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(54) EPOXY ADHESIVE HAVING IMPROVED IMPACT RESISTANCE

(76) Inventors: **Rainer Schoenfeld**, New Berlin, WI (US); **James F. Hubert**, Brookfield, WI (US); **Murteza Erman**, New Berlin, WI (US)

Correspondence Address:
Stephen D. Harper
Law Department
Suite 200
2500 Renaissance Blvd.
Gulph Mills, PA 19406 (US)

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(57) ABSTRACT

In the preparation of an improved adhesive composition, a first reaction product is prepared by the reaction at an elevated temperature of a) 30 to 50 wt-% of an epoxy resin, solid at room temperature, which was prepared from bisphenol A and/or bisphenol F and epichlorohydrin with an epoxide equivalent weight of 400 to 700, b) 10 to 25 wt-% of an epoxy resin, liquid at room temperature, prepared from bisphenol A and/or bisphenol F and epichlorohydrin with an epoxide equivalent weight of 150 to 220, c) 35 to 50 wt-% amino-terminated polyethylene and/or polypropylene glycols and d) a carboxyl-terminated butadiene-nitrile rubber. The first reaction product is mixed with an acrylate terminated urethane resin, glass microspheres, expandable hollow plastic microspheres and a latent curing agent to make an adhesive composition which is pumpable at room temperature and capable of expansion to about 100% with high impact resistance after curing.

EPOXY ADHESIVE HAVING IMPROVED IMPACT RESISTANCE

TECHNICAL FIELD

[0001] This invention relates to methods and compositions useful as adhesives and more particularly to making epoxy based adhesives capable of being employed with or without expansion agents.

BACKGROUND

[0002] Numerous compositions and processes are described in the prior art for making and using a wide variety epoxy-based compositions and other resins and additives in an effort to improve expansion, impact resistance and other key properties of adhesives useful in adhering, filling and making composite structures. For example, various patents describe components and resulting composition and uses such as U.S. Pat. Nos. 5,334,654, 6,270,600, 6,332,731, 5,755,468, and 6,015,865. Nevertheless, significant problems remain prior to the present invention in relation to preparing high impact epoxy based adhesives especially when such adhesives are employed in an expanded state. Further, problems have existed in preparing high impact, expandable adhesives which can be flowed to the application site by pumping, for example, at ambient or moderate temperatures.

BRIEF DESCRIPTION OF THE INVENTION

[0003] We have discovered that unexpectedly improved adhesive formulations can be prepared by pre-reacting a polyepoxide resin having at least two 1,2-epoxy groups per molecule with polyoxy alkylene amine and, optionally, an aduct of carboxy terminated butadiene-nitrile rubber (BNR) to produce a pre-reaction product which is then admixed with an acrylate terminated urethane resin as defined herein, preferably the reaction product of an isocyanate terminated urethane prepolymer and an isocyanate reactive acrylate or methacrylate, a latent curing agent, and optionally with fillers, coloring agents, expanding or blowing agents, or other adjuvants of the type known in the art. When applied to a substrate or carrier the adhesive results in a product having improved impact toughness or impact resistance useful in a wide variety of applications.

[0004] In a preferred embodiment, a curable adhesive is formulated which comprises:

[0005] A) a prepolymer reaction mixture of

[0006] (a) epoxy resin or resins prepared from bisphenol A or bisphenol F and epichlorohydrin having an epoxide equivalent weight of from about 150 to about 700,

[0007] (b) an amino-terminated polyalkylene glycol selected from the group consisting of polyethylene and polypropylene glycols, or a carboxyl terminated butadienenitrile resin, or mixtures thereof,

[0008] B) an acrylate-terminated urethane resin and

[0009] C) a latent curing agent.

DETAILED DESCRIPTION OF THE INVENTION

[0010] In a further preferred embodiment, the pre-reaction products useful in producing adhesive compositions of this invention are prepared in accordance with U.S. Pat. No. 6,015,865 which is hereby incorporated by reference in its entirety. In this preferred embodiment the epoxy resin component is obtained by reacting

[0011] a) an epoxy resin which is solid at room temperature and

[0012] b) an epoxy resin which is liquid at room temperature with

[0013] c) linear amino-terminated polyethylene glycols (ATPEG) or linear and/or trifunctional amino-terminated polypropylene glycols (ATPPG), the epoxy resins a) and b) being used in such a quantity that an excess of epoxide groups over the amino groups is ensured.

[0014] At this point mention is made that the components a), b) and c) can, in each case, also be mixtures of compounds of the given type.

[0015] This pre-reaction product can be modified by adding other modified epoxy resins such as:

[0016] i) adducts of dimeric fatty acids having varying molecular weights with epoxy resins of the diglycidyl ether type of bisphenol A or F (DGEBA or DGEBF) (e.g. Epikote® or EPON® 872),

[0017] ii) adducts of carboxyl-terminated butadiene-nitrile rubber (CTBN) (Hycar® 1300X8, 1300X13; Struktol® with DGEBA or DGEBF

[0018] so that, even at high temperatures (up to +90°. C.) and under ageing conditions (corrosion, moisture), they exhibit permanent strength. Preferably 4 to 40, particularly 5 to 25, e.g. 20% of the epoxide equivalents (EEW) of the total epoxy resin component may be replaced by such adducts.

[0019] When reacting the epoxy resins with the ATPEG/ATPPG, an excess of epoxy groups over the amino groups is preferably employed so that the latter react completely with epoxide groups. Typically, there is a 1.5 to 10-fold excess, for example a 3.5-fold excess of EEW over the active hydrogen equivalents (AHEW) of the amines.

[0020] The epoxy based prepolymer is then admixed with an acrylate terminated urethane resin as described herein and a latent curing agent; and formulated according to known methods to prepare an improved curable adhesive for use in expanded or non-expanded applications where high impact resistance is needed.

[0021] The adhesive made according to this invention results in high T-peel and impact peel strength in the temperature range of −40° C. to +90° C. In the cured state, these adhesives display the degree of flexibility which is necessary especially in the manufacture of automobiles and trucks. The flexibility of the resin matrix may be adjusted by using ATPEG or ATPPG of varying functionality (bi- or trifunctional) and variable chain-length, and by varying the ratio of ATPEG/ATPPG to epoxy resin. The impact toughness and flowability at ambient temperatures may be adjusted by varying the ratio of epoxy-based prepolymer to the acrylate functional urethane resin or resins.

[0022] The weight ratio of epoxy prepolymer to acrylate terminated urethane resin is preferably between about 50:1 to 1:1—and most preferably between about 20:1 to 4:1.

[0023] Surprisingly, the curable adhesives made by combining the epoxy based prepolymers which contain at least two 1,2-epoxy groups per molecule and an amino-terminated polyalkylene glycol and or carboxyl terminated butadiene-nitrile rubber with the acrylate functional urethane resins and a latent curing agent are pumpable at ambient temperatures or slightly higher , e.g., between about 10 to about 50 degrees C., preferably between about 20 and about 40 degrees C. and have improved peel strengths both in the expanded and unexpanded cured state over the prior art.

[0024] In general, a large number of polyepoxides having at least two 1,2-epoxy groups per molecule are suitable as epoxy resins for making the pre-polymer reaction product employed in this invention. The polyepoxides may be saturated, unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic polyepoxide compounds. Examples of suitable polyepoxides include the polyglycidyl ethers, which are prepared by reaction of epichlorohydrin or epibromohydrin with a polyphenol in the presence of alkali. Suitable polyphenols therefor are, for example, resorcinol, pyrocatechol, hydroquinone, bisphenol A (bis(4-hydroxyphenyl)-2,2-propane), bisphenol F (bis(4-hydroxyphenyl)methane), bis(4-hydroxyphenyl)-1,1-isobutane, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)-1,1-ethane, and 1,5-hydroxynaphthalene. Other suitable polyphenols as the basis for the polyglycidyl ethers are the known condensation products of phenol and formaldehyde or acetaldehyde of the novolak resin-type.

