

**IMPROVED PROCESS FOR RESIN TRANSFER MOLDING AND FORMULATIONS USEFUL TO
PRACTICE THE PROCESS**

The present invention relates to resin transfer molding processes and preforms
5 useful in those processes.

Resin transfer molding processes are used to make fiber-reinforced composite materials. Layers of reinforcing material are loaded into a mold, and a thermosetting resin is injected into the mold and cured by ordinary and accepted procedures to provide a finished composite piece.

10 It is difficult and time-consuming to load different layers of fiber into the mold. It was previously necessary to stitch the fibers together in order to provide net-shaped preforms.

A thermoplastic-like resin is sometimes used as a "tackifier" to stiffen the reinforcing material and hold it in place before the molding process begins. See Heck et al., U.S. Patent 4,992,228 (February 12, 1991); and Flonc et al., U.S. Patent 5,080,851
15 (January 14, 1992). ("Thermoplastic-like" means that the resin is a solid, thermosetting resin that exhibits thermoplastic properties, such as a glass-transition temperature and/or a melting point, below the temperature that cures the resin, so that the resin is thermoformable.) In such a process, the individual fiber plies are sprinkled with a solid powder of the tackifier. The powder is heated to fuse it onto the surface of the substrate and then cooled to solidify it. The
20 different plies can be stacked together, heated to fuse the plies together and then cooled leaving a preform. The preform can be placed into the mold and used in an ordinary resin transfer molding process thereafter.

Other tackified substrates are described in Ko et al., U.S. Patent 5,369,192 (November 29, 1994); and Allognot et al., U.S. Patent 5,176,848 (January 5, 1993).

25 It has been recognized that chemical differences between the tackifier and the matrix resin may harm the physical properties of the composite. Therefore, it has been recommended to use a tackifier which is almost identical to the matrix resin. See PCT Publication WO94-26493 (November 24, 1994). However, such tackifiers may not be stable enough for long-term storage of the tackified substrate. What is needed is a material which is
30 more stable for long-term storage, but cures to form a product which is essentially identical to the cured matrix resin.

One aspect of the present invention is a tackified substrate comprising:

- (1) a fibrous substrate suitable for use in a matrix composite; and
- (2) 0.25 to 15 weight percent of a tackifier containing:
 - 35 (a) an epoxy resin,
characterized in that the tackifier further contains:
 - (b) a curing agent for the epoxy resin, but

- (c) 0 to less than 0.5 weight percent of the following compounds which act as catalysts for a curing reaction between Components (a) and (b): amines and ammonium compounds, phosphine and phosphonium compounds, aliphatic sulfonium compounds and arsonium and heterocyclic nitrogen-containing compounds.

5

A second aspect of the present invention is a process to use the tackified substrate comprising the steps of:

- (1) placing one or more of the tackified substrates, individually or as a preform, in a mold;
- 10 (2) injecting into the mold a matrix resin formulation which contains:
 - (a) an epoxy resin,
 - (b) a curing agent for the epoxy resin, and
 - (c) a catalytic amount of catalyst for the reaction between the epoxy resin and the curing agent; and
- 15 (3) curing the matrix resin formulation.

A third aspect is a formulation which is particularly useful as a tackifier in the preforms of the present invention and is useful as a matrix resin formulation in the process of the present invention. The formulation comprises:

- (1) 30 to 50 weight percent epoxy resin derived from a phenol-hydrocarbon resin;
- 20 (2) 20 to 30 weight percent diglycidyl ether of a halogenated dihydric phenol;
- (3) 20 to 40 weight percent polyhydric phenol or phenolic resin;
- (4) optionally, up to 15 weight percent liquid epoxy resin; and
- (5) optionally, a catalytic amount of a catalyst for the reaction of the epoxy resins with the polyphenol resin.

- 25 When the formulation is used as a tackifier, it preferably does not contain Components (4) and (5). When the formulation is used as a matrix resin formulation, it preferably contains Components (4) and (5).

