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(71) Applicant: **DOW GLOBAL TECHNOLOGIES LLC** [US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventors: **MORLEY, Timothy A.**; Wolleraustrasse 15a, CH-8807 Freienbach (CH). **KOENIGER, Rainer**; Wolleraustrasse 15a, CH-8807 Freienbach (CH). **GRUNDER, Sergio**; Bachtobelstrasse 3, CH-8810 Horgen (CH). **VERVOORT, Sylvie**; Ferdinand Lousbergskaai, No. 101, Flat 202, B-9000 Gent (BE). **JELIC, Nebojsa**; Wolleraustrasse 15a, CH-8807 Freienbach (CH).

(74) Agent: **XU, Hong**; The Dow Chemical Company, Intellectual Property, P. O. Box 1967, Midland, Michigan 48641-1967 (US).

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(54) Title: EPOXY RESIN SYSTEM

(57) **Abstract**: A curable resin system comprising 1) an epoxy component having a polyglycidyl ether of a polyphenol having an epoxy equivalent weight of up to about 190; and 2) a hardener component comprising polyethylene tetraamine mixture; wherein the epoxy component has a viscosity of less than 9000 mPa.s at 25°C.

EPOXY RESIN SYSTEM

FIELD OF THE INVENTION

This invention relates to an epoxy based composition and processes for preparing fiber-reinforced composites.

INTRODUCTION

For many reasons, it is in some cases potentially advantageous to replace metal structural parts with reinforced organic polymers. Among the advantages the reinforced organic polymers offer include better resistance to corrosion, the ability to produce parts having complex geometries, and in some cases a superior strength-to-weight ratio. It is this last attribute that has led, and continues to lead, the adoption of reinforced polymers in the transportation industry as replacement for metal structural elements such as chassis members and other structural supports.

Epoxy resin systems are sometimes used as the polymer phase in such composites. Cured epoxy resins are often quite strong and stiff, and adhere well to the reinforcement. An advantage of epoxy resin systems, compared to most thermoplastic systems, is that low molecular weight, low viscosity precursors are used as starting materials. The low viscosity is an important attribute because it allows the resin system to penetrate easily between and wet out the fibers that usually form the reinforcement. This is necessary to avoid cosmetic blemishes such as flow lines to produce a high strength composite, and to reduce voids in the composite structure.

The manufacturing method of choice for making these fiber-reinforced composites is a resin-transfer process, or one of its variants such as vacuum-assisted resin transfer molding (VARTM), the Seeman Composites Resin Infusion Molding Process (SCRIMP), gap resin transfer molding (also known as compression RTM) and wet compression molding. In these processes, the reinforcing fibers are formed into a preform which is placed and impregnated with a mixture of an epoxy resin component and a hardener which flows around and between the fibers, and is cured in a mold to form the composite.

To improve production efficiency, fast curing resin systems are typically desired in manufacturing of composites. Fast curing epoxy resin systems have been developed for the making of composite articles via the RTM and other processes. By their fast curing nature, these resin systems contain highly reactive components and often a significant level of catalysts. The highly reactive systems perform well in the RTM process at elevated molding temperatures (80 to 160°C) and often also with heated components (resin, hardener) to increase reaction speed and to achieve production cycle times desired by the automotive industry. However, during the development phase for a new composite structure for the automotive industry, structure development via the formation of prototypes is often required prior to the final part selection. This enables changes to be more easily made to the design of the composite structures and reduces the extensive financial outlay which would be required for the manufacture of high quality tools required to produce the final parts. Currently, due to their high reactivity, manufacturing prototype parts with fast curing RTM resin systems is extremely challenging due to the insufficient time available to mold the prototype. At lower molding temperatures (e.g., 20 to 40°C), the viscosity of the resin formulation is often too high for efficient impregnation via hand lay-up, winding, pultrusion, infusion, compression, spray or resin transfer molding techniques. At elevated temperatures (e.g., 60 to 100°C), the gelation of the resin systems is too rapid to allow part infusion.

What is desired in the industry is an epoxy resin and hardener formulation that possesses a similar final structure to that of the RTM epoxy system with similar thermal and mechanical performance while also possessing the attributes required to enable the formation of prototype components. These attributes include low viscosity at reduced molding temperatures of less than 60°C and increased latency to enable longer infusion / impregnation time.

SUMMARY OF THE INVENTION

The present invention provides a curable resin system having:

1) an epoxy component containing polyglycidyl ether of a polyphenol having a) an epoxy equivalent weight of less than 190 and b) a reduced mono hydrolyzed resin content of less than 1 wt.% based on the total weight of the polyglycidyl ether of a polyphenol; and

2) a hardener component comprising polyethylene tetraamine mixture.

The epoxy component has a viscosity of less than 9000 mPa.s at 25°C.

DETAILED DESCRIPTION OF THE INVENTION

Applicants have found a unique resin system with the combination of an epoxy component and a hardener component to provide efficient manufacturing of prototypes of composites part. The resin system is mainly a combination of an epoxy component and a hardener component.

