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GB 2478343 A **EP 2426157 A1**
WO 1991/000308 A1 **US 3427282 A**
US 20110294387 A1

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Other: **EPODOC, WPI, CAS ONLINE**

(54) Title of the Invention: **4,4' methylene bis anilines as curing agents for epoxy resins**
Abstract Title: **4,4' methylene bis aniline compounds as curing agents for epoxy resins.**

(57) The use of a 4,4' methylene bis aniline compound as a curing agent for epoxy resins, wherein the 4,4' methylene bis aniline compound is a liquid at 20 °C. The 4,4' methylene bis aniline compound may have one substituent on each aniline ring, preferably the substituent is at the ortho position relative to the amine group. The 4,4' methylene bis aniline compound may also have two substituents on each aniline ring, preferably at the meta position relative to the amine group. Preferably the 4,4' methylene bis aniline compound is M-MIPACDEA, M-DIPACDEA or M-MEACDEA. The epoxy resin may have a functionality of at least two and preferably has an epoxy equivalent weight (EEW) from 80-500. The epoxy resin may also comprise a thermoplastic component that is soluble in the epoxy resin and acts as a toughening agent. The epoxy resin may be used as the matrix of a prepreg comprising a reinforcement. The reinforcement may be carbon fibre, glass fibre or aramid and may be continuous, woven, unwoven or short fibre. Also disclosed is a process for producing a composite comprising an epoxy resin, reinforcing material and a 4,4' methylene bis aniline compound.

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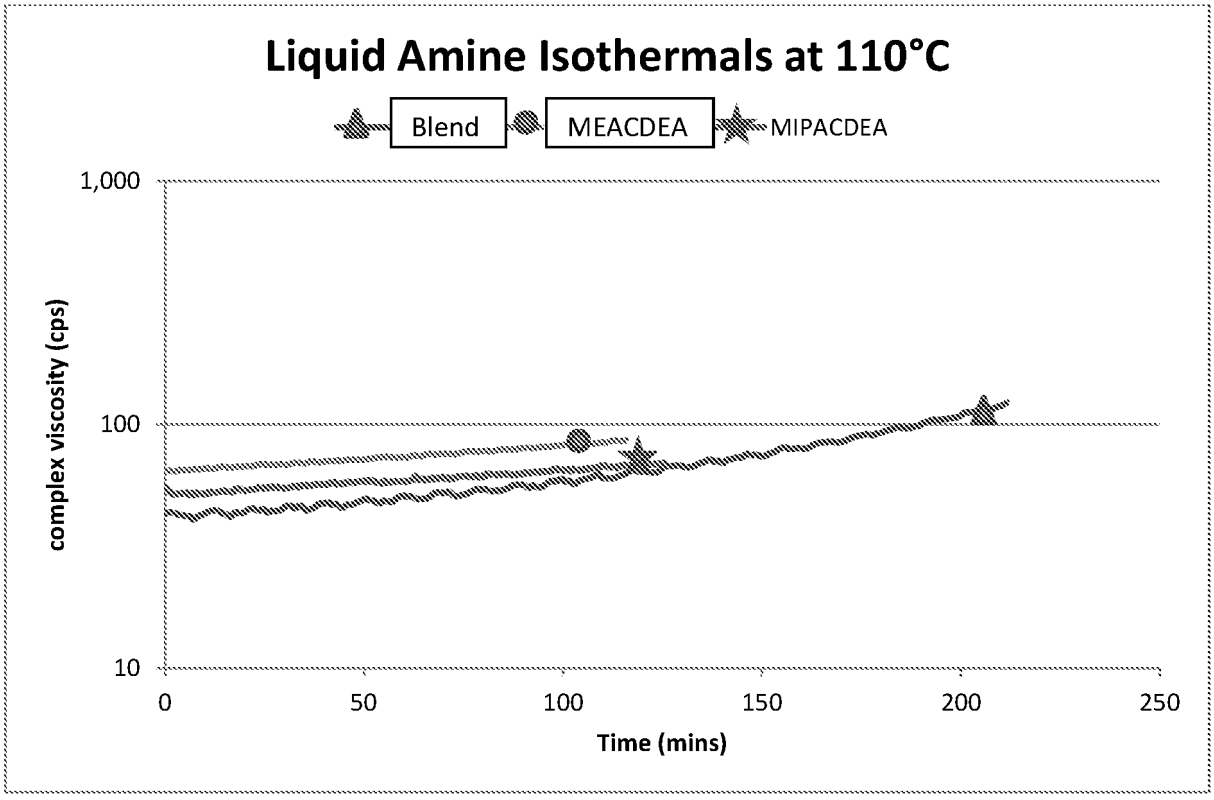

Liquid Amine Isothermals at 110°C
Blend
MEACDEA
MIPACDEA
1,000
100
10
complex viscosity (cps)
0
50
100
150
200
250
Time (mins)

Figure 1

4,4[1] METHYLENE BIS ANILINES AS CURING AGENTS FOR EPOXY RESINS

The present invention relates to curatives for epoxy resins, their use in curing epoxy resins and in epoxy resins containing the curatives. Epoxy resins find widespread use as thermosetting resins in many applications. They are employed as the thermosetting matrix in prepregs consisting of fibres embedded in the thermosetting matrix. They may also be employed in coatings or in reinforcing foams all of which find applications in a wide variety of industries such as the aerospace, automotive, electronics, construction, furniture, green energy and sporting goods industries.

A wide range of epoxy resins are readily available and are available according to their reactivity as required for particular applications. For example, the resins may be solid, liquid or semi solid and may have varying reactivity according to the use to which they are to be put. The reactivity of an epoxy resin is often measured in terms of it's epoxy equivalent weight which is the molecular weight of the resin that contains a single reactive epoxy group. The lower the epoxy equivalent weight the more reactive the epoxy resin.

Different reactivities are required for different uses of epoxy resins but the typical use of an epoxy resin whether it be as the matrix of a fibre reinforced prepreg, an adhesive coating, a structural adhesive is that it is cured by heating. The curing reaction of an epoxy resin is usually an exothermic reaction which needs to be controlled to prevent overheating of the resin perhaps damaging the resin itself, or substrates with which it is used or the moulds in which it may be cured. There is therefore a need to control and preferably reduce the enthalpy of the curing reaction of epoxy resins.

Curing agents are used in order to activate and control the curing of epoxy resins to provide the required cure cycle, the exotherm of the cure and the properties of the final cured resin. A wide range of curing agents for epoxy resins have been proposed and are widely used. For example, amines such as dicyandiamide is a widely used curing agent as are sulfones such as diamino diphenyl sulfone.