The tackifier is useful to make tackified substrates of the present invention. The tackified substrates, matrix resin formulation and process of the present invention are useful to
30 make matrix composites. In addition, the tackifier and matrix resin formulation of the present invention may be useful for other purposes, and the tackified substrates and process may be practiced using different tackifiers and matrix resin formulations.

The present invention uses a reinforcing substrate. Suitable reinforcements are well-known and familiar to persons of ordinary skill in the art. See, for example, Kirk-Othmer,
35 Encyclopedia of Chemical Technology-Supplement, "Composites, High Performance," at 260-281 (J. Wiley & Sons, 1984). The substrate usually contains fibers, such as quartz, aramid, boron, glass, carbon or gel-spun polyethylene fibers. The fibers can be unidirectional or multidirectional. They may be in the form of woven or non-woven mats or in the form of

random short fibers. Preferably, the substrate is in the form of a woven or non-woven fibrous material.

The substrate is contacted with a tackifier under conditions such that the tackifier partially adheres to the fibers. The tackifier should be a solid or a glassy solid up to
5 temperatures of at least 40°C. It preferably becomes flowable and tacky at a temperature of at least 40°C, more preferably up to at least 50°C and most preferably up to at least 60°C. It is preferably an injectable liquid at a temperature of less than 200°C, more preferably at a temperature of less than 175°C and most preferably at a temperature of less than 150°C. (The same temperature criteria are preferably met individually by each component in the tackifier.)

10 The tackifier contains: (a) at least one epoxy resin, and (b) at least one curing agent which is capable of reacting with the epoxy resin, but (c) no catalytic amount of catalyst for the reaction between the epoxy resin and the curing agent.

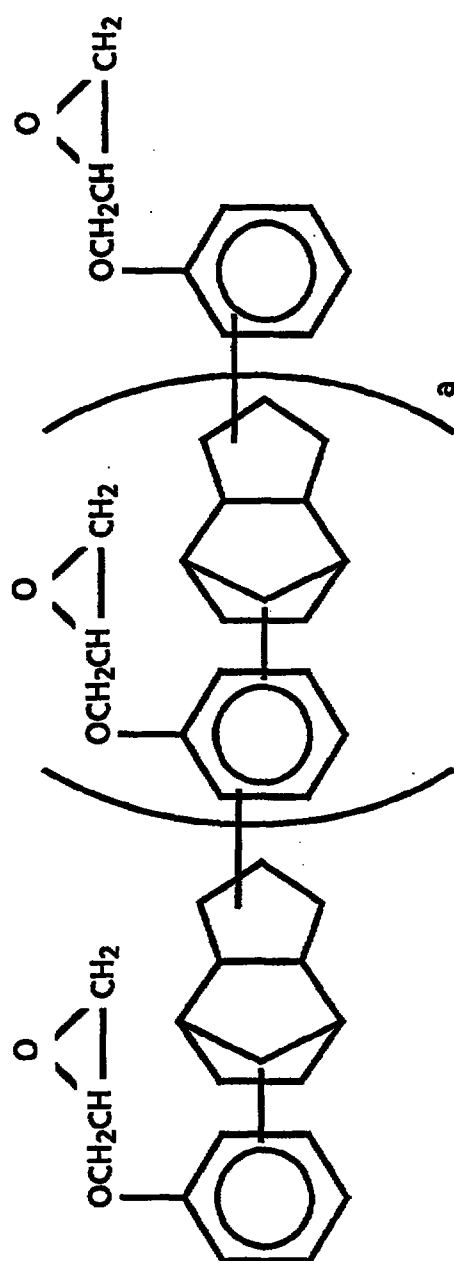
The epoxy resins are preferably poly(glycidyl ethers) of one or more polyhydric phenols, such as biphenols, bisphenols (such as bisphenol A or bisphenol F), novolac resins,
15 phenol-hydrocarbon resins and halogenated variations of those resins. A more preferred epoxy resin mixture contains a mixture of: (1) a poly(glycidyl ether) of a phenol-hydrocarbon resin, and (2) a diglycidyl ether of a halogenated bisphenol.