[0025] Other polyepoxides that are in principle suitable are the polyglycidyl ethers of polyalcohols or diamines. Those polyglycidyl ethers are derived from polyalcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, triethylene glycol, 1,5-pentanediol, 1,6-hexanediol or trimethylolpropane.

[0026] Other polyepoxides are polyglycidyl esters of polycarboxylic acids, for example reaction products of glycidol or epichlorohydrin with aliphatic or aromatic polycarboxylic acids, such as oxalic acid, succinic acid, glutaric acid, terephthalic acid or a dimeric fatty acid.

[0027] Other epoxides are derived from the epoxidation products of olefinically-unsaturated cycloaliphatic compounds or from natural oils and fats.

[0028] Particular preference is given to the epoxy resins derived by reaction of bisphenol A or bisphenol F and epichlorohydrin, the liquid epoxy resins preferably being based on bisphenol A and having a sufficiently low molecular weight. The epoxy resins that are liquid at room temperature generally have weights of from 150 to about 480; particular preference is given to an epoxy equivalent weight range of from 182 to 350.

[0029] The epoxy resins that are solid at room temperature are likewise obtainable from polyphenols and epichlorohydrin; particular preference is given to those based on bisphenol A or bisphenol F having a melting point of from 45 to 130° C., preferably from 50 to 80° C.

[0030] They differ from the liquid epoxy resins substantially by the higher molecular weight thereof, as a result of which they become solid at room temperature. According to the present invention, the solid epoxy resins have an epoxy equivalent weight of $\geqq 400$; particular preference is given to an epoxy equivalent weight of from 450 to about 900.

[0031] There may be used as flexibility-conferring epoxy resins adducts of carboxyl-terminated butadieneacrylonitrile copolymers (CTBN) and liquid epoxy resins based on the diglycidyl ether of bisphenol A. Specific examples are the reaction products of Hycar CTBN 1300 X8, 1300 X13 or 1300 X15 of B. F. Goodrich with liquid epoxy resins. There may also be used the reaction products of amino-terminated polyalkylene glycols (such as those sold under the trademark "JEFFAMINES" by Huntsman Chemical) with an excess of liquid polyepoxides. Such reaction products are disclosed, for example, in U.S. Pat. No. 6,015,865. In principle there may also be used according to the present invention as flexibility-conferring epoxy resins reaction products of mercapto-functional polymers with an excess of polyepoxides. Particular preference is given, however, to the reaction products of polymeric fatty acids, especially of dimeric fatty acids, with epichlorohydrin, glycidol or, especially, the diglycidyl ether of bisphenol A (DGBA).

[0032] Since the curable adhesives of the present invention are preferably one-part or single-component compositions and are to be cured at elevated temperature, they also contain a hardener and/or, in addition, one or more accelerators.

[0033] There may be used as thermally-activatable or latent hardeners for the epoxy resin binder system consisting of components (a), (b) and (c) guanidines, substituted guanidines, substituted ureas, melamine resins, guanamine derivatives, cyclic tertiary amines, aromatic amines and/or mixtures thereof. The hardeners may be involved stoichiometrically in the hardening reaction; they may, however, also be catalytically active. Examples of substituted guanidines are methylguanidine, dimethylguanidine, trimethylguanidine, tetra-methylguanidine, methylisobiguanidine, dimethylisobiguanidine, tetramethylisobiguanidine, hexamethylisobiguanidine, heptamethylisobiguanidine and, more especially, cyanoguanidine (dicyandiamide). Representatives of suitable guanamine derivatives which may be mentioned are alkylated benzoguanamine resins, benzoguanamine resins or methoxymethylethoxymethylbenzoguanamine. For the single-component, thermosetting hot melt adhesives, the selection criterion is, of course, the low solubility of those substances at room temperature in the resin system, so that solid, finely ground hardeners are preferred; dicyandiamide is especially suitable. Good storage stability of the composition is thereby ensured.

[0034] In addition to or instead of the above-mentioned hardeners, catalytically-active substituted ureas may be used. They are especially p-chlorophenyl-N,N-dimethylurea (monuron), 3-phenyl-1,1-dimethylurea (fenuron) or 3,4-dichlorophenyl-N,N-dimethylurea (diuron). In principle, catalytically active tertiary acryl- or alkyl-amines, such as benzyldimethylamine, tris(dimethylamino)phenol, piperidine or piperidine derivatives, may also be used, but they are in many cases too highly soluble in the adhesive system, so that usable storage stability of the single-component system is not achieved. Various imidazole derivatives, preferably solid imidazole derivatives, may also be used as catalytically-active accelerators. Examples which may be mentioned are 2-ethyl-2-methylimidazole, N-butylimidazole, benzimidazole and N-C_1 to C_{12}-alkylimidazoles or

N-arylimidazoles. Particular preference is given to the use of a combination of hardener and accelerator in the form of so-called accelerated dicyandiamides in finely ground form. The separate addition of catalytically-active accelerators to the epoxy hardening system is thus not necessary.

[**0035**] The adhesives according to the present invention may also contain known fillers such as the various ground or precipitated chalks, carbon black, calcium magnesium carbonates, barite and, especially, silicate-like fillers of the aluminum magnesium calcium silicate type, for example wollastonite, chlorite.

[**0036**] When it is desirable to make lightweight structures, the adhesives preferably contain in addition to the above-mentioned fillers so-called lightweight fillers, which are selected from hollow glass spheres, flue ash, hollow plastics spheres based on phenol resins, epoxy resins or polyesters, hollow ceramic spheres, or organic lightweight fillers of natural origin, such as ground nutshells, for example the shells of cashew nuts, coconuts or groundnut shells, as well as cork powder or coke powder. Particular preference is given to such lightweight fillers based on hollow glass or ceramic microspheres.

[**0037**] In another embodiment, the matrix materials for the thermosetting, thermally-expandable molded bodies additionally contain fibers based on aramide fibers, carbon fibers, glass fibers, polyamide fibers, polyethylene fibers or polyester fibers, those fibers preferably being pulp fibers or staple fibers having a fiber length of from 0.5 to 6 mm and a diameter of from 5 to 20 mm. Particular preference is given to polyamide fibers of the aramide fiber type, or to polyester fibers.

[**0038**] Although any suitable expanding agents may be employed, such as, e.g., azo compounds, hydrazides and the like, particular preference is given to the expandable or expanded hollow plastic microspheres based on polyvinylidene chloride copolymers; they are commercially available under the trademark names DUALITE and EXPANCEL from Pierce & Stevens and Casco Nobel, respectively.

[**0039**] The adhesive compositions according to the present invention may also contain other common adjuvants and additives, such as plasticisers, reactive diluents, flow auxiliaries, wetting agents, tackifiers, ageing inhibitors, stabilisers and/or coloring pigments. Depending on the requirements made of the adhesive application in respect of its processing properties, its flexibility, the required rigidifying action and the adhesive bond to the substrates, the relative proportions of the individual components may vary within comparatively wide limits. Typical ranges for the main components of the curable adhesive of the present invention are as follows:

(a) epoxy - based prepolymer	from 10–70 wt. %
(b) acrylate-terminated urethane	from 1–15 wt. %
(c) liquid epoxy resins	from 10 to 50 wt. %
(d) hardener and accelerator	from 0.5 to 10 wt. %
(e) expanding agent	from 0 to 5 wt. %
(f) lightweight filler	from 0 to 50 wt. %
(g) fillers	from 3 to 30 wt. %
(h) fibers	from 0 to 5 wt. %
(i) pigments	from 0 to 1 wt. %

[**0040**] In the cured state, the following improvements are achieved as compared with the prior art:

[**0041**] higher impact resistance or toughness in expanded and unexpanded applications

[**0042**] improved flow characteristics at ambient temperatures which permit pumping to the worksite at temperatures well below cure temperatures

[**0043**] higher resistance to pressure

[**0044**] lower brittleness

[**0045**] improved resistance to cold and heat

[**0046**] reduced temperature dependence of the resistance to pressure from −30° C. to +90° C.