One particular class of curing agents are substituted 4,4[1] methylene bis anilines such as those that are described in US Patents 4,950,792, 4,978,791; European Application Publication Number 2426157 and PCT Publication WO 2002/028323 which describe the nomenclature used to describe the structure of methylene bis anilines.

Epoxy resins are usually employed in formulations containing other additives according to the nature of the use envisaged for the cured epoxy resin. Additives including toughening agents, rubbers, core shell polymers, fillers, optionally blowing agents and the like can be included in the formulations. In order to prepare the epoxy resin formulation it is necessary to produce a homogenous or substantially homogeneous mixture of the various ingredients. In particular it is important that the curing agent be well dispersed throughout the epoxy resin in order to obtain uniform curing of the formulation upon heating so that uniform properties, particularly mechanical properties, are obtained in the cured epoxy resin. Additionally, it is desirable that the formulations can be prepared at temperatures well below the activation temperature of the curing agent to prevent premature activation of the curing agent and cross linking of the epoxy resin. In addition for infusion applications the viscosity of the formulation suitably remains low to promote impregnation of fibrous reinforcement.

It is also preferred that from an economic perspective the formulations can be prepared at low temperatures to reduce the costs of heating the mixtures during compounding of the formulation.

Articles comprising fibre reinforced epoxy resins are typically a fibrous material embedded in a matrix of cured epoxy resin. The articles are usually prepared by shaping the fibrous material and the uncured epoxy resin in a mould and then curing the epoxy resin by heating. There are two main processes that can be used. A process employing what is known as a prepreg in which the fibrous material is first impregnated with the uncured epoxy resin to produce the prepreg. One or more layers of the prepreg are placed in a mould and moulded to the desired shape within the mould and the system then cured. The second process is known as an infusion process where one or more layers of a resin free fibrous material are placed in a mould and infused or injected with the epoxy resin within the mould before or after shaping of the layers and the moulded and resin injected layers are then cured.

Both processes have advantages and disadvantages and the selection of the process to be used depends upon the article to be produced. There are also different requirements for the epoxy resin systems that are used in prepregs and for infusion.

Suitably an infusion resin has a low viscosity at the injection temperatures to allow infusion of a dry fibre reinforcement preform (typically in the range of from 80 to 130°C for aerospace grade resins). In contrast, a prepreg resin should have a higher viscosity at these temperatures to ensure that the preimpregnated fibre reinforcement remains impregnated during storage, transport, handling and lay-up of the prepreg.

Additionally, a prepreg cure schedule typically includes an initial low temperature phase (above room temperature but below curing temperature) to allow the resin to reduce in viscosity so that it will flow to consolidate the preform lay-up. The temperature is then increased to cure the resin.

In an infusion process, following infusion of the preform at the injection temperature, the temperature of the infusion resin is increased to the cure temperature to cure the resin.

Furthermore, an infusion resin is generally prepared where it is used in the moulding process by mixing resins and curatives shortly before it is infused into the fibrous material which may already be formed or may subsequently be formed. The resin is then cured. Infusion must be completed within 1 to 3 hours otherwise the resin will have pre-reacted and the viscosity of the resin will have increased preventing effective infusion of the fibrous material. Infusion resins are generally reactive and is not possible to store the infusion resin for any length of time because it will react and cure. On the other hand, a prepreg resin is designed to remain stable and have a very low rate of cure at low temperatures (typically 40°C or less) for a long period of time, typically 3 weeks up to 6 months to allow for storage and transportation of the prepreg.

There are also hybrid forms of infusion and prepreg technology. In the hybrids the resin is in the form of a highly viscous resin film which is located within a lay-up of dry fibrous reinforcement. Again the temperature is first raised to an initial temperature to reduce the viscosity of the resin film which allows it to flow and impregnate the reinforcement. The resin temperature is then further increased to cure the resin.

The choice of the curative used for curing the epoxy resin will depend upon which process is to be used to produce and process the fibre, uncured epoxy resin system and on the required cure cycle. For example, when the epoxy resin system is to be used in the infusion process the curing agent should not undesirably increase the viscosity of the liquid epoxy resin used for infusion as this could make infusion more difficult requiring greater energy to accomplish infusion and/or leading to inhomogeneous distribution of the liquid epoxy resin throughout the fibrous structure. Since prepregs are often produced in one location and used in another and may be transported and stored between production and use the curing agent used for the epoxy resin system of a prepreg should not therefore be active at low temperatures to cause premature curing of the resin and should have a long outlife at room

temperature (storage time without undesirable pre-reaction). Liquid curing agents may be used in infusion systems and solid curing agents are often used in prepregs.

The requirements of a curing agent for epoxy resins are that it is soluble in the epoxy resins with which it is used at temperatures involved during the cure cycle and that it is easily mixed with the epoxy resin to provide a uniform dispersion of the curing agent throughout the resin. Additionally the curing agent should be activated to provide the desired time/temperature cure cycle for the fibre/epoxy resin system, particularly to provide fast cure but with a low enthalpy of the curing reaction. Furthermore the curing agent should be compatible with other additives such as toughenes that may be included in the system.

There is therefore a continuing need to improve fibre reinforced epoxy resins articles and to find new curing agents that can be used to improve the manufacture and properties of such articles. Examples of properties that we seek to improve are moisture resistance, retention of Tg of the cured resin when subject to heat and/or moisture, improved compression and toughenability. As with many systems it is necessary to obtain the optimum balance of properties and the suitability of the curing agent is governed not only by the manufacturing process to be used but the properties required of the finished cured article.

The present invention aims to obviate or at least mitigate the above described problems and/or to provide improvements generally.

According to the invention there is provided a use, a resin, an article and a process as defined in any one of the accompanying claims.

The present invention addresses these issues and provides a curing agent for the epoxy resin that can be readily formulated and which retains a stable viscosity over time thereby providing a composition which is especially useful in an infusion process. The composition may be readily formulated prior to infusion of a moulding in an infusion process.

The present invention therefore provides the use of a 4,4^1 methylene bis aniline compound as a curing agent for an epoxy resin wherein the 4,4^1 methylene bis aniline compound is a liquid at 20°C.

The invention further provides an epoxy resin containing a 4,4^1 methylene bis aniline compound which is a liquid at 20°C.

The invention further provides an article comprising an epoxy resin containing a 4,4[1] methylene bis aniline compound which is a liquid at 20°C.