Examples of phenol-hydrocarbon resins, their glycidyl ethers and processes to make them are described in Nelson et al., U.S. Patent 4,390,680 (June 28, 1983); Nelson,
20 U.S. Patent 4,394,497 (July 19, 1983); and Bogan et al., U.S. Patent 4,710,429 (December 1, 1987). The phenol-hydrocarbon resin is highly preferably a condensation product of dicyclopentadiene and phenol, such as is represented in the following formula:

25

30

35



wherein "a" represents an average number of repeating units which is preferably 0 to 10, more preferably 0 to 5 and most preferably 0 to 2. The epoxy-equivalent weight (EEW) of the phenol-hydrocarbon resin is preferably between 175 and 400, and more preferably between 200 and 260.

- 5 The diglycidyl ether of a halogenated bisphenol is preferably a diglycidyl ether of a brominated bisphenol, more preferably a diglycidyl ether of brominated bisphenol A and most preferably a diglycidyl ether of tetrabromobisphenol A.

- The curing agent is preferably selected such that it will not substantially cure with the epoxy resin at ambient temperatures without a catalyst. Examples of preferred curing
10 agents include: polyhydric phenols and/or phenolic resins, carboxylic acids, carboxylic acid anhydrides or mixtures thereof.

- Polyhydric phenols and/or phenolic resins which are useful as curing agents preferably contain on average more than 2 phenolic hydroxyl groups per molecule and more preferably at least 3 phenolic hydroxyl groups per molecule. The maximum number of
15 phenolic hydroxyl groups is not critical, but is limited by practical considerations, such as viscosity and glass-transition temperature. In most cases, the polyhydric phenol or phenolic resin preferably contains on average no more than 12 phenolic hydroxyl groups per molecule and more preferably contains on average no more than 8 phenolic hydroxyl groups per molecule. The polyphenol is preferably a novolac resin and more preferably a cresol-novolac
20 resin.

 The tackifier may optionally contain other, non-catalytic components. For instance, the tackifier may contain thermoplastic polymers, rubbers or elastomers, or other modifiers.

- The tackifier should not contain a catalytic amount of any catalyst for the reaction
25 between the curing agent and the epoxy resin. Examples of catalysts include: amines and ammonium compounds, phosphine and phosphonium compounds, aliphatic sulfonium and arsonium compounds, and heterocyclic nitrogen-containing compounds. More specific examples of catalysts are described in: Bertram et al., U.S. Patent 4,594,291 (June 10, 1986) (Column 8, line 59 to Column 9, line 11); and Bertram et al., U.S. Patent 5,134,239 (July 28, 1992)
30 (Column 2, line 15 to Column 23, line 29). The tackifier preferably contains less than 0.05 weight percent catalyst, more preferably less than 0.01 weight percent catalyst and most preferably about 0 weight percent catalyst.

- The epoxy resins, curing agents and other components are blended to make the tackifier. They are preferably melt-blended, cooled to solidify the melt and then ground to a
35 powder. The average particle diameter of the tackifier is preferably no more than 150 μm , more preferably no more than 100 μm and most preferably no more than 75 μm . The minimum average particle diameter is not critical and is limited by practical considerations, such as handling and application. In most cases, the average particle diameter is preferably at least

45 μm and more preferably at least 50 μm . It is theorized (without intending to be bound) that in the curing step, the catalyst in the matrix resin formulation can initiate curing reactions at the surface of the particle, which continue into the center of the particle. Therefore, it is advantageous to use a small particle size.

5 The tackifier should be applied to the substrate in a quantity great enough to hold the fibers in the desired shape and position, but small enough to leave the resulting preform porous, so that, later, the matrix resin formulation can infuse throughout the substrate. The quantity of tackifier is preferably at least 0.25 weight percent of the substrate, more preferably at least 1 weight percent and most preferably at least 3 weight percent. The
10 quantity of tackifier is preferably no more than 15 weight percent of the substrate, more preferably no more than 8 weight percent and most preferably no more than 5 weight percent.