1. The Epoxy Component

In the present invention, the epoxy component contains at least 40% by weight of polyglycidyl ether of a polyphenol having an epoxy equivalent weight less than 190. In the resin system of the present invention, the epoxy component contains about, based on the total weight of the epoxy component, more than 40 wt. %, preferably more than 50 wt. %, and more preferably more than 60 wt. % of such polyglycidyl ethers of a polyphenol resin.

The polyglycidyl ether of a polyphenol resin useful in the present invention has a lower mono hydrolyzed resin content. The resin may contain, for example and based on the total weight of the polyglycidyl ether of a polyphenol resin, no more than 1 wt. %, preferably no more than 0.75 wt. % and still more preferably no more than 0.5 wt. % of mono hydrolyzed resin content. Mono hydrolyzed resins are α-glycol compounds formed by the addition of a molecule of water to an epoxide group. The presence of significant quantities of mono hydrolyzed content tends to increase the viscosity of the epoxy component, and in turn that of the epoxy resin/hardener mixture. In addition, it is believed that these species may contribute to a reduction in open time.

The epoxy component may also contain optional ingredients. Among these are solvents or reactive diluents such as are described in WO 2008/140906, pigments, antioxidants, preservatives, impact modifiers, short (up to about 6 inches (15.24 cm) in length, preferably up to 2 inches (5.08 cm) in length, more preferably up to about ½ inch (1.27 cm) in length) reinforcing fibers, non-fibrous particulate fillers including micron- and nano-particles, wetting agents and the like. An electro-conductive filler may be present in the epoxy component.

The epoxy resin component has a viscosity of less than 9000 and preferably about 4000 to 6000 mPa.s at 25°C.

2. The Hardener Component

The hardener component of the present resin system may be a polyethylene tetraamine mixture. By "polyethylene tetraamime mixture", it is meant a mixture of polyethylene polyamine compounds, of which at least 95% by weight, based on the total weight of the mixture, have exactly four amine nitrogen atoms. For purposes of this invention, those polyethylene polyamine compounds having exactly four amine nitrogen atoms are referred to as "polyethylene tetraamine" compounds.

The polyethylene tetraamine compound can be linear, branched and/or or cyclic. At least 40% of the weight of the polyethylene tetraamine mixture is linear triethylene tetraamine, that is:

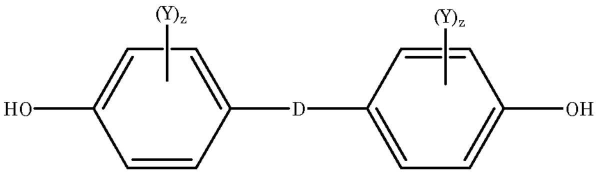
$$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2$$

Linear triethylene tetraamine may constitute at least 60%, preferably at least 90%, more preferably at least 95%, and most preferably up to 100%, of the weight of the polyethylene tetraamine mixture, based on the total weight of the mixture.

The polyethylene tetraamine mixture may include other polyethylene tetraamine compounds such as, for example, N,N'-bis(2aminoethyl)piperazine, (piperazinoethyl)ethylenediamine and tris(aminoethyl)amine. These polyethylene tetraamine compounds are commonly present in significant amounts (up to, for example 55% or up to 35% by weight based on total weight of the hardener component in the aggregate) in commercially available TETA (triethylene tetraamine) products.

The polyethylene tetraamine mixture may include small amounts of other aliphatic or cycloaliphatic amine compounds having three or fewer amine nitrogen atoms or five or more amine nitrogen atoms. These compounds preferably constitute at most 5% by weight, preferably at most 2% by weight and more preferably at most 1% by weight of the polyethylene tetraamine mixture. The polyethylene tetraamine mixture preferably contains no more than 0.3% by weight of aminoethylethanol amine.

In a preferred embodiment, the polyethylene tetraamine mixture is the only hardener in the resin system. If other hardeners are present, they preferably constitute no more than 20%, more preferably no more than 10% and still more preferably no more than 5% by weight of the hardener component. Among the other hardeners that can be used are, for example, dicyandiamide, phenylene diamine (particularly the meta-isomer), bis(4-amino-3,5-dimethylphenyl)-1,4-diiso-propylbenzene,bis(4-amino-phenyl)1,4-diiospropylbenzene, diethyl toluene diamine, methylene dianiline, mixtures of methylene dianiline and polymethylene polyaniline compounds (sometimes referred to as PMDA, including commercially available products such as DL-50 from Air Products and Chemicals), diaminodiphenylsulfone, phenolic hardeners including those represented by the structure (III)



(III)

where each Y independently represents a halogen atom, each z is independently an integer from 0 to 4 and D is a divalent hydrocarbon group as described with regard to structure I above. Examples of suitable phenolic hardeners include dihydric phenols such as bisphenol A, bisphenol K, bisphenol F, bisphenol S and bisphenol AD, and mixtures thereof, and their mono-, di-, tri- and tetra-brominated counterparts and amino-functional polyamides. These are available commercially under as Versamide® 100, 115, 125 and 140, from Henkel, and Ancamide® 100, 220, 260A and 350A, from Air Products and Chemicals.