The liquid 4,4[1] methylene bis aniline can be readily formulated with epoxy resins and also with the other traditional ingredients that are used in epoxy resin formulations. In a two component infusion process, the liquid bis-aniline compound advantageously may be processed more readily than a solid amine. A solid amine typically needs to be melted before injection and the processing equipment for the infusion may need to be heated throughout to reduce or prevent any recrystallization of the amine in the equipment. Furthermore, a solid or crystalline amine will require heating to melt the amine adding a further step which may be costly and time-consuming. The liquid bis-aniline compound suitably requires no heating or only moderate heating in order to be processable in an infusion process.

The liquid 4,4[1] methylene bis anilines compounds used in this invention may be obtained by appropriate selection of the substituent groups on the aromatic rings of the compound, and they may be asymmetric 4,4[1] methylene bis anilines by which is meant compounds containing different substituents on each of the aromatic rings and which may be symmetrical or asymmetrical. The liquids may also be mixtures of two or more 4,4[1] methylene bis anilines. By a liquid 4,4[1] methylene bis aniline is meant one that remains a liquid at 20°C without crystallisation for at least 30 days.

Within this application the nomenclature employed to describe the aniline molecules from which the 4,4[1] methylene bis anilines are derived is as follows.

XXXA where XXX represents the substituents on the aniline molecule. For example

DIPA is Diisopropyl aniline
DEA is Diethyl aniline
MEA is methyl ethyl aniline
CEA is chloro ethyl aniline
CDEA is chlorodiethyl aniline
FDEA is fluorodiethyl aniline

Suitably, any alkyl groups are in the ortho position in relation to the amine group of the aniline and any halogen containing group that is present may be in the meta position.

Where the 4,4^1 methylene bis anilines are hybrids derived from two different anilines they are referred to as

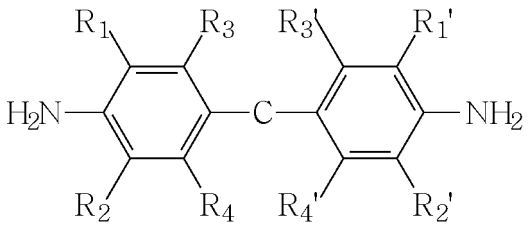
M-XXXAX^{1}X^{1}X^{1}A

where XXXA is one of the aniline molecules employed and X^{1}X^{1}X^{1}A is the other. For example

M-MEACDEA is 4,4'-methylene-2'-methyl-2,6,6'-triethyl-3-chloro dianiline).

The 4,4^1 methylene bis anilines used in this invention may be prepared by any suitable techniques such as those described in European Patent Publication 2426157 and PCT Publication WO 2002/028323.

In a preferred embodiment, the 4,4^1 methylene bis aniline compound is a liquid at 20°C and has the formula I below:



wherein R_1, R_2, R_3, R_4, $R_{1'}$, $R_{2'}$, $R_{3'}$, and $R_{4'}$ are independently selected from:

hydrogen;

C_1 to C_6 alkyl, preferably C_1 to C_4 alkyl, where the alkyl group may be linear or branched and optionally substituted, for example methyl, ethyl, isopropyl and trifluoro methyl;

halogen, for example chlorine;

amide;

ester;

fluoroalkyl.

The bis aniline compound may be symmetrical and comprise one substituent for example an alkyl group or a fluoroalkyl group on each aniline ring, preferably at the ortho position relative to the amine group.

In another embodiment, the bis aniline compound may be symmetrical and comprise two substituents for example an alkyl group or a fluoroalkyl group on each aniline ring, preferably at the meta position relative to the amine group.

In a further embodiment R_1, and $R_{1'}$ are different and/or R_4, and $R_{4''}$ are different. In another embodiment R_2, $R_{2'}$, R_3, and $R_{3'}$ are not chlorine.

We have found that by appropriate selection of the substituent groups on the aniline molecules liquid materials that are particularly useful as curing agents for epoxy resins can be obtained. In order to demonstrate the effect of substituents and the products various symmetric and asymmetric materials of the following formula were prepared from mixtures of aniline molecules as set out in Table 1.

Aniline	DIPA	DEA	MEA	CDEA
MIPA	No crystals after 12 days	crystallised	crystallised	Liquid 6 months at RT
DIPA		crystallised	crystallised	Prepared (liq for 39 days)
DEA			Not prepared	Prepared - crystallised
MEA				Prepared (liq for 31 days)

Table 1

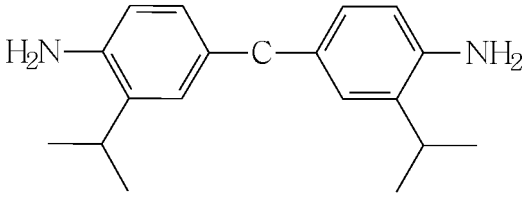
The hybrids of DEA, DIPA and MEA with CDEA were also prepared as admixtures with the two homo-coupled anilines. Compositions of the admixtures were determined by HPLC with the hybrid constituting greater than 60 wt % for all the mixtures the compositions obtained are given in Table 2.

Composition	Hybrid % w:w	M-CDEA % w:w	Other % w:w
M-DEACDEA	65.0	20.4	14.7 (M-DEA)
M-MEACDEA	60.4	23.5	16.1 (M-MEA)
M-DIPACDEA	~69	~16	~15 (M-DIPA)
M-MIPACDEA	63.3	21.3	15.5 (M-MIPA)

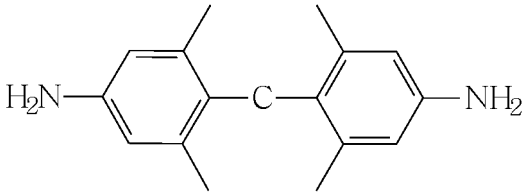
Table 2

The hybrid M-DEACDEA crystallised after 1 day whereas M-DIPACDEA was a stable liquid for 39 days. M-MEACDEA remained liquid for 31 days.

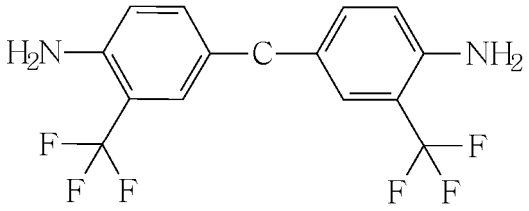
The effect of substituents on the aniline molecules was again shown in the preparation of alternative substituted anilines both as hybrids and as homo-coupled 4,4' methylene bis anilines. 4,4' methylene bis (2-isopropyl aniline) [M-IPA], 4,4' methylene bis (3,5-dimethyl aniline) [M-3,5DMA], and ,4'-methylene bis (2-trifluoromethyl aniline) [M-TFMA] have been prepared as shown below.