 The tackifier may be applied by known methods for powders, such as by sprinkling or electrostatic application. It is preferably applied substantially evenly across the substrate. The tackifier is heated above its glass-transition temperature to cause it to adhere to
15 the fibers and to adhere the fibers together. This step may be carried out either when the tackifier is applied or afterward. The temperature is preferably low enough that the tackifier does not cure substantially. The temperature is preferably between 40°C and 150°C, and more preferably between 80°C and 110°C.

 Individual plies of tackified substrate are preferably shaped and/or laminated
20 together to make a preform after the tackifier is applied and before the composite is made. For instance, multiple plies may be pressed together at a temperature above the glass-transition temperature of the tackifier. Likewise, individual plies or laminated preforms may be molded or shaped at a temperature that is above the glass-transition temperature of the tackifier and that does not fully cure the tackifier. The temperature is preferably as previously
25 described for adhering the tackifier. Examples of shaping and laminating different preforms are described in: Heck, U.S. Patent 4,992,228 (February 12, 1991); and Flonc, U.S. Patent 5,080,851 (January 14, 1992).

 The preforms are used for resin transfer molding by: (1) loading the preform into a mold; (2) injecting a matrix resin formulation into the mold; and (3) curing the matrix resin
30 formulation. (Theoretically, the tackifier cures simultaneously with the matrix resin, although direct observation to verify simultaneous curing is difficult.) The matrix resin formulation contains at least one epoxy resin and at least one curing agent. The description and preferred embodiments of the epoxy resin and curing agent are the same as previously described for the tackifier. However, the matrix resin formulation optionally contains some resins of lower
35 molecular weight which reduces the melt viscosity of the formulation. Moreover, the matrix resin formulation should contain a catalytic amount of a catalyst for the reaction between the epoxy resin and the curing agent.

The epoxy resin(s) and curing agent(s) in the matrix resin formulation are preferably essentially identical to the epoxy resin(s) and curing agent(s) in the tackifier, so that the tackifier and matrix resin formulation cure to provide essentially equivalent cured polymers. For instance, the epoxy resin and curing agent components of the tackifier and the

5 matrix resin formulation:

- (a) preferably contain essentially the same reactive sites as the curing agent;
- (b) preferably have in common at least 50 percent of backbone units that link the reactive sites, more preferably at least 80 or 90 percent, and most preferably essentially all;
- 10 (c) preferably have weight average molecular weights that differ from each other by no more than a 5:1 ratio, more preferably no more than a 3:1 ratio and most preferably no more than a 2:1 ratio;
- (d) preferably have average equivalent weights that differ from each other by no more than a 5:1 ratio, more preferably no more than a 3:1 ratio, more highly
- 15 preferably no more than a 2:1 ratio and most preferably by no more than a 1.5:1 ratio; and
- (e) preferably differ by no more than 50 percent, more preferably no more than 25 percent and most preferably no more than 10 percent in their concentration in the formulation.

20 Suitable catalysts for the matrix resin formulation have already been described and are well known in the art. The catalyst is preferably an amine, a phosphonium salt or an imidazole. It more preferably contains a 2-alkylimidazole, a tetraalkylphosphonium salt or an alkyl tritolylphosphonium salt. The concentration of catalyst is preferably at least 0.05 weight percent and more preferably at least 0.1 weight percent. The maximum concentration of

25 catalyst is not critical and is limited primarily by practical considerations, such as cost, cure time and properties of the cured resin. In most cases, the concentration of catalyst is preferably no more than 5 weight percent and more preferably no more than 2 weight percent.

The quantity of matrix resin formulation should be sufficient to hold the fibers together, to maintain fiber alignment and, preferably, to transfer loads around broken fibers.

30 It is usually preferable to minimize the quantity of matrix resin formulation in the composite. After curing, the matrix resin formulation and tackifier preferably make up at least 25 volume percent of the composite and more preferably make up at least 35 volume percent. The matrix resin formulation and tackifier are preferably no more than 75 volume percent of the composite, more preferably no more than 45 volume percent and most preferably no more

35 than 40 volume percent.