[**0047**] constant force level over the deformation path

[**0048**] reduction in density (specific weight)

[**0049**] low water absorption.

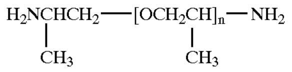
[**0050**] In the preparation of the epoxy prepolymer reaction product, the following compounds may be used as amino-terminated polyethylene glycols (ATPEG) or polypropylene glycols (ATPPG):

[**0051**] 1. linear amino-terminated polyethylene glycols (ATPEG) having the formula

$$H_2N—(CH_2)_2—[O—(CH_2)_2—O—(CH_2)_2]_n—NH_2$$

[**0052**] in which n=17 to 27.

[**0053**] 2. linear amino-terminated polypropylene glycols (ATPPG) having the formula:

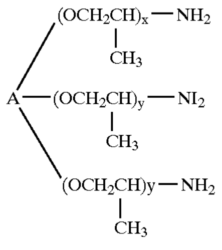


$$H_2N\underset{\substack{|\\CH_3}}{CH}CH_2—[OCH_2\underset{\substack{|\\CH_3}}{CH}]_n—NH_2$$

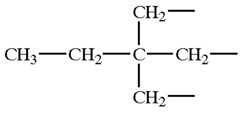
[**0054**] in which n is 5 to 100. They are obtainable under the trade name Jeffamine® of the D-series.

Jeffamine ® Type	n	approx. molecular weight
D-400	5–6	400
D-2000	33	2000
D-4000	68	4000

[**0055**] 3. trifunctional compounds having the formula

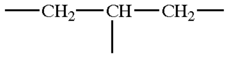


[0056] in which A is



$$CH_3-CH_2-\underset{|\atop CH_2-}{\overset{CH_2-\atop |}{C}}-CH_2-$$

[0057] or a



$$-CH_2-\underset{|}{CH}-CH_2-$$

[0058] group and x, y and z independently of each other are 1 to 40 and x+y+z are preferably >6. They are obtainable under the trade name Jeffamine® of the T-series.

Jeffamine ® Type	A (initiator)	approx. molecular weight
T-403	trimethylol propane	440
T-3000	glycerin	3000
T-5000	glycerin	5000

[0059] Amino-terminated polyalkylene glycols containing both oxyethylene and oxypropylene repeating units may also be utilized.

[0060] As already mentioned, the properties of the curable adhesive can be controlled by varying the ratios of the resin components especially the ratio of the epoxy based prepolymer and the acylate terminated urethane resin according to the present invention. Referring to the epoxy based prepolymer in a preferred embodiment, 0.5 to 1 equivalent (30 to 50 wt-%) of epoxy resin a) which is solid at room temperature and 0.5 to 1 equivalent (10 to 25 wt-%) of epoxy resin b) which is liquid at room temperature are reacted with 0.125 to 0.5 equivalent (35 to 50 wt-%) of the amino-terminated polyethylene or polypropylene glycols, it being possible for 0.5 to 10 wt-% to be a trifunctional ATPPG. The heat-resistance of this cold-flexible resin component can be further improved by adding dimeric acid and/or butadiene-nitrile rubber/DGEBA or DGEBF adducts. More specifically, this reaction product can be modified by adding other modified epoxy resins such as:

[0061] i) adducts of dimeric fatty acids having varying molecular weights with epoxy resins of the diglycidyl ether type of bisphenol A or F (DGEBA or DGEBF) (e.g. Epikote® or EPON® 872); and/or

[0062] ii) adducts of carboxyl-terminated butadiene-nitrile rubber (CTBN) (Hycar® 1300X8, 1300X13;Struktol®) with DGEBA or DGEBF

[0063] When reacting the epoxy resins with the ATPEG/ATPPG, an excess of epoxy groups over the amino groups is used so that the latter react completely with epoxide groups. Typically, there is a 1.5 to 10-fold excess, for example a 3.5-fold excess of EEW over the active hydrogen equivalents (AHEW) of the amines.

[0064] In preparing the curable adhesive according to the present invention, the expoxy-based prepolymer resin component is initially prepared in a first stage. To this end, preferably, the solid epoxy resin a) and the liquid epoxy resin b) are reacted with the ETPEG or ATPPG c) in the desired ratio. The reaction takes place at high temperature, preferably at 90 to 130° C., for example at approximately 120° C., for a duration of e.g. three hours.

[0065] The resultant resin is generally solid or viscous at room temperature. It can be directly further processed by admixture with the acrylate terminated urethane resin and latent curing agent to obtain the curable adhesive according to this invention. However, it is also possible to prepare the resin in advance and to store it until further processing. For further processing, first of all it is necessary to heat the resin in order to lower its viscosity to such a degree that it can be mixed with the other constituents of the reactive hot melt adhesive. The resin is preferably heated to a temperature above 50° C., for example 60 to 110° C., particularly 70 to 95° C. Then the other modified resins including the acrylate terminated urethane resin are added and homogeneously mixed. It must be ensured that heating is not carried out to a temperature at which the added latent curing agent would be activated. For heating the resin and mixing with the other constituents of the reactive adhesive, a heated kneader or planetary mixer is suitably used. It is preferred to incorporate the latent curing agent in the mixture last after the other constituents. It is further preferred to cool the mixture, prior to adding the latent curing agent, to a temperature at the lower limit of the temperature range which is suitable for processing. In accordance with this invention, the epoxy-prepolymer mixture prepared as described above is mixed with an acrylate functional urethane resin and more preferably with acrylate terminated urethane such as those described in U.S. Pat. Nos. 3,297,745; 4,390,662; 4,719,268; 4,486,582 and 4,618,658, and 5,334,654, and 5,700,891 which are hereby incorporated by reference in their entirety. Acrylate-terminated urethane resins comprise the reaction product of an isocyanate terminated urethane prepolymer and an isocyanate reactive acrylate or methacrylate. Isocyanate terminated prepolymers are prepared by reacting a polyfunctional isocyanate, typically an aromatic diisocyanate, with a polyol, preferably a long chain polyether or polyester polyol, such as the ethylene and propyleneoxide adducts of C_2 to C_4 polyalcohols, polytetramethylene glycol (polyTHF), and polycaprolactone. For enhanced flexibilization of the polyepoxide resin, the molecular number average weight of the polyol should range from about 400 to 4000, preferably 700 to 2000. Flexibilizers utilizing a polyol having a number average molecular weight of less than 1000 generally lead to extremely viscous flexibilizers. Higher molecular weight polyols tend to cause premature phase separation in the formulated epoxy leading to poor physical properties. The preferred isocyanate-terminated urethane prepolymer is prepared by any known means, for example, a 2000 mw polypropylene glycol is reacted with an 80/20 2,4/2,6-toluenediisocyanate mixture. Any polyisocyanate such as methylenediphenyldiisocyanate (MDI), isophorone-diisocyanate, (IPDI) or paraphenylenediisocyanate (PPDI) is also suitable.

[0066] The isocyanate-reactive acrylates and methacrylates typically used to prepare the acrylate terminated urethane prepolymers are hydroxy alkylacrylates and methacrylates and these include: hydroxyacrylates such as hydroxyethyl acrylate or methacrylate, hydroxypropyl acrylate or methacrylate, hydroxypentyl acrylate or methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl hexyl methacrylate, hydroxybutyl methacrylate and the like. Typically the ester portion of the acrylate or methacrylate is from a C_2-C_8 alcohol.