M-IPA



M-3,5-DMA



M-TFMA

M-IPA was prepared in good yield and was a liquid at room temperature. No noticeable crystallisation has occurred after 37 days. M-3,5 DMA was a solid at room temperature.

With M-TFMA the crude product is isolated as a liquid but purification yields a low melting point solid.

The liquid 4,4[1] methylene bis anilines are used as curatives for any epoxy resin. In preferred formulations the epoxy resin has a functionality at least 2 and has a high reactivity. The epoxy equivalent weight (EEW) of the resin is preferably in the range from 80 to 1500, preferably of from 80 to 500. Suitable epoxy resins may comprise blends of two or more epoxy resins selected from monofunctional, difunctional, trifunctional and/or tetrafunctional epoxy resins. The liquid 4,4[1] methylene bis anilines are particularly useful with epoxy resins that are liquid at ambient temperature.

Difunctional epoxy resins with which the liquid 4,4[1] methylene bis anilines may be used include those based on: diglycidyl ether of bisphenol F, diglycidyl ether of bisphenol A (optionally brominated), phenol and cresol epoxy novolacs, glycidyl ethers of phenol-aldehyde adducts, glycidyl ethers of aliphatic diols, diglycidyl ether, diethylene glycol digicidyl ether, aromatic epoxy resins, aliphatic polyglycidyl ethers, epoxidised olefins, brominated resins, aromatic glycidyl amines, heterocyclic glycidyl imidines and amides, glycidyl ethers, fluorinated epoxy resins, glycidyl esters or any combination thereof.

Difunctional epoxy resins may be selected from diglycidyl ether of bisphenol F, diglycidyl ether of bisphenol A, diglycidyl dihydroxy naphthalene, or any combination thereof.

Trifunctional epoxy resins with which the liquid 4,4[1] methylene bis anilines may be used include those based upon phenol and cresol epoxy novolacs, glycidyl ethers of phenol-aldehyde adducts, aromatic epoxy resins, aliphatic triglycidyl ethers, dialphatic triglycidyl ethers, aliphatic polyglycidyl amines, heterocyclic glycidyl imidines and amides, glycidyl ethers, fluorinated epoxy resins, or any combination thereof. Suitable trifunctional epoxy resins are available from Huntsman Advanced Material (Monthey, Switzerland) under the tradenames MY0500 and MY0510 (triglycidyl para-aminophenol) and MY0600 and MY0610 (triglycidul meta-aminophenol). Triglycidyl meta-aminophenol is also available from Sumitomo Chemical Co. (Osaka, Japan) under the tradename ELM-120.

Tetrafunctional epoxy resins with which the liquid 4,4[1] methylene bis anilines may be used include N,N, N,[1],N[1]-tetraglycidyl-m-xylenediamine (available commercially from Mitsubishi Gas Chemical Company under the name Tetrad-X, and as Erisys GA-240 from CVC Chemicals), and N,N,N[1],N[1]-tetraglycidylmethylenedianline (e.g. MY720 and MY721 from Huntsman Advanced Materials). Other suitable multifunctional epoxy resins include DEN438 (from Dow Chemicals, Midland, MI) DEN439 (from Dow Chemicals), Araldite ECN 1273 (from Hunstman Advanced Materials), and Araldite ECN 1299 (from Huntsman Advanced Materials).

The epoxy resin formulation of the present invention comprising the epoxy resin and the liquid 4,4[1] methylene bis aniline may also include a thermoplastic component that is soluble in the epoxy resin and acts as a toughening agent. Any suitable soluble thermoplastic polymer that has been used as toughening agent may be used. Typically, the thermoplastic polymer is added to the resin mix as particles that are dissolved in the resin mixture by heating prior to addition of any insoluble particles and the curing agent. Once the thermoplastic agent is substantially dissolved in the hot matrix resin precursor (i.e. the blend

of epoxy resins), the precursor is cooled and the remaining ingredients (curing agent and insoluble particles) are added.

Exemplary thermoplastics that can be used as the soluble thermoplastic component include any polyethersulfone, polyetherimide and polysulphone which are soluble in the epoxy resin.

Polyethersulfone (PES) is preferred for use as the soluble thermoplastic component. PES is sold under the trade name Sumikaexcel 5003P, which is commercially available from Sumitomo Chemicals. Alternatives to 5003P are Solvay polyethersulphone 105RP, or the non-hydroxyl terminated grades such as Solvay 1054P. It is preferred that the uncured resin formulation include from 10 to 20 weight percent of the thermoplastic component. More preferred are uncured resin formulation that contain from 12 to 18 wt % soluble thermoplastic component. Most preferred are resin formulation that contain from 13 to 15 wt % soluble thermoplastic component. Other additives may be present in the resin; the additives may have a small particle of less than 1 micron, preferably less than 0.5 micron so as not too increase the viscosity of the resin significantly. Examples of suitable additive particles are nanocore shell rubbers and nano silica particles.

The uncured resin formulation may also include an insoluble particle component that is composed of a combination of elastic particles and rigid particles. The amount of insoluble particles in the uncured resin formulation is preferably from 8 to 30 wt %. More preferred are resin formulations that contain from 8 to 25 wt % insoluble particles. Most preferred are resin formulations that contain form 8 to 20 wt % insoluble particles.

Examples of suitable rigid particles include polyamideimide (PAI) and polyamide (PA). Rigid particles have glass transition temperatures (T_g) that are above room temperature (22°C). Rigid particles are harder than the elastic particles. In addition, rigid particles are not as easily deformed as the elastic particles. Rigid particles have a Young's modulus of between 100 and 1000 ksi. Preferably, the Young's modulus of the rigid particles is between 200 and 800 ksi.

Polyamide particles come in a variety of grades that have different melting temperatures depending upon the particular polyamide and the molecular weight of the polyamide. Polyamide particles used in the formulations of the present invention preferably have melting points of above 190°C and below 240°C. This is well above typical epoxy curing temperatures. So that little, if any, dissolution of the particles occurs during cure. It is preferred that the polyamide particles have a Young's modulus of between 200 and 400 ksi with a modulus of about 300 ksi being particularly preferred.