The matrix resin formulation is preferably applied under sufficient pressure to force it throughout the preform, so that the preform is impregnated with resin and voids within the cured composite are minimized. The matrix resin formulation is preferably applied

at pressures from a vacuum of 600 psig. There is frequently a pressure drop across the mold, so that pressure at the inlet may be as high as 400 psig while pressure at the outlet is 50 psig or lower. The cured composite preferably contains no more than 5 volume percent voids, more preferably no more than 2 volume percent voids and most preferably no more than 1 volume percent voids.

The matrix resin formulation and tackifier are then subjected to temperature and other conditions suitable to fully cure them. Again, the optimum time and temperature varies widely depending upon the matrix resin formulation and tackifier used and will be familiar to persons skilled in the art. The final curing step is preferably 30 to 120 minutes at a temperature of 90°C to 180°C. However, for some matrix formulations, the best curing temperature may be as high as 250°C or more. The final curing step is preferably completed in a mold that can provide a composite of the desired shape.

The resulting cured composite can be cooled, finished and used in the ordinary manner for matrix composites.

A preferred resin formulation for use in tackifiers and matrix resins contains:

- (1) 30 to 50 weight percent epoxy resin derived from a phenol-hydrocarbon resin, more preferable 35 to 45 weight percent and most preferably 40 to 43 weight percent;
- (2) 20 to 30 weight percent diglycidyl ether of a halogenated dihydric phenol and more preferably 25 to 30 weight percent;
- (3) 20 to 40 weight percent polyphenol resin, more preferably 25 to 35 weight percent and most preferably 27 to 33 weight percent; and
- (4) optionally, up to 15 weight percent liquid epoxy resin, more preferably up to 10 weight percent and most preferably up to 4 weight percent.

The foregoing percentages are excluding the weight of solvent, if any. The formulation may further contain organic solvent when it is used as a matrix resin formulation, but it preferably does not. The solids concentration is preferably at least 50 weight percent, more preferably at least 75 weight percent and most preferably at least 99 weight percent. When the formulation is used as a tackifier, Element (4) is preferably not used. When the formulation is used as a matrix resin, Element (4) is preferably used. Formulations which contain liquid epoxy resin - Element (4) - preferably contain at least 1 weight percent. The formulation may also contain catalyst, optionally. The preferred minimum quantities of catalyst are as discussed previously.

The process of the present invention is more fully illustrated in the following examples.

Examples

The following example is for illustrative purposes only and should not be taken as limiting the scope of either the Specification or the Claims. Unless otherwise stated, all parts and percentages are by weight.

5 The following materials are used in the example:

Epoxy Resin A - is a diglycidyl ether of tetrabromobisphenol having an epoxide equivalent weight (EEW) of 305 to 355, that is commercially available from The Dow Chemical Company as D.E.R.* 542 epoxy resin.

10 Epoxy Resin B - is the polyglycidyl ether of a dicyclopentadiene-phenol oligomer. Epoxy Resin B contains on average about 3.2 epoxy groups per molecule and has an EEW of about 255.

Epoxy Resin C - is the polyglycidyl ether of a dicyclopentadiene-phenol oligomer. Epoxy Resin C contains on average about 2.2 epoxy groups per molecule and has an EEW of 215 to 235. It is commercially available from The Dow Chemical Company as TACTIX* 556 epoxy resin.

Epoxy Resin D - is liquid diglycidyl ether of bisphenol A having an EEW of 172 to 176.

15 Novolac Resin E - is a cresol novolac resin containing about 6 phenolic hydroxyl groups per molecule, which is commercially available from Schenectady Chemicals, Inc. as CRJ-406.

Catalyst F - is a product obtained by mixing tetrabutylphosphonium acetate-acetic acid complex and fluoboric acid.

20 Example 1 - Process Using Mixture of Phenol-Hydrocarbon Epoxy Resin and Halogenated Epoxy Resin.

A tackifier was made by the following procedure. A 5,663 g quantity of Epoxy Resin A and a 3,215.5 g quantity of Epoxy Resin B were melted separately at 150°C. Both resins were mixed in a reactor at 145°C. An additional 7,014.5 g of Resin B flakes were added to the molten mixture and 6,770 g of Novolac E flakes were added. The mixture was stirred for
25 50 minutes and then drained onto foil and cooled to room temperature to solidify. The solid mixture was broken, ground and sieved to an average particle diameter of no more than 106 μ m.