[0067] Additional materials which can be used to prepare substances which we choose to describe as included within the definition of acrylate terminated urethane resins include the following:

> **[0068]** 1) prepolymers having number average molecular weights of 250-10,000, preferably 700-4000, and having glass transition temperatures below about 10 degrees C., preferably below about minus 10 degrees C. The average functionality of these prepolymers is at least 2, preferably 2 to 6 and particularly preferably 2 to 3. The terminal functional groups of the prepolymer may be amino or hydroxyl or carboxyl or mercapto, preferably, hydroxyl.

[0069] Particularly preferred prepolymers include linear and branched polypropylene glycols having number average molecular weights about 700 to about 4000;linear and branched polytetrahydrofurans having number average molecular weights between about 700 and about 4000;linear and branched poly(1,2-buyleneoxide) having number average molecular weights between about 700 and about 4000;and hydroxyterminated polyesters having number average molecular weights between about 700 and about 4000.

> **[0070]** 2) polyisocyanates, preferably diisocyanates or triisocyanates such as isophonoronediisocyanate, methylenediphenyldiisocyanate, toluenediisocyanate, hexamethylenediisocyanate,tetramethylxylylenediisocyanate, and the like.
>
> **[0071]** 3) isocyanate-reactive acrylates or methacylates, preferably hydroxyacrylates or—methacrylates such as hydroxyethylacrylate, hydroxypropylacrylate, hydroxyethylmethacrylate, hydroxypropylmethacylate, and the like.

[0072] Chain lengtheners such as diols and triols like 1,4 butanediol, 1,1,1 -trimethylolpropane, glycerol, 1,2,6-hexanetriol, pentaerythritol and the like optionally may be employed, preferably, from 0.01 to about 5% by weight.

[0073] Accordingly, one may react the NCO-reactive prepolymer with excess of polyisocyanate to yield an NCO-tipped prepolymer. When triol chain lengtheners, as described above, are added during this reaction and a suitable amount of polyisocyanate is used, branched NCO-tipped prepolymers are produced. Diol chain lengtheners can be used to control the molecular weight of the resulting prepolymer. This NCO-functional polymer is then reacted with the NCO-reactive acrylate or methacrylate to yield materials which are described for the purposes of this invention as (meth)acrylate terminated urethanes.

[0074] In another embodiment within the scope of this invention, the acrylate terminated urethane resins as described herein may also be employed as an adduct onto an epoxy resin.

[0075] It should be further understood that in yet another embodiment within the scope of the present invention, an acrylate terminated urethane resin is employed to produce a cureable adhesive composition without employing the amine-terminated glycol materials described above by admixing an epoxide resin having at least two 1,2-epoxide groups per molecule as described herein, a copolymer based on at least one 1,3-diene and at least one polar, ethyleneically unsaturated comonomer, such as acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, or esters of acrylic or methacrylic acid with C1-C6 alcohols and a latent epoxide curing agent as described herein.

[0076] The reactive adhesive according to the invention is suitable for glueing or adhering parts made of different materials. It is preferably used for the glueing of metal parts and particularly for the glueing of steel sheets. These can also be electro-galvanized, hot-dip galvanized or zinc/nickel-coated steel sheets.

[0077] The adhesive is usually deposited in the form of a melt on one side, i.e. onto one of the two parts which are to be glued together. It is advantageous that the curable adhesive composition of this invention can be flowed or pumped to the work site at ambient temperatures or slightly above since, in most applications, it is preferable to ensure that the adhesive is heated only up to a temperature at which the latent curing agent is not yet activated. The two parts are joined together immediately after deposition of the adhesive mass and provisionally bonds the two parts to each other.

[0078] The resultant bond already has sufficient strength, e.g., so that the still uncured adhesive is not washed out if the metal sheets which are provisionally bonded to each other are treated for de-greasing purposes in a wash bath and then in a phosphating bath.

[0079] The adhesive is preferably finally cured in an oven at a temperature which lies clearly above the temperature at which the adhesive melt was applied to the parts to be bonded and at or above the temperature at which the hardener and/or accelerators are activated (i.e., become reactive towards the other components of the adhesive). Curing preferably takes place at a temperature above 150° C., for example at 170° C., for about 30 minutes.

EXAMPLE 1

Preparation of Epoxy Pre-Polymer SF 65

[0080] The reaction products of linear and trifunctional ATPPG with DGEBA can be prepared separately or in the mixture. Resins A to J were prepared from the following constituents, the formulation size being 1 kg in each case:

			Preparation of modified epoxy resins (in equivalents)								
	EEW	AHEW	A	B	C	D	E	F	G	H	J
liquid DGEBA	187		0.765	0.765	0.765	0.765	0.69	0.765	—	1.785	—
semisolid	255		—	—	—	—	—	—	1.122	—	1.122

-continued

Preparation of modified epoxy resins (in equivalents)											
	EEW	AHEW	A	B	C	D	E	F	G	H	J
DGEBA solid	475		0.765	0.765	0.765	0.765	0.692	—	—	—	—
DGEBA solid	537		—	—	—	—	—	0.266	—	—	—
DGEBA CTBN adduct	325		0.17	0.17	0.17	0.17	—	—	0.147	—	—
CTBN adduct	190*		—	—	—	—	—	0.125	—	—	0.125
Dimeric acid adduct	650		—	—	—	—	0.34	—	—	—	—
Linear ATPPG		1000	0.44	0.43	0.44	0.43	0.43	—	—	—	—
Linear ATPPG		500	—	—	—	—	—	0.334	0.286	0.238	0.334
trifunct. ATPPG		500	0.08	0.023	—	—	0.013	—	—	0.048	—
trifunct. ATPPG		75	—	—	0.011	0.023	—	—	—	—	—
Viscosity at 80° C. [Pa · s]			36	37	28	33	34	17	6.3	0.59	7.8

*5% CTBN, 95% DGEBA

[0081] Resin mixtures A to J were melted at approximately 80° C. and introduced first into the kneader with delivery screw. then the additional resin (CTBN adduct or dimeric acid adduct) was added and homogeneously mixed at 80° C.

[0082] Abbreviations used herein are defined as follows:

[0083] CTBN=carboxyl-terminated butadiene-nitrile rubber

[0084] ATPPG=amino-terminated polypropylene glycol

[0085] DGEBA=diglycidyl ether of bisphenol A

[0086] EEW=epoxide equivalent weight

[0087] AHEW=active hydrogen equivalent weight

[0088] TSS=tensile shearing strength

[0089] TPS=t-peel strength

[0090] SF-65 =the pre-polymer product resulting from the above procedure

EXAMPLE 2

Preparation of the Acrylate Terminated Urethane

[0091] The NCO-reactive prepolymers are mixed for 45 min at 90-100° C. and 0.1-2 mbar to remove water. The polyisocyanate is then added in one portion under nitrogen at 50° C. The reaction mixture is mixed under nitrogen at 70-80° C. to a constant NCO-value. Then the NCO-reactive acrylate is added together with a polymerization inhibitor. 0.01% DBTL is added after 1 hour at 80° C. and the mixing is continued for additional 2 h, then the epoxy resin is added.

