à la chaleur est obtenu en tant que matériau composite renforcé par des fibres par retrait primaire de la matrice mère après durcissement primaire, et durcissement secondaire dans un état autoporteur.

7. Procédé pour produire un matériau composite renforcé par des fibres selon l'une quelconque des revendications 1 à 5, dans lequel un matériau structurel résistant à la chaleur est obtenu en tant que matériau composite renforcé par des fibres par retrait primaire de la matrice mère après durcissement primaire, et durcissement secondaire dans un état autoporteur.

8. Matériau de moule résistant à la chaleur obtenu par le procédé de la revendication 6.

9. Matériau structurel résistant à la chaleur obtenu par le procédé de la revendication 7.

Fig.1

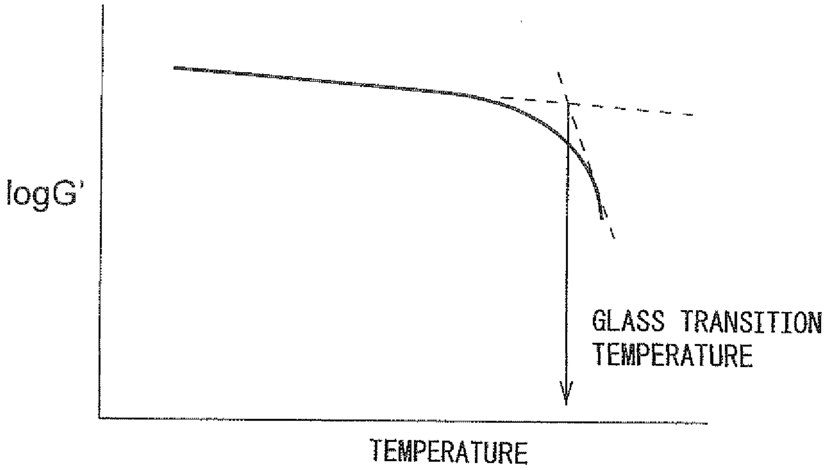

logG'
GLASS TRANSITION
TEMPERATURE
TEMPERATURE

Fig.2

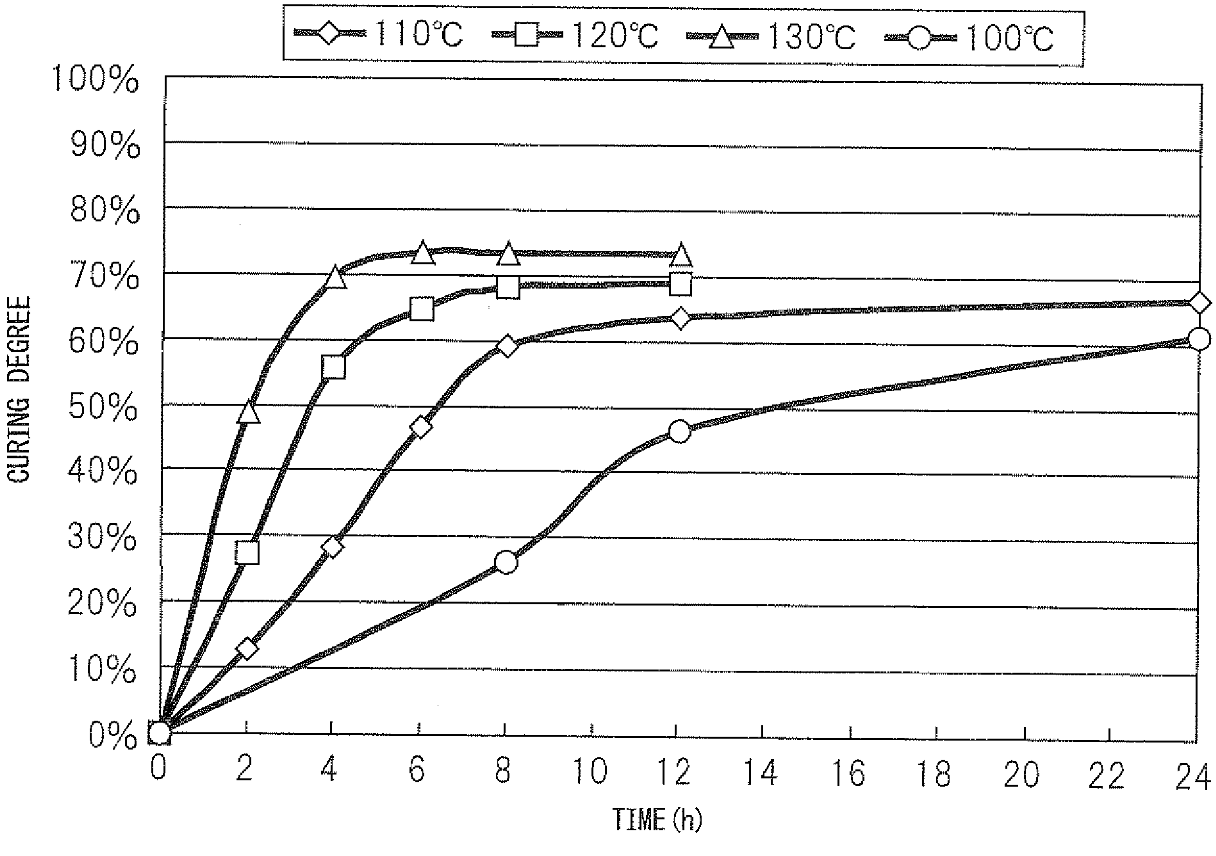
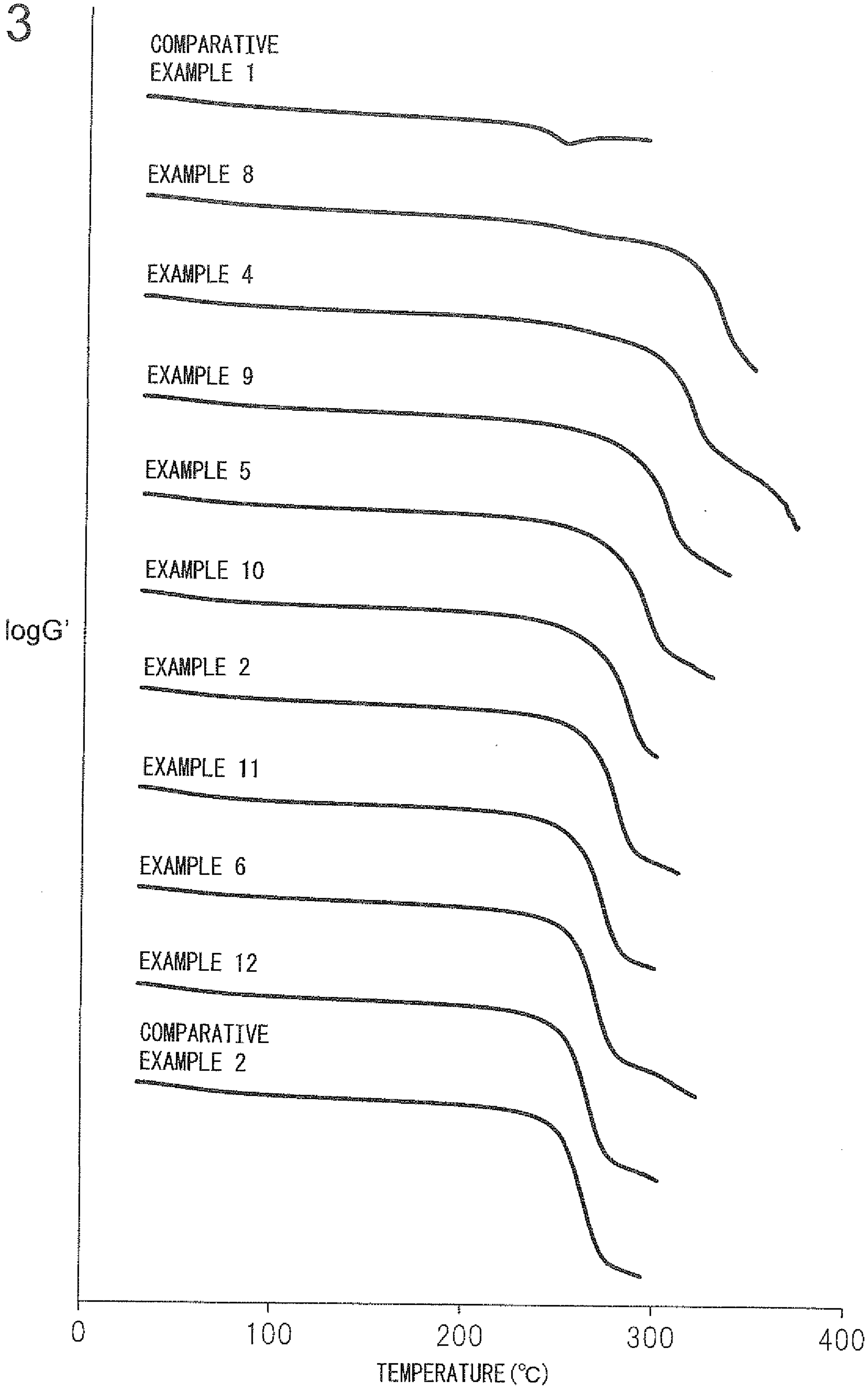

110℃
120℃
130℃
100℃
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
CURING DEGREE
0
2
4
6
8
10
12
14
16
18
20
22
24
TIME (h)

Fig.3


COMPARATIVE EXAMPLE 1
EXAMPLE 8
EXAMPLE 4
EXAMPLE 9
EXAMPLE 5
EXAMPLE 10
EXAMPLE 2
EXAMPLE 11
EXAMPLE 6
EXAMPLE 12
COMPARATIVE EXAMPLE 2
logG'
0
100
200
300
400
TEMPERATURE (°C)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2003096163 A **[0013]**
- EP 1275674 A **[0014]**