In one preferred embodiment, the hardener component of the present invention contains over 90 wt. % of triethylenetetramine and the rest being 1,4-diaza-bicyclo[2,2,2]octane, based on the total weight of the hardener component.

3. The Resin System

The hardener component and epoxy component are combined in amounts such that at least 0.8 epoxy equivalents are provided to the reaction mixture of the two components per amine hydrogen equivalent provided by the epoxy component. A preferred amount is at least 0.9 epoxy equivalents per amine hydrogen equivalent and a still more preferred amount is at least 1.0 epoxy equivalents per amine hydrogen equivalent. The epoxy component can be provided in large excess, such as up to 10 epoxy equivalents per amine hydrogen equivalent provided to the reaction mixture, but preferably there are no more than 2, more preferably no more than 1.25 and still more preferably no more than 1.10 epoxy equivalents provided per amine hydrogen equivalent. Embodiments in which the hardener is present in a small excess (for example from 0.0 to 0.80 epoxy equivalents per equivalent of amine hydrogens) often exhibit particularly short demold times while producing a cured resin having a high glass transition temperature. In general the weight ratio between epoxy component to hardener component is between 100:11 to 100:20 but preferably between 100:12 to 100:19.

In one embodiment, triethylene diamine is provided to the reaction mixture of epoxy and hardener components and performs a catalytic role. A suitable amount is about 0.01 to 0.5 moles of triethylene diamine per part per mole of per mole of primary and/or secondary amine compounds in the amine hardener. A preferred lower amount is 0.025 moles and a more preferred lower amount is 0.05 moles of triethylene diamine per mole of per mole of primary and/or secondary amine compounds in the amine hardener. A preferred upper amount is up to 0.25 moles and a more preferred upper amount is up to 0.20 moles of triethylene diamine, in each case per mole of primary and/or secondary amine compounds in the amine hardener. An especially preferred amount is 0.09 to 0.175 moles of triethylene diamine per mole of primary and/or secondary amine compounds in the amine hardener.

The catalyst can be used in conjunction with one or more other catalysts. If such an added catalyst is used, suitable such catalysts include those described in, for example, U.S. Patent Nos. 3,306,872, 3,341,580, 3,379,684, 3,477,990, 3,547,881, 3,637,590, 3,843,605, 3,948,855, 3,956,237, 4,048,141, 4,093,650, 4,131,633, 4,132,706, 4,171,420, 4,177,216, 4,302,574, 4,320,222, 4,358,578, 4,366,295, and 4,389,520, and WO 2008/140906, all incorporated herein by reference. Examples of suitable catalysts are imidazoles such as 2-methylimidazole; 2-ethyl-4-methylimidazole; 2-phenyl imidazole; tertiary amines such as triethylamine, tripropylamine, N,N-dimethyl-1-phenylmethaneamine and 2,4,6-tris((dimethylamino)methyl)phenol and tributylamine; phosphonium salts such as ethyltriphenylphosphonium chloride, ethyltriphenyl-phosphonium bromide and ethyltriphenyl-phosphonium acetate; ammonium salts such as benzyltrimethylammonium chloride and benzyltrimethylammonium hydroxide; various carboxylic acid compounds, and mixtures any two or more thereof.

In some other embodiments, the triethylene diamine is the sole catalyst provided to the reaction mixture. It is noted that the hardener components are not, for purposes of this invention, considered as catalysts.

In some embodiments, the reaction mixture, that is, the resin system of the present invention, contains water and/or a compound having at least one hydroxyl group and an equivalent weight per hydroxyl group of up to 75, preferably up to 50. This compound, if present, is suitably present in small amounts, such as from 0.1 to 10 parts by weight, preferably from 0.25 to 5 parts and still more preferably from 1 to 3 parts by weight per part by weight of triethylene diamine. Besides water, suitable such compounds include, for example, alkanols such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, neopentanol, 1-hexanol and the like; alkylene glycols such as ethylene glycol, 1,2-propane diol, 1,3-propane diol, 1,4-butane diol, and neopentyl glycol; poly(alkylene glycols) such as diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol and the like; glycol monoethers such as ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, 1,2-propane diol monomethyl ether, dipropylene glycol monomethyl ether, as well as the corresponding ethyl ethers; glycol monoesters such as ethylene glycol monacetate, diethylene glycol monoacetate, 1,2-propane diol monoacetate, dipropylene glycol monoacetate; higher functionality polyols such as glycerin, oligomers of glycerin, trimethylolpropane, trimethylolethane, pentaerythritol, erythritol, sorbitol, sucrose and the like; and mono- di- or trialkanolamines such as monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine, aminoethylethanolamine and the like.