Acrylate Terminated Urethane Resin A:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Capa 305	275	10.7	Polycaprolactone	Solvay Interox
Capa 220	672	26.2	Polycaprolactone	Solvay Interox
MDI	538	21.0	Methylenediphenyldiisocyanate	
HPMA	310	12.1	Hydroxypropyl methacrylate	
Epon 828	769	30.0	DGEBA	

[0092]

Acrylate Terminated Urethane Resin B:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PTHF 650	392	39.0	Polytetrahydrofuran	
MDI	225	22.4	Methylenediphenyldiisocyanate	
HPMA	86	8.6	Hydroxypropyl methacrylate	
Epon 828	301	30.0	DGEBA	

[0093]

Acrylate Terminated Urethane Resin C:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PTHF 650	398	40.0	Polytetrahydrofuran	
MDI	225	22.6	Methylenediphenyldiisocyanate	
HEA	73	7.3	Hydroxyethyl acrylate	
Epon 828	298	30.0	DGEBA	

[0094]

Acrylate Terminated Urethane Resin D:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Capa 305	110	11.0	Polycaprolactone	Solvay Interox
Capa 220	267	26.7	Polycaprolactone	Solvay Interox
MDI	217	21.7	Methylenediphenyldiisocyanate	
HEA	106	10.6	Hydroxyethyl acrylate	
Epon 828	300	30.0	DGEBA	

[0095]

Acrylate Terminated Urethane Resin E:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Dynacoll 7250	612	61.2	Polyester	Degussa
MDI	59	5.9	Methylenediphenyldiisocyanate	
HEA	29	2.9	Hydroxyethyl acrylate	
Epon 818	300	30.0	DGEBA	

[0096]

Acrylate Terminated Urethane Resin F:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Dynacoll 7360	589	58.9	Polyester Polyol	Degussa
MDI	75	7.5	Methylenediphenyldiisocyanate	
HEA	36	3.6	Hydroxyethyl acrylate	
Epon 828	300	30.0	DGEBA	

[0097]

Acrylate Terminated Urethane Resin G:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Pluriol P 900	551	45.4	Polypropyleneglycol	BASF
MDI	225	18.5	Methylenediphenyldiisocyanate	
HEA	73	6.0	Hydroxyethyl acrylate	
Epon 828	364	30.0	DGEBA	

[0098]

Acrylate Terminated Urethane Resin H:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Pluriol P 2000	1225	56.3	Polypropylene glycol	BASF
MDI	225	10.3	Methylenediphenyldiisocyanate	
HEA	73	3.4	Hydroxyethyl acrylate	
Epon 828	653	30.0	DGEBA	

[0099]

Acrylate Terminated Urethane Resin J:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Pluriol P 900	551	46.8	polypropylene glycol	BASF
IPDI	200	17.0	isophorone diisocyanate	
HEA	73	6.2	Hydroxyethyl acrylate	
Epon 828	353	30.0	DGEBA	

[0100]

Acrylate Terminated Urethane Resin K:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Pluriol P 2000	1225	57.2	polypropylene glycol	BASF
IPDI	200	9.3	isophorone diisocyanate	
HEA	73	3.4	Hydroxyethyl acrylate	
Epon 828	642	30.0	DGEBA	

[0101]

Acrylate Terminated Urethane Resin L:				
Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Pluriol P 900	551	49.8	polypropylene glycol	BASF
HDI	151	13.6	hexamethylene diisocyanate	
HEA	73	6.6	Hydroxyethyl acrylate	
Epon 828	332	30.0	DGEBA	

[0102]

Acrylate Terminated Urethane Resin M:				
Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Pluriol P 2000	425	54.8	polypropylene glycol	BASF
Trimethylol propane	2.2	0.28		
HDI	65	8.4	hexamethylene diisocyanate	
HEA	51	6.6	hydroxyethyl acrylate	
Epon 828	233	30.0	DGEBA	

[0103]

Acrylate Terminated Urethane Resin N:				
Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
Ancarez 2364	1000	100.0	acrylate-functional urethane resin	Air Products

EXAMPLE 3

Preparation of the Curable Adhesive

[0104] Curable adhesives are prepared by admixing SF-65 with an acrylate-terminated urethane resin and other components listed in Table 1 below with mixing for 45 minutes at a temperature controlled between 27-38 degrees C. (80-100 degrees F.) and pressure of 0.3-3 psi.

TABLE 1

all data in Grams												
Component/ Adhesive	1	2	3	4	5	6	7	8	9	10	11	12
SF-65 A (Example 1)	500									500	500	500
SF-65 B (Example 1)		500										
SF-65 C (Example 1)			500									
SF-65 D (Example 1)				500								
SF-65 E (Example 1)					500							
SF-65 F (Example 1)						500						
SF-65 G (Example 1)							500					
SF-65 H (Example 1)								500				
SF-65 J (Example 1)									500			
Polydis 3604												
EPON 828	100	100	100	100	100	100	100	100	100	100	100	100
EPON 834												
DER 351	100	100	100	100	100	100	100	100	100	100	100	100
DER 354												
Resin A (Example 2)										100		
Resin B											100	

TABLE 1-continued

all data in Grams

(Example 2)												
Resin C (Example 2)												100
Resin D (Example 2)												
Resin E (Example 2)												
Resin F (Example 2)												
Resin G (Example 2)												
Resin H (Example 2)												
Resin J (Example 2)	100	100	100	100	100	100	100	100	100			
Resin K (Example 2)												
Resin L (Example 2)												
Resin M (Example 2)												
Resin N (Example 2)												
AMICURE CG 1400	50	50	50	50	50	50	50	50	50	50	50	50
DE 83R	20	20	20	20	20	20	20	20	20	20	20	20
BUSAN 11-M1	10	10	10	10	10	10	10	10	10	10	10	10
Calcium Oxide	10	10	10	10	10	10	10	10	10	10	10	10
MONARCH 280	5	5	5	5	5	5	5	5	5	5	5	5
ULTRA PFLEX	29	29	29	29	29	29	29	29	29	29	29	29
DYHARD UR 300	6	6	6	6	6	6	6	6	6	6	6	6
EXPANCEL 551	10	10	10	10	10	10	10	10	10	10	10	10
Cab-O-Sil TS 720	30	30	30	30	30	30	30	30	30	30	30	30
EPODIL 749	30	30	30	30	30	30	30	30	30	30	30	30

Component/ Adhesive	13	14	15	16	17	18	19	20	21	22	23	24
SF-65 A (Example 1)	500	500	500	500	500	500	500	500	500	480		
SF-65 B (Example 1)												
SF-65 C (Example 1)											480	
SF-65 D (Example 1)												
SF-65 E (Example 1)												
SF-65 F (Example 1)												
SF-65 G (Example 1)												
SF-65 H (Example 1)												480
SF-65 J (Example 1)												
Polydis 3604										106	106	106
EPON 828	100	100	100	100	100	100	100	100	100	106	106	106
EPON 834												
DER 351	100	100	100	100	100	100	100	100	100			
DER 354												
Resin A (Example 2)										89		
Resin B (Example 2)												
Resin C (Example 2)												
Resin D (Example 2)	100											