Suitable polyamide particles contain polyamide 6 (caprolactam – PA6) as the main ingredient having a melt temperature of 220 °C, but may also contain polyamide 12 (laurolactame - PA 12), polyamide 11, provided that the melting temperature of the particle remains above the cure temperature of the resin formulation. The particles should have particle sizes of below 100 microns. It is preferred that the particles range in size from 5 to 60 microns and more preferably from 10 to 30 microns. It is preferred that the average particle size be around 20 microns. The particles should be substantially spherical. The particles can be made by anionic polymerization in accordance with PCT application WO2006/051222, by co-extrusion, precipitation polymerization, emulsion polymerization or by cryogenic grinding. Suitable polyamide particles that may be used as rigid particles in accordance with the present invention are available commercially from Arkema of France under the trade name Orgasol.

It is preferred that the resin formulation include PA particles and that the amount of PA particles be in the range of 8 to 55 wt % of the total resin formulation. More preferred are PA particle amounts in the range of 8-20 wt %.

The uncured resin formulation may also include at least one other curing agent in addition to the 4,4[1] methylene bis anilines. Suitable additional curing agents are those which facilitate the curing of the epoxy-functional compounds and, particularly, facilitate the ring opening polymerization of such epoxy compounds.

Suitable additional curing agents include anhydrides, particularly polycarboxylic anhydrides, such as nadic anhydride (NA), methylnadic anhydride (MNA - available from Aldrich), phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride (HHPA - available from Anhydrides and Chemicals Inc., Newark, N.J.), methyltetrahydrophthalic anhydride (MTHPA -available from Anhydrides and Chemicals Inc.), methylhexahydrophthalic anhydride (MHHPA -available from Anhydrides and Chemicals Inc.), endomethylenetetrahydrophthalic anhydride, hexachloroendomethylene-tetrahydrophthalic anhydride (Chlorentic Anhydride - available from Velsicol Chemical Corporation, Rosemont, 111.), trimellitic anhydride, pyromellitic dianhydride, maleic anhydride (MA - available from Aldrich), succinic anhydride (SA), nonenylsuccinic anhydride, dodecenylsuccinic anhydride (DDSA - available from Anhydrides and Chemicals Inc.), polysebacic polyanhydride, and polyazelaic polyanhydride.

Further suitable additional curing agents include the amines, including other aromatic amines, e.g., 1,3-diaminobenzene, 1,4-diaminobenzene, 4,4'-diamino-diphenylmethane, and the polyaminosulphones, such as 4,4'-diaminodiphenyl sulphone (4,4'-DDS - available from

Huntsman), 4-aminophenyl sulphone, and 3,3'- diaminodiphenyl sulphone (3,3'-DDS). Other suitable additional curing agents include 4,4'-methylene bis chlorodiethylaniline (MCDEA), 4,4'-methylene bis diethylaniline (MDEA) and 4,4'-methylene bis methyl isopropyl aniline which are especially useful in resin transfer moulding (RTM).

Suitable additional curing agents may also include polyols, such as ethylene glycol (EG - available from Aldrich), poly(propylene glycol), and polyvinyl alcohol); and the phenol-formaldehyde resins, such as the phenol-formaldehyde resin having an average molecular weight of about 550-650, the p-t-butylphenol-formaldehyde resin having an average molecular weight of about 600-700, and the p-n-octylphenol-formaldehyde resin, having an average molecular weight of about 1200-1400, these being available as HRJ 2210, HRJ-2255, and SP-1068, respectively, from Schenectady Chemicals, Inc., Schenectady, N.Y.). Further as to phenol-formaldehyde resins, a combination of CTU guanamine, and phenol-formaldehyde resin having a molecular weight of 398, which is commercially available as CG-125 from Ajinomoto USA Inc. (Teaneck, N.J.), is also suitable.

The uncured formulation resin may also include additional ingredients, such as performance enhancing or modifying agents and additional thermoplastic polymers provided they do not adversely affect the tack and outlife of the formulation or the strength and damage tolerance of cured composite parts obtained from the formulation. The performance enhancing or modifying agents, for example, may be selected from flexibilizers, toughening agents/particles, accelerators, core shell rubbers, flame retardants, wetting agents, pigments/dyes, UV absorbers, anti-fungal compounds, fillers, conducting particles, and viscosity modifiers.

Suitable curing agent accelerators are any of the urone compounds that have been commonly used. Specific examples of accelerators, which may be used alone or in combination, include N,N-dimethyl, N'-3,4-dichlorphenyl urea (Diuron), N'-3-chlorophenyl urea (Monuron), and preferably N,N-(4-methyl-m-phenylene bis[N',N'-dimethylurea] (e.g. Dyhard UR500 available from Degussa).

Uncured resin formulations in accordance with the present invention may be used in a wide variety of situations where a cured epoxy resin is desired. Although the uncured epoxy resin compositions may be used alone, the formulations of this invention are generally combined with a fibrous support to form composite materials. The composite materials may be in the form of a prepreg, partially cured prepreg or a completely cured final part. Prepreg is the term used to describe fibre reinforced materials embedded in a matrix of uncured epoxy resin. The fibrous reinforcement may be carbon fibre, glass fibre or aramid and may be

continuous, woven or unwoven or short fibre. The term "uncured", when used herein in connection with prepreg, formulation resin or composite material, is intended to covers items that may have been subjected to some curing, but which have not been completely cured to form the final composite part or structure.

The liquid 4,4[1] methylene bis aniline compound employed as a curing agent for an epoxy resin is especially suitable for the production of a composite by an infusion process. The liquid aniline enables the uncured resin composition to retain a suitable viscosity whereby it may be drawn into a mould to form a resin or a composite. In an infusion process, the reinforcing material, for example a fabric or a fibrous material, is first placed in the mould and the liquid resin is drawn into the mould perhaps under pressure or by vacuum to encase the reinforcing material within the mould. Suitably the uncured resin drawn into the mould comprises the epoxy resin, liquid 4,4[1] methylene bis aniline compound and optionally other components The reinforcing material may have been preshaped in the mould or maybe shaped once impregnated with the resin and the resin impregnated reinforcing material may then be cured in the mould.

The speed and distance of the infusion of the reinforcing material is dependent on its permeability, the pressure gradient acting on the infused resin and the viscosity of the resin composition. Suitably the resin is drawn through the reinforcing material at a temperature of 80 to 130 ^{o}C. Once the resin has been drawn through the reinforcing material, the temperature is suitably raised to around 150 to 190 ^{o}C to cure the resin.