The curable reaction mixture may also contain other optional components such as impact modifiers, internal mold release agents (IMR), pigments, antioxidants, preservatives, reinforcing fibers short (up to about 6 inches (15.24 cm) in length, preferably up to 2 inches (5.08 cm) in length, more preferably up to about ½ inch (1.27 cm) in length), non-fibrous particulate fillers including micron- and nanoparticles, wetting agents, internal mold release agents and the like. An electroconductive filler may be present in the hardener mixture.

Suitable impact modifiers include natural or synthetic polymers having a T_g of lower than -40°C. These include natural rubber, styrene-butadiene rubbers, polybutadiene rubbers, isoprene rubbers, polyethers such as poly(propylene oxide), poly(tetrahydrofuran) and butylene oxide-ethylene oxide block copolymers, core-shell rubbers, mixtures of any two or more of the foregoing, and the like. The rubbers are preferably present in the form of small particles that become dispersed in the polymer phase of the resin system. The rubber particles can be dispersed within the epoxy resin or hardener and preheated together with the epoxy resin or hardener prior to forming the hot reaction mixture.

It is generally preferred to cure the epoxy resin and the hardener mixture in the presence of an internal mold release agent. Such an internal mold release agent may constitute up to 5%, more preferably up to about 1% of the total weight of the reaction mixture. Suitable internal mold release agents are well known and commercially available, including those marketed as Marbalease™ by Rexco-USA, Mold-Wiz™ by Axel Plastics Research Laboratories, Inc., Chemlease™ by Chem-Trend, PAT™ by Würtz GmbH, Waterworks Aerospace Release by Zyvax and Kantstik™ by Specialty Products Co. In addition to (or instead of) adding the internal mold release agent during mixing, it is also possible to combine such an internal mold release agent into the epoxy component and/or the hardener component before the epoxy component and the hardener component are brought together.

Suitable particulate fillers have an aspect ratio of less than 5, preferably less than 2, and do not melt or thermally degrade under the conditions of the curing reaction. Suitable fillers include, for example, glass flakes, aramid particles, carbon black, carbon nanotubes, various clays such as montmorillonite, and other mineral fillers such as wollastonite, talc, mica, titanium dioxide, barium sulfate, calcium carbonate, calcium silicate, flint powder, carborundum, molybdenum silicate, sand, and the like. Some fillers are somewhat electroconductive, and their presence in the composite can increase the electroconductivity of the composite. In some applications, notably automotive applications, it is preferred that the composite is sufficiently electroconductive that coatings can be applied to the composite using so-called “e-coat” methods, in which an electrical charge is applied to the composite and the coating becomes electrostatically attracted to the composite. Conductive fillers of this type include metal particles (such as aluminum and copper), carbon black, carbon nanotubes, graphite and the like.

In some embodiments, the present resin system has, when cured at least one temperature between 100 and 150°C, a gel time of at least 10 seconds, at least 15 seconds, or preferably at least 20 seconds, and a demold time no greater than 300 seconds, preferably no greater than 240 seconds and still more preferably no greater than 120 seconds. In some embodiments, the demold time is no greater than 120 seconds or no greater than 60 seconds at this temperature. Gel time and demold time are for purposes of this invention measured by using a KraussMaffei Rim Star RTM 4/4 high-pressure injection machine where the gel time is measured during a curing evaluation test as described in the testing methods section of this application.

Thermoset resins are formed from the resin system of the invention by mixing the epoxy component and hardener component at proportions as described above and curing the resulting mixture. Either or both of the components can be preheated if desired before they are mixed with each other. It is generally necessary to heat the mixture to an elevated temperature to obtain a rapid cure. In a molding process such as the process for making molded composites, the curable reaction mixture is introduced into a mold, which may be, together with any reinforcing fibers and/or inserts as may be contained in the mold, preheated. The curing temperature may be, for example, from 60 to 180°C. When a long (at least 10 seconds, preferably at least 20 seconds) gel time is desirable, the curing temperature preferably is not greater than

160°C. When both a long gel time and a short demold time is wanted, a suitable curing temperature is 80 to 160°C, preferably 100 to 150°C and especially 110 to 140°C.

It is preferred to continue the cure until the resulting resin system attains a glass transition temperature in excess of the cure temperature. The glass transition temperature at the time of demolding is preferably at least 120°C, more preferably at least 130°C, still more preferably at least 140°C and even more preferably at least 150°C. An advantage of this invention is that such glass transition temperatures can be obtained with short curing times. This allows for short cycle times. Demold times at cure temperatures of 100 to 150°C, especially 110 to 140°C, are typically 300 seconds or less, preferably are 240 seconds or less and more preferably 180 seconds or less. In some embodiments, the demold time at such temperatures is no more than 120 seconds or no more than 60 seconds.