TABLE 1-continued

all data in Grams												
Resin E (Example 2)		100										
Resin F (Example 2)			100									
Resin G (Example 2)				100								
Resin H (Example 2)					100						89	89
Resin J (Example 2)												
Resin K (Example 2)						100						
Resin L (Example 2)							100					
Resin M (Example 2)								100				
Resin N (Example 2)									100			
AMICURE CG 1400	50	50	50	50	50	50	50	50	50	65	65	65
DE 83R	20	20	20	20	20	20	20	20	20			
BUSAN 11-M1	10	10	10	10	10	10	10	10	10	37	37	37
Calcium Oxide	10	10	10	10	10	10	10	10	10			
MONARCH 280	5	5	5	5	5	5	5	5	5	7	7	7
ULTRA PFLEX	29	29	29	29	29	29	29	29	29	300	300	300
DYHARD UR 300	6	6	6	6	6	6	6	6	6	7	7	7
EXPANCEL 551	10	10	10	10	10	10	10	10	10	8.4	8.4	8.4
Cab-O-Sil TS 720	30	30	30	30	30	30	30	30	30	41	41	41
EPODIL 749	30	30	30	30	30	30	30	30	30	37	37	37
Component/ Adhesive	25	26	27	28	29	30	31	32	33	34	35	36
SF-65 A (Example 1)												778
SF-65 B (Example 1)						230						
SF-65 C (Example 1)	480		480									
SF-65 D (Example 1)												865
SF-65 E (Example 1)								500	500			
SF-65 F (Example 1)					190					628		
SF-65 G (Example 1)												
SF-65 H (Example 1)		480		480								
SF-65 J (Example 1)							271					
Polydis 3604	106	106	106	106	80	50		90	90			
EPON 828	106	106	106	106	150	200	388	600	600	600	250	
EPON 834					60			120	120	108	100	
DER 351					60							300
DER 354							33			100	200	
Resin A (Example 2)												
Resin B (Example 2)												
Resin C (Example 2)			89	89								
Resin D (Example 2)												
Resin E (Example 2)												
Resin F (Example 2)												
Resin G (Example 2)					130							
Resin H (Example 2)												
Resin J												

TABLE 1-continued

all data in Grams

(Example 2)												
Resin K (Example 2)												
Resin L (Example 2)												
Resin M (Example 2)	89	89							200		130	280
Resin N (Example 2)						80	50	200		100		
AMICURE CG 1400	65	65	65	65	55	50	57	100	100	110	90	100
DE 83R					15		50			80	70	100
BUSAN 11-M1	37	37	37	37	20	20	10	25	25	20	15	20
Calcium Oxide					20	10	5	20	20	10	20	15
MONARCH 280	7	7	7	7	10	5	10	5	5	10	10	10
ULTRA PFLEX	300	300	300	300	180	300	80	213	213	127	146	158
DYHARD UR 300	7	7	7	7	6	10	4	10	10	20	16	16
EXPANCEL 551	8.4	8.4	8.4	8.4	8.8	9.5	7.8	13.4	13.4	18.8	19.1	17.8
Cab-O-Sil TS 720	41	41	41	41	30	32	34	64	64	66	65	62
EPODIL 749	37	37	37	37	15	20	10	40	40	20	50	50
Component/ Adhesive	**37**	**38**	**39**	**40**	**41**	**42**	**43**	**44**	**45**	**46**	**47**	**48**
SF-65 A (Example 1)												778
SF-65 B (Example 1)							230					
SF-65 C (Example 1)												
SF-65 D (Example 1)	865											
SF-65 E (Example 1)									500	500		
SF-65 F (Example 1)						190					314	
SF-65 G (Example 1)												
SF-65 H (Example 1)					480							
SF-65 J (Example 1)								271				
Polydis 3604		225	300	380	106	80	50		90	90		
EPON 828		615	800	800	106	150	200	388	600	600	300	250
EPON 834						60			120	120	54	100
DER 351	300					60						
DER 354		135						33			50	200
Resin A (Example 2)												
Resin B (Example 2)												
Resin C (Example 2)		150			89							
Resin D (Example 2)												
Resin E (Example 2)												
Resin F (Example 2)												
Resin G (Example 2)						130						
Resin H (Example 2)												
Resin J (Example 2)												
Resin K (Example 2)												
Resin L (Example 2)												
Resin M (Example 2)			260							200		130
Resin N (Example 2)	280			380			80	50	200		50	

TABLE 1-continued

all data in Grams

AMICURE CG 1400	100	106	128	140	65	55	50	57	100	100	55	90
DE 83R	100	60	100			15		50			40	70
BUSAN 11-M1	20	15	30	40	37	20	20	10	25	25	10	15
Calcium Oxide	15	15	10			20	10	5	20	20	29	20
MONARCH 280	10	8	10	10	7	10	5	10	5	5	5	10
ULTRA PFLEX	158	150	260	100	300	180	300	80	213	213	50	146
DYHARD UR 300	16	8	14	60	7	6	10	4	10	10	10	16
EXPANCEL 551	17.8	8.0	14.2	13.8								
Cab-O-Sil TS 720	62	49	72	72	41	30	32	34	64	64	33	65
EPODIL 749	50				37	15	20	10	40	40		50

Component/ Adhesive	49	50	51	52
SF-65 A (Example 1)				
SF-65 B (Example 1)				
SF-65 C (Example 1)				
SF-65 D (Example 1)	865			
SF-65 E (Example 1)				
SF-65 F (Example 1)				
SF-65 G (Example 1)				
SF-65 H (Example 1)				
SF-65 J (Example 1)				
Polydis 3604		225	300	380
EPON 828		615	800	800
EPON 834				
DER 351	300			
DER 354		135		
Resin A (Example 2)				
Resin B (Example 2)				
Resin C (Example 2)		150		
Resin D (Example 2)				
Resin E (Example 2)				
Resin F (Example 2)				
Resin G (Example 2)				
Resin H (Example 2)				
Resin J (Example 2)				
Resin K (Example 2)				
Resin L (Example 2)				
Resin M (Example 2)	280		260	
Resin N (Example 2)				380
AMICURE CG 1400	100	106	128	140
DE 83R	100	60	100	
BUSAN 11-M1	20	15	30	40
Calcium Oxide	15	15	10	
MONARCH 280	10	8	10	10
ULTRA PFLEX	158	150	260	100
DYHARD UR 300	16	8	14	60
EXPANCEL 551				

TABLE 1-continued

	all data in Grams			
Cab-O-Sil TS 720	62	49	72	72
EPODIL 749	50			

[0105]

TABLE 2

Component	Chemical name of component	Tradename of Company
SF-65	Polyoxyalkyleneamine epoxy adduct	
Polydis 3604	CTBN-Epoxy adduct	Struktol
EPON 828	diglycidylether of bisphenol A	Resolution Performance Products
EPON 834	diglycidylether of bisphenol A	Resolution Performance Products
DER 351	diglycidylether of bisphenol A and F	Dow
DER 354	diglycidylether of bisphenol F	Dow
Resin A-N (Example 2)	acrylate functional urethane	
AMICURE CG 1400	Dicyandiamide	Air Products
DE 83R	decabromodiphenyl ether	Great Lakes Chemical Corp
BUSAN 11-M1	Barium metaborate monohydrate	Buckman Laboratories
Calcium Oxide	Calcium Oxide	
MONARCH 280	carbon black	Cabot
ULTRA PFLEX	coated precipitated calcium carbonate	Pfizer
DYHARD UR 300	Fenuron	SKW Trostberg
EXPANCEL 551	Poly(acrylonitril-co-vinylidene chloride), isobutane	Akzo Nobel
Cab-O-Sil TS 720	treated fumed silica	Cabot
Epodil 749	Neopentyl glycol diglycidyl ether	Air Products

[0106] Curing: Fix bond with clips and place specimens for 20 min in an air-circulating oven at160° C.

[0107] Table 3 below describes the properties of the above described adhesives following curing.