As the 4,4[1] methylene bis aniline compound in the present invention is liquid at room temperature, the compound and epoxy resin suitably provide a low viscosity composition which is infusable. The composition may readily be drawn through the reinforcing material at a temperature of 80 to 130 ^{o}C to provide a composite with excellent mechanical properties. The liquid infusion process advantageously allows composites to be formed with reduced manufacturing costs due to the material being cured in an out of autoclave process.

Advantageously, the resin composition has a viscosity of less than 100 cPoise preferably 60 to 80 cPoise at a temperature of 110°C.

Improved homogeneity of the cured resin provides a high quality and consistent composite product enabling the composite to be employed in applications where it will be subjected to high stresses for example in space, aeronautical and turbine applications.Such composite materials may be used for any intended purpose, they are preferably used in automotive and aerospace vehicles and particularly preferred for use in commercial and military aircraft. For

example, the composite materials may be used to make non-primary (secondary) aircraft structures. However the preferred use of the composite material is for structural applications, such as primary aircraft structures. Primary aircraft structures or parts are those elements of either fixed-wing or rotary wing aircraft that undergo significant stress during flight and which are essential for the aircraft to maintain controlled flight. The composite materials may also be used for other structural applications to make load-bearing parts and structures in general, for example they may be used in wind turbine blades and sporting goods such as skis.

Where the liquid 4,4[1] methylene bis anilines of this invention are used as curing agents in pre-impregnated composite material, the materials are composed of reinforcing fibres and the uncured resin formulation as a matrix to contain the fibres. The reinforcing fibres can be any of the conventional fibre configurations that are used in the prepreg industry. The matrix includes an epoxy resin component which may include difunctional epoxy resins, but preferably includes a combination of trifunctional and tetrafunctional aromatic epoxy resins. The resin matrix for such a use preferably further includes a soluble thermoplastic component and an insoluble particulate component and a curing agent.

The uncured resin formulation of this invention may be made in accordance with standard processing techniques. The various epoxy resins may be mixed together at room temperature or above (depending upon resin viscosities) to form a resin mix to which the thermoplastic component is added. This mixture is then heated to an elevated temperature (typically around 120°C - 130°C) for a sufficient time to substantially dissolve the thermoplastic(s). The mixture is then cooled down to around 80°C - 90°C or below (depending upon the viscosity of the mixture) and the insoluble thermoplastic particles and other additives, if any, are then mixed into the resin. The resin is then further cooled to around 70°C - 80°C or below, if necessary, and the liquid 4,4[1] methylene bis aniline and any other curing agents are added to form the final formulation which may then be impregnated into the fiber reinforcement. In a preferred process, once the soluble thermoplastic has been dissolved, the mixture is cooled to around 80°C and all of the remaining ingredients, including the curing agent are added.

The compounds of the present invention, when used in a resin for a prepreg, allow for the resin to be mixed at a lower temperature than when using conventional prepreg curatives. This eliminates any premature reaction that may occur during the mixing phase. The reinforcing fibres used in the composites or prepregs based on the formulations of this invention may be synthetic or natural fibres or any other form of material or combination of

materials that, combined with the resin composition of the invention, forms a composite product. The reinforcement web can either be provided via spools of fibre that are unwound or from a roll of textile. Exemplary fibres include glass, carbon, graphite, boron, ceramic and aramid. Preferred fibres are carbon and glass fibres particularly carbon fibres. Hybrid or mixed fibre systems may also be envisaged. The use of cracked (i.e. stretch-broken) or selectively discontinuous fibres may be advantageous to facilitate lay-up of the product and improve its capability of being shaped. Although a unidirectional fibre alignment is preferable, other forms may also be used. Typical textile forms include simple textile fabrics, knit fabrics, twill fabrics and satin weaves. It is also possible to envisage using non-woven or non-crimped fibre layers. The surface mass of fibres within the fibrous reinforcement is generally 80-4000 g/m^2, preferably 100-2500 g/m^2, and especially preferably 150-2000 g/m^2. The number of carbon filaments per tow can vary from 3000 to 320,000, again preferably from 6,000 to 160,000 and most preferably from 12,000 to 48,000. For fibreglass reinforcements, fibres of 600-2400 tex are particularly adapted.

Exemplary layers of unidirectional fibrous tows are made from HexTow® carbon fibres, which are available from Hexcel Corporation. Suitable HexTow® carbon fibres for use in making unidirectional fibre tows include: IM7 carbon fibres, which are available as tows that contain 6,000 or 12,000 filaments and weight 0,223 g/m and 0.446 g/m respectively; IM8-IM10 carbon fibres, which are available as tows that contain 12,000 filaments and weigh from 0.446 g/m to 0.324 g/m; and AS7 carbon fibres, which are available in tows that contain 12,000 filaments and weigh 0.800 g/m, tows containing up to 80,000 or 50,000 (50K) filaments may be used such as those containing about 25,000 filaments available from Toray and those containing about 50,000 filaments available from Zoltek. The tows typically have a width of from 3 to 7 mm and are fed for impregnation on equipment employing combs to hold the tows and keep them parallel and unidirectional.

For structural applications, it is generally preferred that the fibres be unidirectional in orientation. When unidirectional fibre layers are used, the orientation of the fibre can vary throughout the prepreg stack. However, this is only one of many possible orientations for stacks of unidirectional fibre layers. For example, unidirectional fibres in neighbouring layers may be arranged orthogonal to each other in a so-called 0/90 arrangement, which signifies the angles between neighbouring fibre layers. Other arrangements, such as 0/+45/-45/90 are of course possible, among many other arrangements.

The structural fibres of the prepregs will be substantially impregnated with the epoxy resin and prepregs with a resin content of from 20 to 85 wt % of the total prepreg weight are

preferred more preferably with 30 to 50 wt % resin based on the weight of the prepreg, and most preferably between 35 to 38 wt % resin based on the weight of the prepreg.

The % of impregnation of a prepreg which is impregnated with resin is measured by means of the water pick up test.

The water pick up test is conducted as follows. Six strips of prepreg are cut of size 100 (+/-2) mm x 100 (+/-2) mm. Any backing sheet material is removed. The samples are weighed near the nearest 0.001 g (W1). The strips are located between PTFE backed aluminium plates so that 15 mm of the prepreg strip protrudes from the assembly of PTFE backed plates on one end and whereby the fiber orientation of the prepreg is extends along the protruding part. A clamp is placed on the opposite end, and 5 mm of the protruding part is immersed in water having a temperature of 23 °C, relative air humidity of 50% +/- 35%, and at an ambient temperature of 23 °C. After 5 minutes of immersion the sample is removed from the water and any exterior water is removed with blotting paper. The sample is then weighed again W2. The percentage of water uptake WPU (%) is then calculated by averaging the measured weights for the six samples as follows:

WPU (%) = (<W2>-<W1>) / <W1>) x 100.