30 A tackified cloth was made by sprinkling the tackifier on carbon cloth, heating the tackifier to 200°F to melt it and then cooling the tackifier. The cloth contained 4 weight percent tackifier at the end of the procedure.

A preform was made using 8 plies of tackified cloth. The plies were stacked in a vacuum bag apparatus and a vacuum was pulled to put 1 atmospheric pressure on the stack of plies. The plies were then heated to 200°F (93°C) and cooled to room temperature to make a preform.

35 A composite was made using the preform. The preform was placed into a matched die mold, which was sealed and placed under vacuum. A matrix resin formulation was injected into the mold. The formulation contained: 26 weight percent Epoxy Resin A, 42 weight percent Epoxy resin C, 3 weight percent Epoxy Resin D, 30 weight percent Novolac

Resin E and 1 weight percent Catalyst F. The panel was cured for three hours at 177°C. The product is a composite panel.

5

10

15

20

25

30

35



THIS SHEET HAS BEEN
REPLACED

WO 96/37354

PCT/US96/07161

CLAIMS:

1. A tackified substrate comprising:
 - (1) a fibrous substrate suitable for use in a matrix composite; and
 - (2) 0.25 to 15 weight percent of a tackifier containing:
 - 5 (a) at least one epoxy resin;
 characterized in that the tackifier substrate further contains:
 - (b) at least one curing agent for the epoxy resin; but
 - (c) 0 to less than 0.5 weight percent of the following compounds which act as catalysts for a curing reaction between Components (a) and (b): amines and ammonium compounds, phosphine and phosphonium compounds, aliphatic sulfonium compounds and arsonium, and heterocyclic nitrogen-containing compounds.
2. A tackified substrate as described in Claim 1 wherein curing agent of Component (b) contains any one or more of: a polyhydric phenol or phenolic resin, a carboxylic acid or a carboxylic acid anhydride.
3. The tackified substrate of Claim 2 wherein the tackifier becomes flowable and tacky at a temperature between 40°C and 200°C.
4. The tackified substrate of Claim 2 wherein at least one epoxy resin is a glycidyl ether derivative of a phenol-hydrocarbon resin.
- 20 5. A tackified substrate as described in Claim 2 wherein the curing agent is a polyhydric phenol or phenolic resin.
6. A tackified substrate as described in Claim 2 wherein the tackifier contains:
 - (1) 30 to 50 weight percent epoxy resin derived from a phenol-hydrocarbon resin;
 - (2) 20 to 30 weight percent diglycidyl ether of a halogenated dihydric phenol; and
 - 25 (3) 20 to 40 weight percent polyhydric phenol or phenolic resin.
7. A method to use a tackified substrate as described in any of Claims 1 to 6 comprising the steps of:
 - (1) placing one or more of the tackified substrates as described in any of Claims 1 to 6, individually or as a preform, in a mold;
 - 30 (2) injecting into the mold one or more matrix resin formulations which contain:
 - (a) an epoxy resin, and
 - (b) a curing agent for the epoxy resin, and
 - (c) a catalytic amount of catalyst for the reaction between the epoxy resin and the curing agent; and
 - 35 (3) curing the matrix resin formulation.
8. A formulation comprising:
 - (1) 30 to 50 weight percent epoxy resin derived from a phenol-hydrocarbon resin;
 - (2) 20 to 30 weight percent diglycidyl ether of a halogenated dihydric phenol;



THIS SHEET HAS BEEN
REPLACED

WO 96/37354

PCT/US96/07161

- (3) 20 to 40 weight percent polyhydric phenol or phenolic resin;
(4) optionally, up to 15 weight percent liquid epoxy resin; and
wherein such weight percentages exclude the weight of solvent, if any.

9. A formulation as described in Claim 8 which does not contain any of
5 Components (4) or (5).

10. A formulation as described in Claim 8 which contains 1 to 15 weight percent
of liquid epoxy resin and which contains 0.05 to 5 weight percent of at least one catalyst.