4. The Composites and the Process of Making the Composite

The curable epoxy resin system of the invention is particularly useful for making fiber-reinforced composites by curing the system in the presence of reinforcing fibers. These composites are in general made by mixing the epoxy component with the hardener component to form a mixture or the resin system of the present invention, wetting the fibers with the mixture, and then curing the mixture in the presence of the catalyst and the reinforcing fibers.

The reinforcing fibers are thermally stable and have a high melting temperature, such that the reinforcing fibers do not degrade or melt during the curing process. Suitable fiber materials include, for example, glass, quartz, polyamide resins, boron, carbon, wheat straw, hemp, sisal, cotton, bamboo and gel-spun polyethylene fibers.

The reinforcing fibers can be provided in the form of short (0.5 to 15 cm) fibers, long (greater than 15 cm) fibers or continuous rovings. The fibers can be provided in the form of a mat or other preform if desired; such mats or preforms may in some embodiments be formed by entangling, weaving and/or stitching the fibers, or by binding the fibers together using an adhesive binder. Preforms may approximate the size and shape of the finished composite article (or portion thereof that requires reinforcement). Mats of continuous or shorter fibers can be stacked and pressed together, typically with the aid of a tackifier, to form preforms of various thicknesses, if required.

Suitable tackifiers for preparing preforms (from either continuous or shorter fibers) include heat-softenable polymers such as described, for example, in U. S. Patent Nos. 4,992,228, 5,080,851 and 5,698,318. The tackifier should be compatible with and/or react with the polymer phase of the composite, so that there is good adhesion between the polymer and reinforcing fibers. A heat-softenable epoxy resin or mixture thereof with a hardener, as described in U. S. Patent No. 5,698,318, is especially suitable. The tackifier may contain other components, such as one or more catalysts, a thermoplastic polymer, a rubber, or other modifiers.

A sizing or other useful coating may be applied onto the surface of the fibers before they are introduced into the mold. A sizing often promotes adhesion between the cured epoxy resin and the fiber surfaces.

The composite may be formed in a mold. In such a case, the reinforcing fibers may be introduced into the mold before the epoxy/hardener mixture. This is normally the case when a fiber preform is used. The fiber preform is placed into the mold, the mold is closed, and the epoxy resin/hardener mixture is then introduced into the mold, where it penetrates between the fibers in the preform, fills the cavity, and then cures to form a composite product.

Alternatively, the fibers (including a preform) can be deposited into an open mold, and the reaction mixture can be sprayed, poured or injected onto the preform and into the mold. After the mold is filled in this manner, the mold is closed and the resin system cured. An example of a process of this type is gap compression resin transfer molding, in which the mold containing the fibers is kept open with a gap which may be, for examples 10 to 100% or more of the original cavity thickness. The gap permits lower flow resistance, which makes mold filling easier and facilitates penetration of the reaction mixture around and between the fibers.

Short fibers can be introduced into the mold with the resin system. Such short fibers may be, for example, blended with the epoxy component or hardener component (or both) prior to forming the reaction mixture. Alternatively, the short fibers may be added into the reaction mixture at the same time as the epoxy and hardener are mixed, or afterward but prior to introducing the hot reaction mixture into the mold.

Alternatively, short fibers can be sprayed into a mold. In such cases, the reaction mixture can also be sprayed into the mold, at the same time or after the short fibers are sprayed in. When the fibers and reaction mixture are sprayed simultaneously, they can be mixed together prior to spraying. Alternatively, the fibers and reaction mixture can be sprayed into the mold separately but simultaneously. The sprayed materials may be spread and/or leveled using a doctor blade or similar device before closing the mold and performing the cure. In a process of particular interest, long fibers are chopped into short lengths and the chopped fibers are sprayed into the mold, when or immediately before the hot reaction mixture is sprayed in. Mesh materials often function as flow promoters.

A wet compression process can be used, in which the reaction mixture is applied directly to a fiber preform or stack without injection by spraying (as in the PUpreg or Baypreg processes), or by laying it down as “bands” of system, which are being fed through a wider slit die, which could have a width of 1 cm to 50 cm or more. Sufficient material is applied to reach the desired fiber volume content in the final product. The reaction mixture can be applied to the fibers inside an open mold, or outside the mold. The reaction mixture may instead be applied to the center layer of a build up, by wetting a layer of fibers with the reaction mixture and then putting a second layer of fibers onto the wetted surface, therefore sandwiching the resin layer in between two layers of fibers. The fiber mats can be made out of non crimped fiber buildups, of woven fabric, of random fiber build-ups or preforms. If the reaction mixture is applied to the fibers outside of the mold, it is typically applied at a somewhat low temperature, to prevent premature curing, and to increase the viscosity of the reaction mixture so it does not drip off the fibers before they are transferred into the mold. The wetted preform is then placed into the lower half of a hot mold, the mold is closed and the material cured under compression.

Composites made in accordance with the invention may have fiber contents of at least 10 volume percent, preferably at least 25 volume percent or at least 35 volume percent, up to 80 volume percent, preferably up to 70 volume percent, more preferably up to 60 volume percent.