The WPU (%) is indicative of the Degree of Resin Impregnation (DRI).

Water pick up values for the uncured prepreg moulding material and tows of the invention may be in the range of from 1 to 90%, 5 to 85%, 10 to 80%, 15 to 75%, 15 to 70%, 15 to 60%, 15 to 50%, 15 to 40%, 15 to 35%, 15 to 30%, 20 to 30%, 25 to 30% and/or combinations of the aforesaid ranges.

The prepregs of this invention can be produced by impregnating the fibrous material with the resin. In order to increase the rate of impregnation, the process is preferably carried out at an elevated temperature so that the viscosity of the resin is reduced. However it must not be so hot for sufficient length of time that premature curing of the resin occurs. Thus, the impregnation process is preferably carried out at temperatures in the range of from 10°C to 90°C. Beneficially, resins comprising compounds of the present invention can be processed at lower temperatures, such as from 20 to 30 °C. The resin may be applied to the fibrous material at a temperature in these ranges and consolidated into the fibrous material by pressure such as that exerted by passage through one or more pairs of nip rollers.

The prepreg of the present invention may be prepared by feeding the components to a continuous mixer where a homogenous mixture is formed. The mixing is typically performed

at a temperature in the range 20 to 80°C. The mixture may then be cooled and pelletized or flaked for storage. Alternatively the mixture may be fed directly from the continuous mixer onto a prepreg line where it is deposited onto a moving fibrous layer and consolidated into the fibrous layer, usually by passage through nip rollers. The prepreg may then be rolled and stored, or transported to the location at which it is to be used. Curing at a pressure close to atmospheric pressure can be achieved by the so-called vacuum bag technique. This involves placing the prepreg or prepreg stack in an air-tight bag and creating a vacuum on the inside of the bag, the bag may be placed in a mould prior or after creating the vacuum and the resin then cured by externally applied heat to produce the moulded laminate. The use of the vacuum bag has the effect that the prepreg stack experiences a consolidation pressure of up to atmospheric pressure, depending on the degree of vacuum applied.

Upon curing, the prepreg or prepreg stack becomes a composite laminate, suitable for use in a structural application, such as for example an automotive, marine vehicle or an aerospace structure or a wind turbine structure such as a shell for a blade or a spar or in sporting goods such as skis. Such composite laminates can comprise structural fibres at a level of from 80% to 15% by volume, preferably from 58% to 65% by volume.

The present invention is illustrated but in no way limited by reference to the following Examples in which the 4,4[1] methylene bis anilines previously described were employed as curing agents with the epoxy resin MY721 (EEW 113, obtained from Huntsman Advanced Materials) and LY3581 (EEW 160 to 170, obtained from Huntsman Advanced Materials).

Examples

Formulations as outlined in Table 3 were prepared by mixing 35.5g of MY721 with 27.8g of a curative at 60 °C. The curatives included M-DIPACDEA, M-MEACDEA, M-MIPACDEA and a blend of M-MIPA and M-DEA. The mixtures were then cured at 130 °C for one hour followed by 180 °C for two hours. Dynamic scanning calorimetry (DSC) was performed using a TA Q100 instrument to determine onset temperatures, enthalpy and residual cure using a heating rate of 10°C/min. Dynamic mechanical analysis (DMA) was performed using a Q800 instrument on cured resin to determine glass transition temperatures at a heating rate of 5 °C/min and at a frequency of 1 Hz. Hot/wet resistance was determined of the neat resin by immersing cured DMA specimens in a water bath for two weeks at 70 °C. Water uptake and Tg were then determined. Compression modulus was performed using an Instron mechanical test machine on neat resin cylinders (6 cm long 1-1.5 cm in diameter) that were machined to parallel ends.

The results are shown in Table 3.

Table 3

Curative with MY721	Onset of cure (°C)	Enthalpy (J/g)	E' Tg (°C)	Wet Tg (°C)	Water uptake (%)	Modulus (GPa)
M-DIPACDEA	221	465	196	172	1.80	3.6
M-MEACDEA	211	452	208	172	1.64	3.9
M-MIPACDEA	217	392	208	186	2.31	3.7
*Blend M-MIPA and M-DEA	211	411	208	169	2.60	3.3

*Blend of curatives M-MIPA (6g) and M-DEA (13g)

These compositions were held at a temperature of 110 °C and their complex viscosity was determined over time. The results are illustrated graphically in Figure 1. The M-MEACDEA and M-IPACDEA containing compositions remained stable for longer at this temperature as compared to the blend of curatives M-MIPA and M-DEA which is progressing more quickly to cure as shown by the increasing viscosity. As the viscosity of the formulations of the invention remain stable for a longer period, there is more time to infuse the composition to form a resin before it starts to cure and increase in viscosity. As viscosity increases, the infusion process is slowed down or further infusion is prevented.

When used to cure the epoxy resin MY721, M-DIPACDEA produced a cured resin having a slightly lower T_g than when used with the blend of curatives M-MIPA and M-DEA and also a lower Tg than when the hybrid M-MIPACDEA was used.

M-MEACDEA showed very similar properties to that of the cured blend of curatives with MY721 with the exception of modulus, which was improved by 0.6 GPa.

35.71g of MY721 was mixed with 23.51g of M-IPA at 60 °C. The mixtures were then cured at 130 °C for one hour followed by 180 °C for two hours. The use of M-IPA resulted in a product with a T_g similar to that of the blend and some of the liquid hybrids when cured with MY721 but gave a lower temperature for the onset of cure. Compression modulus is nearly 1

GPa higher than the the blend of curatives M-MIPA and M-DEA with MY721 as shown in Table 4

Table 4.

Epoxy with M-IPA	Onset of cure (°C)	Enthalpy (J/g)	E' Tg (°C)	Wet Tg (°C)	Water uptake (%)	Modulus (GPa)
MY721	188	321	207	164	2.21	4.24
LY3581	147	351	121			

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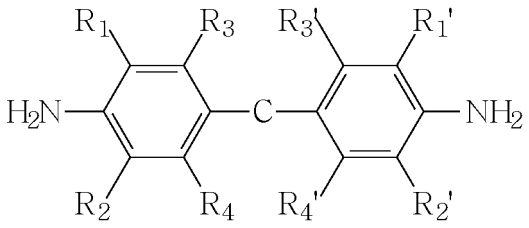
CLAIMS

1. The use of a 4,4[1] methylene bis aniline compound as a curing agent for epoxy resins wherein the 4,4[1] methylene bis aniline compound is a liquid at 20°C.