10

15

20

This Sheet Has Been Replaced



25

30

35



2061

THIS SHEET HAS BEEN
REPLACED

1. A tackified substrate comprising:

(1) a fibrous substrate suitable for use in a matrix composite; and

(2) 0.25 to 15 weight percent of a tackifier containing:

(a) at least one epoxy resin;

This Sheet Has Been Replaced



5 characterized in that the tackifier substrate further contains:

(b) at least one curing agent for the epoxy resin wherein the curing agent is a polyhydric phenol, phenolic resin, carboxylic acid or mixtures thereof; and

10 (c) 0 to less than 0.5 weight percent of the following compounds which act as catalysts for a curing reaction between Components (a) and (b): amines and ammonium compounds, phosphine and phosphonium compounds, aliphatic sulfonium compounds and arsonium, and heterocyclic nitrogen-containing compounds.

15 2. A tackified substrate as described in Claim 1 wherein curing agent of Component (b) contains any one or more of: a polyhydric phenol or phenolic resin, a carboxylic acid or a carboxylic acid anhydride.

3. The tackified substrate of Claim 2 wherein the tackifier becomes flowable and tacky at a temperature between 40°C and 200°C.

4. The tackified substrate of Claim 2 wherein at least one epoxy resin is a glycidyl ether derivative of a phenol-hydrocarbon resin.

20 5. A tackified substrate as described in Claim 2 wherein the curing agent is a polyhydric phenol or phenolic resin.

6. A tackified substrate as described in Claim 2 wherein the tackifier contains:

(1) 30 to 50 weight percent epoxy resin derived from a phenol-hydrocarbon resin;

25 (2) 20 to 30 weight percent diglycidyl ether of a halogenated dihydric phenol; and

(3) 20 to 40 weight percent polyhydric phenol or phenolic resin.



42061.

THIS SHEET HAS BEEN
REPLACED

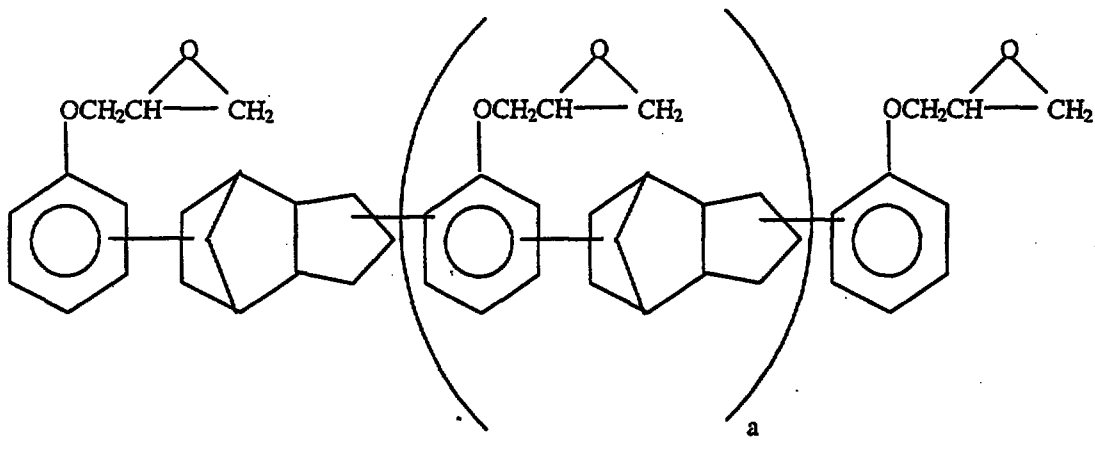
7. A method to use a tackified substrate as described in any of Claims 1 to 6 comprising the steps of:

- (1) placing one or more of the tackified substrates as described in any of Claims 1 to 6, individually or as a preform, in a mold;
- 5 (2) injecting into the mold one or more matrix resin formulations which contain:
 - (a) an epoxy resin, and
 - (b) a curing agent for the epoxy resin wherein the curing agent is a polyhydric phenol, phenolic resin, carboxylic acid or mixtures thereof; and
 - (c) a catalytic amount of catalyst for the reaction between the epoxy resin
- 10 (3) curing the matrix resin formulation.