TABLE 3

	PROPERTIES			
Adhesive #	Viscosity (Flow at 80 psi, 0.104 inch)	Expansion@ 160 C./ 20 min.	Shear Strength w/oil 160 C. for 20 min.	T-Peel Strength w/oil 160 C. for 20 min.
1	110 sec/20 gms @ 32.1 C.	AVE. = 97%	EZG: AVE. = 13.8 MPa	EZG: 151 N/25 mm
	25.8 sec/20 gms @ 39.0 C.		HDG: AVE. = 13.0 MPa	HDG: 133 N/25 mm
2	138 sec/20 gms @ 33.3 C.	AVE. = 89%	EZG: AVE. = 9.1 MPa	EZG: 107 N/25 mm
	31.4 sec/20 gms @ 40.1 C.		HDG: AVE. = 6.6 MPa	HDG: 94 N/25 mm
3	98.2 sec/20 gms @ 32.4 C.	AVE. = 99%	EZG: AVE. = 13.6 MPa	EZG: 150 N/25 mm
	20.8 sec/20 gms @ 38.4 C.		HDG: AVE. = 13.3 MPa	HDG: 138 N/25 mm
4	107 sec/20 gms @ 32.0 C.	AVE. = 90%	EZG: AVE. = 11.4 MPa	EZG: 153 N/25 mm
	23.8 sec/20 gms @ 38.9 C.		HDG: AVE. = 10.0 MPa	HDG: 129 N/25 mm

TABLE 3-continued

	PROPERTIES			
Adhesive #	Viscosity (Flow at 80 psi, 0.104 inch)	Expansion@ 160 C./ 20 min.	Shear Strength w/oil 160 C. for 20 min.	T-Peel Strength w/oil 160 C. for 20 min.
5	110 sec/20 gms @ 31.8	AVE. = 103%	EZG: AVE. = 12.5 MPa	EZG: 147 N/25 mm
	20.0 sec/20 gms @ 39.5 C.		HDG: AVE. = 12.1 MPa	HDG: 130 N/25 mm
6	59.9 sec/20 gms @ 32.0 C.	AVE. = 118%	EZG: AVE. = 13.5 MPa	EZG: 139 N/25 mm
	14.5 sec/20 gms @ 39.3 C.		HDG: AVE. = 12.1 MPa	HDG: 125 N/25 mm
7	23.7 sec/20 gms @ 32.2 C.	AVE. = 79%	EZG: AVE. = 15.1 MPa	EZG: 126 N/25 mm
	7.3 sec/20 gms @ 39.5 C.		HDG: AVE. = 14.2 MPa	HDG: 112 N/25 mm
8	10.1 sec/20 gms @ 32.5	AVE. = 47%	EZG: AVE. = 18.6 MPa	EZG: 107 N/25 mm
	5.9 sec/20 gms @ 39.8 C.		HDG: AVE. = 12.7 MPa	HDG: 87 N/25 mm
9	28.0 sec/20 gms @ 32.0 C.	AVE. = 81%	EZG: AVE. = 15.6 MPa	EZG: 118 N/25 mm
	9.4 sec/20 gms @ 39.1 C.		HDG: AVE. = 14.9 MPa	HDG: 102 N/25 mm
10	100 sec/20 gms @ 32.2 C.	AVE. = 99%	EZG: AVE. = 14.4 MPa	EZG: 140 N/25 mm
	23.7 sec/20 gms @ 39.0 C.		HDG: AVE. = 13.8 MPa	HDG: 123 N/25 mm
11	144 sec/20 gms @ 30.9 C.	AVE. = 106%	EZG: AVE. = 11.9 MPa	EZG: 135 N/25 mm
	26.1 sec/20 gms @ 40.2 C.		HDG: AVE. = 11.2 MPa	HDG: 122 N/25 mm
12	138 sec/20 gms @ 31.5 C.	AVE. = 96%	EZG: AVE. = 14.1 MPa	EZG: 156 N/25 mm
	25.8 sec/20 gms @ 39.0 C.		HDG: AVE. = 13.5 MPa	HDG: 144 N/25 mm
13	115 sec/20 gms @ 31.9 C.	AVE. = 99%	EZG: AVE. = 13.8 MPa	EZG: 150 N/25 mm
	29.8 sec/20 gms @ 38.1 C.		HDG: AVE. = 12.7 MPa	HDG: 135 N/25 mm
14	96.0 sec/20 gms @ 31.3 C.	AVE. = 87%	EZG: AVE. = 8.1 MPa	EZG: 72 N/25 mm
	20.8 sec/20 gms @ 39.1 C.		HDG: AVE. = 8.3 MPa	HDG: 72 N/25 mm
15	101.6 sec/20 gms @ 31.5 C.	AVE. = 92%	EZG: AVE. = 4.5 MPa	EZG: 58 N/25 mm
	23.0 sec/20 gms @ 39.0 C.		HDG: AVE. = 4.8 MPa	HDG: 53 N/25 mm
16	95.6 sec/20 gms @ 32.3 C.	AVE. = 101%	EZG: AVE. = 16.8 MPa	EZG: 166 N/25 mm
	25.8 sec/20 gms @ 39.0 C.		HDG: AVE. = 14.3 MPa	HDG: 131 N/25 mm
17	91.1 sec/20 gms @ 32.3 C.	AVE. = 108%	EZG: AVE. = 14.6 MPa	EZG: 170 N/25 mm
	25.4 sec/20 gms @ 37.8 C.		HDG: AVE. = 13.0 MPa	HDG: 143 N/25 mm
18	101 sec/20 gms @ 32.2 C.	AVE. = 92%	EZG: AVE. = 13.0 MPa	EZG: 150 N/25 mm
	25.4 sec/20 gms @ 38.8 C.		HDG: AVE. = 13.0 MPa	HDG: 139 N/25 mm
19	106 sec/20 gms @ 32.3 C.	AVE. = 95%	EZG: AVE. = 13.5 MPa	EZG: 148 N/25 mm
	28.1 sec/20 gms @ 38.5 C.		HDG: AVE. = 13.2 MPa	HDG: 135 N/25 mm
20	136 sec/20 gms @ 32.4 C.	AVE. = 109%	EZG: AVE. = 15.2 MPa	EZG: 168 N/25 mm
	36.8 sec/20 gms @ 38.8 C.		HDG: AVE. = 14.5 MPa	HDG: 157 N/25 mm
21	102 sec/20 gms @ 32.4 C.	AVE. = 97%	EZG: AVE. = 13.8 MPa	EZG: 148 N/25 mm
	22.0 sec/20 gms @ 40.0 C.		HDG: AVE. = 12.9 MPa	HDG: 135 N/25 mm