The mold may contain, in addition to the reinforcing fibers, one or more inserts. Such inserts may function as reinforcements, may function as flow promoters, and in some cases may be present for weight reduction purposes. Examples of such inserts include, for example, wood, plywood, metals, various polymeric materials, or glass, which may be foamed or unfoamed, such as polyethylene, polypropylene, another polyolefin, a polyurethane, polystyrene, a polyamide, a polyimide, a polyester, polyvinylchloride and the like, various types of composite materials, and the like, that do not become distorted or degraded at the temperatures encountered during the molding step.

The reinforcing fibers and core material, if any, may be enclosed in a bag or film such as is commonly used in vacuum assisted processes.

The mold and the preform (and any other inserts, if any) may be heated to the curing temperature or some other useful elevated temperatures prior to contacting them with the reaction mixture. The mold surface may be treated with an external mold release agent, which may be solvent or water-based.

The particular equipment that is used to mix the components of the reaction mixture and transfer the mixture to the mold is not considered to be critical to the invention, provided the reaction mixture can be transferred to the mold before it attains a high viscosity or develops significant amounts of gels. The process of the invention is amenable to RTM, VARTM, RFI, gap compression resin transfer molding and SCRIMP processing methods and equipment (in some cases with equipment modification to provide the requisite heating at the various stages of the process), as well as to other methods such as wet compression.

The mixing apparatus can be of any type that can produce a highly homogeneous mixture of the epoxy component and hardener component (and any optional materials that are also mixed in at this time). Mechanical mixers and stirrers of various types may be used. Two preferred types of mixers are static mixers and impingement mixers.

In some embodiments, the mixing and dispensing apparatus is an impingement mixer. Mixers of this type are commonly used in so-called reaction injection molding processes to form polyurethane and polyurea moldings. The epoxy component and the hardener component (and other materials which are mixed in at this time) are pumped under pressure into a mixing head where they are rapidly mixed together. Operating pressures in high pressure machines may range from 1,000 to 29,000 psi or higher (6.9 to 200 MPa or higher), although some low pressure machines can operate at significantly lower pressures. The resulting mixture is then preferably passed through a static mixing device to provide further additional mixing, and then transferred into the mold cavity. The static mixing device may be designed into the mold. This has the advantage of allowing the static mixing device to be opened easily for cleaning.

In certain specific embodiments, the epoxy component and the hardener component are mixed as just described, by pumping them under pressure into a mixing head. Impingement mixing may be used. The catalyst is introduced with the epoxy resin, the hardener, or as a separate stream. The operating pressure of the incoming epoxy resin and hardener streams may range from a somewhat low value (for example, from about 1 to about 6.9 MPa) or a high value (such as, for example, from 6.9 to 200 MPa). The resulting mixture of epoxy resin, hardener and catalyst is then introduced into the mold at a somewhat low operating pressure, such as up to 5 MPa or up to about 1.035 MPa). In such embodiments, the mixture of epoxy resin, hardener and catalyst is typically passed through a static mixer before entering the mold. Some or all the pressure drop between the mix-head and the mold injection port often will take place through such a static mixer. An especially preferred apparatus for conducting the process is a reaction injection molding machine, such as is commonly used to processes large polyurethane and polyurea moldings. Such machines are available commercially from Krauss Maffei Corporation and Cannon or Hennecke.

In other embodiments, the reaction mixture is mixed as before, and then sprayed into the mold. Temperatures are maintained in the spray zone such that the temperature of the hot reaction mixture is maintained as described before.

The mold is typically a metal mold, but it may be ceramic or a polymer composite provided the mold is capable of withstanding the pressure and temperature conditions of the molding process. The mold contains one or more inlets, in liquid communication with the mixer(s), through which the reaction mixture is introduced. The mold may contain vents to allow gases to escape as the reaction mixture is injected.

The mold is typically held in a press or other apparatus which allows it to be opened and closed, and which can apply pressure on the mold to keep it closed during the filling and curing operations. The mold or press is provided with means by which heat or cooling can be provided.

In some embodiments of the foregoing process, the molded composite is demolded in no more than 5 minutes, preferably from 1 to 5 minutes, more preferably from 1 to 3 minutes, after the epoxy resin system has been introduced into the mold. In such processes, the introduced resin system flows around and between the reinforcing fibers and fills the mold and then cures in the mold, preferably forming a polymer having a glass transition temperature of at least 120°C (more preferably at least 130°C or at least 140°C) within three minutes, more preferably within two minutes, after the reaction mixture has been introduced into the mold.

The process of the invention is useful to make a wide variety of composite products, including various types of automotive or other transportation parts. Examples of these parts include vertical and horizontal body panels, automobile and truck chassis components, and so-called “body-in-white” structural components.