This Sheet Has Been Replaced



1. A tackified substrate comprising:
- (1) a fibrous substrate suitable for use in a matrix composite; and
 - (2) about 0.25 to 15 weight percent of a tackifier containing:
 - (a) a phenol-hydrocarbon resin glycidyl derivative represented by the formula:



wherein "a" represents an average number of repeating units which is 0 to 10.

- (b) at least one curing agent containing at least one compound selected from the group consisting of a polyhydric phenol or phenolic resin, a carboxylic acid or a carboxylic acid anhydride, and
- (c) 0 to less than 0.05 weight percent of a catalyst selected from the group consisting of amines and ammonium compounds, phosphine and phosphonium compounds, aliphatic sulfonium and arsonium compounds and heterocyclic nitrogen-containing compounds, said catalyst present in the tackifier in amounts such that the catalyst does not promote a curing reaction between Components (a) and (b).



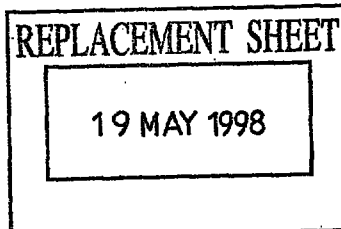
2. A tackified substrate as described in Claim 1 wherein curing agent of Component (b) contains any one or more of : a polyhydric phenol or phenolic resin, a carboxylic acid or a carboxylic acid anhydride.

3. The tackified substrate of Claim 2 wherein the tackifier becomes flowable and tacky at a temperature between 40°C and 200°C.

4. A tackified substrate as described in Claim 2 wherein the curing agent is a polyhydric phenol or phenolic resin.

5. A method to use a tackified substrate as described in any of Claims 1 to 4 comprising the steps of:

- (1) placing one or more of the tackified substrates as described in any of Claims 1 to 4, individually or as a preform, in a mold;
- (2) injecting into the mold one or more matrix resin formulations which contain:
 - (a) an epoxy resin; and
 - (b) a curing agent for the epoxy resin wherein the curing agent is polyhydric phenol, phenolic resin, carboxylic acid or mixtures thereof; and
 - (c) a catalytic amount of catalyst for the reaction between the epoxy resin and the curing agent; and
- (3) curing the matrix resin formulation.





PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B29B 11/16, B29C 70/48, C08G 59/38	A2	(11) International Publication Number: WO 96/37354 (43) International Publication Date: 28 November 1996 (28.11.96)
(21) International Application Number: PCT/US96/07161 (22) International Filing Date: 17 May 1996 (17.05.96) (30) Priority Data: 08/449,378 23 May 1995 (23.05.95) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: BURTON, Bruce, L.; 55 Flag Court, Lake Jackson, TX 77566 (US). HUNTER, Douglas, L.; R.R. 3, 410 Austin Drive, Angleton, TX 77515 (US). PUCKETT, Paul, M.; 115 Poinciana, Lake Jackson, TX 77566 (US). (74) Agent: MAURER, Charles, J., III; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641- 1967 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: IMPROVED PROCESS FOR RESIN TRANSFER MOLDING AND FORMULATIONS USEFUL TO PRACTISE THE PROCESS (57) Abstract An improved tackifier for making tackified substrates contains: (a) at least one epoxy resin, and (b) at least one curing agent for the epoxy resin, but (c) no catalytic amount of catalyst for the reaction between the epoxy resin and the curing agent. The tackified substrates are used to make composites by: (1) placing one or more of the tackified substrates in a mold; (2) injecting into the mold a matrix resin formulation which is chemically-similar to the tackifier, except that it contains a catalytic amount of catalyst for the reaction between the epoxy resin and the curing agent; and (3) curing the matrix resin formulation. The tackifiers are more storage-stable than similar tackifiers which contain catalyst, and the resulting composites have and/or retain physical properties better than composites made using tackifiers without curing agent.		