2. The use according to Claim 1 wherein the 4,4[1] methylene bis aniline compound has the formula I below:



wherein R_1, R_2, R_3, R_4, $R_{1'}$, $R_{2'}$, $R_{3'}$, and $R_{4'}$ are independently selected from:

hydrogen;

C_1 to C_6 alkyl where the alkyl group is linear or branched and optionally substituted;

halogen;

amide;

ester;

fluoroalkyl.

3. The use according to Claim 2 wherein R_1, and $R_{1'}$ are different and/or R_4, and $R_{4''}$ are different.

4. The use according to Claim 2 or Claim 3 wherein R_2, $R_{2'}$, R_3, and $R_{3'}$ are not chlorine.

5. The use according to Claim 1 or Claim 2 wherein the 4,4[1] methylene bis aniline compound is symmetrical.

6. The use according to any of the preceding claims wherein the 4,4[1] methylene bis aniline compound has one substituent on each aniline ring

7. The use according to Claim 6 wherein the substituent is selected from $C_{1\text{-}4}$ alkyl and trifluoroalkyl.

8. The use according to Claim 6 or Claim 7 wherein the substituent is at the ortho position relative to the amine group.

9. The use according to any of Claims 1 to 5 wherein the 4,4[1] methylene bis aniline compound has two substituents on each aniline ring

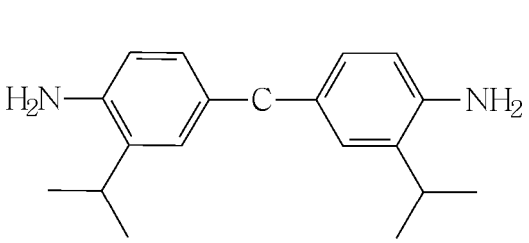
10. The use according to Claim 9 wherein the substituents are at the meta position relative to the amine group.

11. The use according to Claim 1 or Claim 2 in which the 4,4[1] methylene bis aniline is M-MIPACDEA.

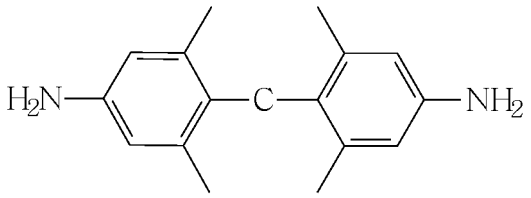
12. The use according to Claim 1 in which the 4,4[1] methylene bis aniline is M-DIPACDEA.

13. The use according to Claim 1 in which the 4,4[1] methylene bis aniline is M-MEACDEA.

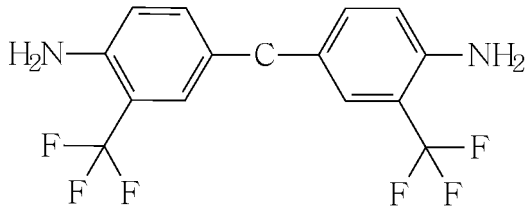
14. The use according to Claim 1 in which the 4,4[1] methylene bis aniline is selected from



M-IPA



M-3,5-DMA



M-TFMA

15. An epoxy resin containing a 4,4[1] methylene bis aniline compound which is a liquid at 20°C.

16. An epoxy resin according to Claim 15 in which the epoxy resin has a functionality of at least 2.

17. An epoxy resin composition according to any of Claims 15 or 16 in which the liquid 4,4[1] methylene bis aniline compound is selected from M-MIPACDEA, M-DIPACDEA, M-MEACDEA, M-IPA, M-DMA or M-TFMA.

18. An epoxy resin according to any of Claims 15 to 17 in which the epoxy equivalent weight (EEW) of the resin is in the range from 80 to 500.

19. An epoxy resin according to any of Claims 15 to 18 including a thermoplastic component that is soluble in the epoxy resin and acts as a toughening agent. 20 An epoxy resin according to any of Claims 15 to 19 in which the resin composition has a viscosity of less than 100 cPoise at a temperature of 110°C.

20 The use of an epoxy resin formulation according to any of Claims 15 to 19 as the matrix of a prepreg comprising a reinforcement.

21. The use according to Claim 20 in which the reinforcement in the prepreg comprises carbon fibre, glass fibre or aramid and may be continuous, woven or unwoven or short fibre.

22. An article comprising an epoxy resin cured with a 4,4[1] methylene bis aniline compound which is a liquid at 20°C.

23. A process for producing a composite comprising an epoxy resin and a reinforcing material comprising providing a reinforcing material, infusing the reinforcing material with an uncured, flowable epoxy resin composition comprising an epoxy resin and a curing agent comprising a liquid 4,4[1] methylene bis aniline compound and optionally other components, drawing the uncured epoxy resin through the reinforcing material located in a mould at a temperature of 80 to 130 °C and raising the temperature to 150 to 190 °C to cure the resin.

24. A process according to Claim 23 wherein the resin composition has a viscosity of less than 100 cPoise at a temperature of 110 °C.

Intellectual Property Office

Application No:	GB1502006.8	**Examiner:**	Dr Kerri Stenning
Claims searched:	1-24	**Date of search:**	27 July 2015

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-3, 11, 12, 15-24	GB2478343 A (HEXCEL COMPOSITES LTD) see particularly example 4 and 6.
X	1, 2, 4-9, 14-18, 22	US3427282 A (UNIROYAL INC) see particularly the examples and the claims.
X	1, 2, 4, 5, 9, 15, 16, 18-24	US2011/294387 A1 (HEXCEL COMPOSITES LTD) see particularly paragraph [0081] and the examples.
X	1, 2, 4, 5, 9, 15, 16, 18, 19, 22	EP2426157 A1 (LONZA AG) see particularly the examples and paragraph [0039].
X	1, 2, 4, 5, 9, 15, 16, 19, 22	WO91/00308 A1 (MARTIN MARIETTA ENERGY SYSTEMS) see particularly example 2.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

C08G; C08J; C08K; C08L

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI, CAS ONLINE

Intellectual Property Office

International Classification:

Subclass	Subgroup	Valid From
C08G	0059/50	01/01/2006
C08G	0059/40	01/01/2006
C08J	0005/24	01/01/2006
C08K	0005/17	01/01/2006
C08K	0005/18	01/01/2006
C08L	0063/00	01/01/2006