Body panel applications include fenders, door skins, hoods, roof skins, decklids, tailgates and the like. Body panels often require a so-called “class A” automotive surface which has a high distinctness of image (DOI). For this reason, the filler in many body panel applications will include a material such as mica or wollastonite. Parts made in accordance with this invention may be in some cases subjected to high temperatures. For example, certain protective coatings as are commonly used in automotive manufacturing processes often are applied electrostatically in a so-called “ecoat” process, and then subjected to a bake cure. In such a bake cure, the composite may be subject to a temperature of 140 to 220°C, for a period of 10 to 60 minutes. Resin system and composites made in accordance with this invention which are to be coated in such a manner should have a high enough glass transition temperature as to be able to withstand the high temperature of the bake temperature. In addition, an electroconductive filler may be incorporated into the composite to increase the electrical conductivity of the part, to facilitate the electrodeposition process.

The following examples are provided to illustrate the invention, but not limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

Testing Methods

Viscosity:

Standard test method of ASTM D445 was used to measure viscosity of various samples at 25°C. The unit is mPa.s.

To measure the combined resin and hardener viscosities, comparative and inventive samples were placed in a preheated shear rheometer (MCR301, Anton Paar) equipped with parallel plates (25 mm diameter, gap 1 mm) and their viscosity was measured under isothermal conditions at 55°C with a shear rate of 10 s^{-1}.

Differential Scanning Calorimetry (DSC):

Dynamic DSC was used to determine the Tg value of the resin systems. In a heating ramp of 10°C/min the samples were heated from 25 to 220°C, kept isothermal at 220°C for three minutes, cooled in a ramp of 10°C to 25°C, kept isothermal at 25°C for three minutes, then heated again with a heating ramp of 10°C to 220°C, kept isothermal at 220°C for 3 minutes, and cooled in a ramp of 10°C to 25°C. Tg onset and Tg midpoint are determined from the second heating segment.

Comparative Samples

CS 1 uses a diglycidyl ether of a polyphenol having an epoxy equivalent weight of about 250 and less than 1% by weight of mono hydrolyzed resin (commercially available from The Dow Chemical Company as VORAFORCE 5310™). The resin component has a viscosity of about 7000 to 10500 mPa.s at 25°C. The resin is mixed with hardener component at a weight ratio of 100 to 14.7.

CS2 uses the same epoxy resin and hardener with a weight ratio of 100:16.2.

The hardener used is a blend of a triethylene tetraamine mixture commercially available as D.E.H. 24 by The Dow Chemical Company and triethylene diamine at a mole ratio of 1:0.1.

Inventive Samples

IS 1 uses, as the epoxy component, a diglycidyl ether of polyphenol having an epoxy equivalent weight of about 190 and less than 0.5% by weight of mono hydrolyzed resin (commercially available from The Dow Chemical Company as VORATRON™ ER 104). The epoxy resin component has a viscosity of about 4000 to 6000 mPa.s at 25°C. The resin is mixed with hardener component at a weight ratio of 100 to 14.7.

IS 2 uses the same epoxy resin and hardener with a weight ratio of 100:16.2.

The hardener used is a blend of a triethylene tetraamine mixture commercially available as D.E.H. 24 by The Dow Chemical Company and triethylene diamine at a mole ratio of 1:0.1.

Results

Samples were measured for the time required to reach 250 mPa.s and 500 mPa.s. respectively. To do this, both Comparative Samples (with an initial viscosity of about 110 mPa.s at 55°C) and Inventive Samples with an initial viscosity of about 90 mPa.s at 55°C were placed in a preheated shear rheometer (MCR301, Anton Paar) equipped with parallel plates (25 mm diameter, gap 1 mm) and their viscosity was measured under isothermal conditions at 55 °C and at a shear rate of 10 s^{-1}.

Table 1 Time required to reach a certain level of viscosity at plate temperature 55 °C

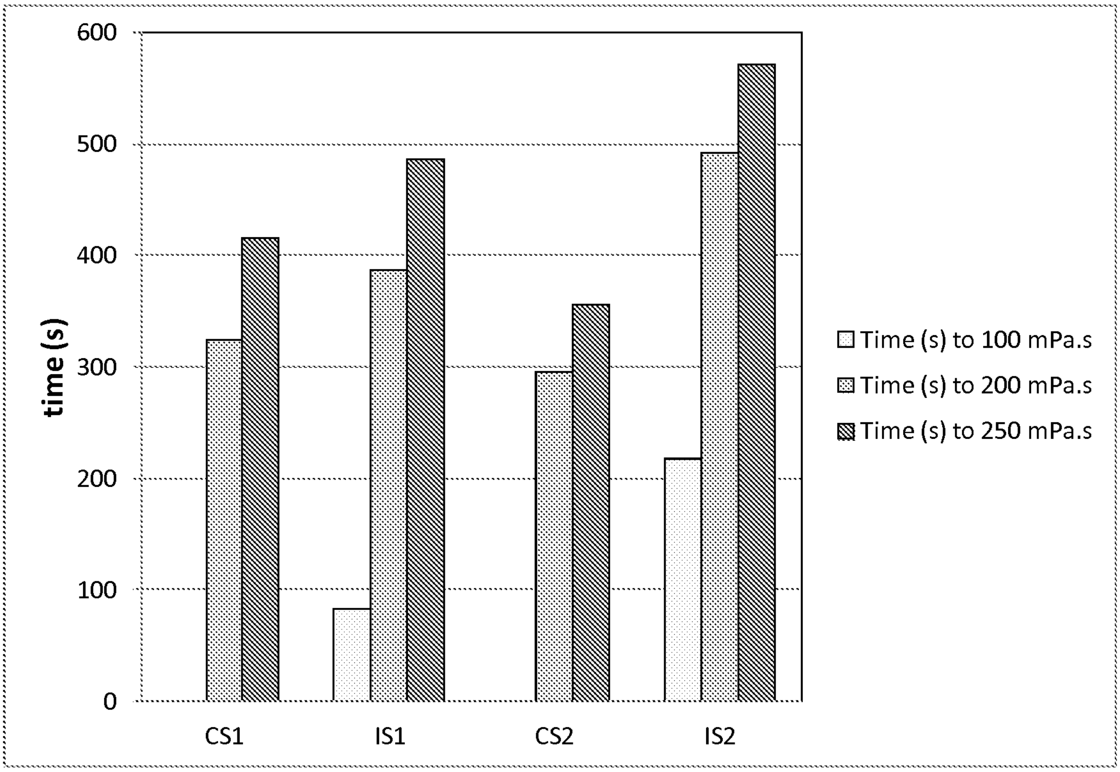


Table 2 Summary of time recorded to reach 250 and 500 mPa.s respectively for comparative and inventive samples at plate temperature 55 °C

Sample	Time (mins) to 250 mPa.s	Time (mins) to 500 mPa.s
CS1	6.9	10.9
CS2	5.9	9.9
IS1	8.1	12.2
IS2	9.5	13.1

In relation to the fabrication of a prototype composite article an important feature of any suitable resin system is that during the filling phase the system should demonstrate sufficient open time as to enable the efficient filling of complex articles with a low void content. Sufficient open time can be defined by the time to reach a critical viscosity such as 250 or in some cases up to 500 mPa.s above which the filling of complex geometries with a low void content can be extremely challenging. Therefore any suitable resin system for the fabrication of prototype composite articles should demonstrate a low viscosity for as long as possible during the filling phase of the manufacture. Currently, due to their high reactivity, manufacturing prototype parts with fast curing RTM resin systems is extremely challenging due to the insufficient time available to mold the prototype. The data shown in Table's 1 and 2 demonstrates that by using the proposed inventive system versus the comparative system surprisingly, the time to 250 and 500 mPa.s respectively can be substantially lengthened to provide greater time to complete the fabrication of the composite article.

Glass transition temperatures (Tg value) of the resin systems were also measured and the results provided in Table 3.

Table 3 Tg values of the resin systems

	Glass Transition Temperature onset °C	**Glass Transition Temperature mid point °C**
CS 2	125	131
IS 2	123	129

Furthermore, the glass transition temperatures measured for the Comparative and Inventive Samples demonstrated that the thermal performance of the two resin compositions is very similar while greater latency and hence longer fabrication time is available by the use of the Inventive Sample.

CLAIMS:

1. A curable resin system, comprising

1) an epoxy component having polyglycidyl ethers of a polyphenol having an epoxy equivalent weight of up to about 190;

2) a hardener component comprising polyethylene tetraamine mixture;

wherein the epoxy component has a viscosity of less than 9000 mPa.s at 25°C.

2. The curable resin system of claim 1, wherein the polyglycidyl ethers of a polyphenol comprises no more than 1 wt. %, based on total weight of the polyglycidyl ethers of a polyphenol, of mono hydrolyzed resin content.

3. The curable resin system of claim 1, wherein the weight ratio between the epoxy component to the hardener component is between 100:11 to 100:20.

4. The curable resin system of claim 1, wherein at least 40% of the weight of the polyethylene tetraamine mixture is a linear triethylene tetraamine with a chemical structure of:

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2.$$

5. The curable resin system of claim 1, wherein the hardener component comprises over 90 wt. % of triethylenetetramine and the rest being 1,4-di-azabicyclo[2,2,2]octane, based on the total weight of the hardener component.

6. The curable resin system of claims 1 to 5 further comprising an internal mold release agent.

7. A cured fiber-reinforced composite made from the resin system of claims 1 to 6.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/020852

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G59/50
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/107512 A1 (BASF SE [DE]; SUTER DOMINIC [DE]; KINSCHERFF MANFRED [DE]; DAHMEN KIRS) 9 September 2011 (2011-09-09) the whole document -----	1-7

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 May 2015	20/05/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Siemens, Thomas

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/020852

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011107512 A1	09-09-2011	CN 102782002 A	14-11-2012
		EP 2542609 A1	09-01-2013
		JP 2013521257 A	10-06-2013
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