TABLE 3-continued

PROPERTIES

Adhesive #	Viscosity (Flow at 80 psi, 0.104 inch)	Expansion@ 160 C./ 20 min.	Shear Strength w/oil 160 C. for 20 min.	T-Peel Strength w/oil 160 C. for 20 min.
22	220 sec/20 gms @ 32.4 C.	AVE. = 112%	EZG: AVE. = 16.9 MPa	EZG: 131 N/25 mm
	40.1 sec/20 gms @ 38.6 C.		HDG: AVE. = 15.4 MPa	HDG: 133 N/25 mm
23	184 sec/20 gms @ 32.3 C.	AVE. = 116%	EZG: AVE. = 15.7 MPa	EZG: 129 N/25 mm
	31.8 sec/20 gms @ 38.4 C.		HDG: AVE. = 14.9 MPa	HDG: 124 N/25 mm
24	18.1 sec/20 gms @ 32.3	AVE. = 116%	EZG: AVE. = 17.6 MPa	EZG: 118 N/25 mm
	8.7 sec/20 gms @ 39.8 C.		HDG: AVE. = 14.3 MPa	HDG: 111 N/25 mm
25	198 sec/20 gms @ 32.0 C.	AVE. = 90%	EZG: AVE. = 16.6 MPa	EZG: 125 N/25 mm
	40.0 sec/20 gms @ 38.3 C.		HDG: AVE. = 15.3 MPa	HDG: 125 N/25 mm
26	14.3 sec/20 gms @ 33.0	AVE. = 107%	EZG: AVE. = 17.8 MPa	EZG: 120 N/25 mm
	8.8 sec/20 gms @ 39.2 C.		HDG: AVE. = 15.0 MPa	HDG: 122 N/25 mm
27	214 sec/20 gms @ 32.5 C.	AVE. = 92%	EZG: AVE. = 15.4 MPa	EZG: 133 N/25 mm
	40.8 sec/20 gms @ 38. C.		HDG: AVE. = 14.0 MPa	HDG: 127 N/25 mm
28	15.5 sec/20 gms @ 32.6	AVE. = 102%	EZG: AVE. = 17.0 MPa	EZG: 109 N/25 mm
	9.5 sec/20 gms @ 38.8 C.		HDG: AVE. = 14.6 MPa	HDG: 98 N/25 mm
29	71.8 sec/20 gms @ 32.1 C.	AVE. = 98%	EZG: AVE. = 16.8 MPa	EZG: 129 N/25 mm
	23.8 sec/20 gms @ 39.2 C.		HDG: AVE. = 15.6 MPa	HDG: 128 N/25 mm
30	67.6 sec/20 gms @ 31.9 C.	AVE. = 107%	EZG: AVE. = 16.5 MPa	EZG: 130 N/25 mm
	23.3 sec/20 gms @ 39.0 C.		HDG: AVE. = 15.5 MPa	HDG: 126 N/25 mm
31	82.4 sec/20 gms @ 32.0 C.	AVE. = 103%	EZG: AVE. = 16.9 MPa	EZG: 125 N/25 mm
	27.5 sec/20 gms @ 39.2 C.		HDG: AVE. = 15.7 MPa	HDG: 127 N/25 mm
32	70.5 sec/20 gms @ 31.8 C.	AVE. = 96%	EZG: AVE. = 16.7 MPa	EZG: 132 N/25 mm
	20.9 sec/20 gms @ 39.2 C.		HDG: AVE. = 15.5 MPa	HDG: 120 N/25 mm
33	90.2 sec/20 gms @ 31.9 C.	AVE. = 92%	EZG: AVE. = 17.3 MPa	EZG: 138 N/25 mm
	24.7 sec/20 gms @ 39.1 C.		HDG: AVE. = 15.9 MPa	HDG: 128 N/25 mm
34	74.4 sec/20 gms @ 32.0 C.	AVE. = 106%	EZG: AVE. = 16.7 MPa	EZG: 130 N/25 mm
	17.4 sec/20 gms @ 39.3 C.		HDG: AVE. = 15.2 MPa	HDG: 127 N/25 mm
35	76.1 sec/20 gms @ 32.0 C.	AVE. = 103%	EZG: AVE. = 14.7 MPa	EZG: 150 N/25 mm
	19.0 sec/20 gms @ 39.4 C.		HDG: AVE. = 14.3 MPa	HDG: 139 N/25 mm
36	71.0 sec/20 gms @ 31.8 C.	AVE. = 100%	EZG: AVE. = 15.9 MPa	EZG: 132 N/25 mm
	15.5 sec/20 gms @ 39.3 C.		HDG: AVE. = 14.8 MPa	HDG: 129 N/25 mm
37	65.9 sec/20 gms @ 32.2 C.	AVE. = 105%	EZG: AVE. = 16.1 MPa	EZG: 130 N/25 mm
	14.1 sec/20 gms @ 39.0C		HDG: AVE. = 15.5 MPa	HDG: 130 N/25 mm
38	14.2 sec/20 gms @ 32.0 C.	AVE. = 117%	EZG: AVE. = 16.6 MPa	EZG: 100 N/25 mm
	4.3 sec/20 gms @ 39.1 C.		HDG: AVE. = 15.5 MPa	HDG: 94 N/25 mm

TABLE 3-continued

		PROPERTIES		
Adhesive #	Viscosity (Flow at 80 psi, 0.104 inch)	Expansion@ 160 C./ 20 min.	Shear Strength w/oil 160 C. for 20 min.	T-Peel Strength w/oil 160 C. for 20 min.
39	16.2 sec/20 gms @ 31.8 C. 6.6 sec/20 gms @ 39.0 C.	AVE. = 121%	EZG: AVE. = 16.9 MPa HDG: AVE. = 15.4 MPa	EZG: 113 N/25 mm HDG: 102 N/25 mm
40	12.9 sec/20 gms @ 31.9 C. 4.0 sec/20 gms @ 38.7 C.	AVE. = 106%	EZG: AVE. = 15.7 MPa HDG: AVE. = 15.0 MPa	EZG: 130 N/25 mm HDG: 121 N/25 mm
41	16.1 sec/20 gms @ 32.2 9.1 sec/20 gms @ 39.0 C.		EZG: AVE. = 26.3 MPa HDG: AVE. = 18.9 MPa	EZG: 186 N/25 mm HDG: 164 N/25 mm
42	70.0 sec/20 gms @ 32.3 C. 23.5 sec/20 gms @ 39.0 C.		EZG: AVE. = 27.0 MPa HDG: AVE. = 21.9 MPa	EZG: 201 N/25 mm HDG: 172 N/25 mm
43	67.0 sec/20 gms @ 32.09 C. 24.7 sec/20 gms @ 38.8 C.		EZG: AVE. = 26.9 MPa HDG: AVE. = 22.2 MPa	EZG: 190 N/25 mm HDG: 166 N/25 mm
44	80.1 sec/20 gms @ 32.0 C. 31.9 sec/20 gms @ 39.0 C.		EZG: AVE. = 27.1 MPa HDG: AVE. = 20.4 MPa	EZG: 196 N/25 mm HDG: 167 N/25 mm
45	65.2 sec/20 gms @ 31.9 C. 19.7 sec/20 gms @ 39.0 C.		EZG: AVE. = 25.7 MPa HDG: AVE. = 20.5 MPa	EZG: 202 N/25 mm HDG: 160 N/25 mm
46	100.1 sec/20 gms @ 31.8 C. 28.1 sec/20 gms @ 38.7 C.		EZG: AVE. = 26.6 MPa HDG: AVE. = 21.5 MPa	EZG: 196 N/25 mm
47	150.0 sec/20 gms @ 35.0 C. 76.8 sec/20 gms @ 39.2 C.		EZG: AVE. = 25.1 MPa HDG: AVE. = 19.4 MPa	EZG: 191 N/25 mm HDG: 168 N/25 mm
48	42.6 sec/20 gms @ 35.0 C. 19.5 sec/20 gms @ 39.2 C.		EZG: AVE. = 24.3 MPa HDG: AVE. = 19.0 MPa	EZG: 203 N/25 mm
49	37.2 sec/20 gms @ 35.1 C. 15.5 sec/20 gms @ 39.3 C.		EZG: AVE. = 24.7 MPa HDG: AVE. = 19.3 MPa	EZG: 223 N/25 mm
50	9.0 sec/20 gms @ 34.9 C. 4.5 sec/20 gms @ 39.0 C.		EZG: AVE. = 28.0 MPa HDG: AVE. = 20.9 MPa	EZG: 167 N/25 mm
51	13.4 sec/20 gms @ 35.1 C. 6.2 sec/20 gms @ 38.9 C.		EZG: AVE. = 27.6 MPa HDG: AVE. = 22.7 MPa	EZG: 188 N/25 mm
52	10.0 sec/20 gms @ 32.0 C. 4.0 sec/20 gms @ 38.7 C.		EZG: AVE. = 25.6 MPa HDG: AVE. = 21.8 MPa	EZG: 214 N/25 mm

What is claimed is:

1. A curable adhesive which comprises:

A) a prepolymer reaction mixture of

(a) epoxy resin or resins prepared from bisphenol A or bisphenol F and epichlorohydrin having an epoxide equivalent weight of from about 150 to about 700;and

(b) an amino-terminated polyalkylene glycol, or a carboxyl terminated butadiene nitrile resin, or mixtures thereof;

B) an acrylate terminated urethane resin; and

C) a latent curing agent.

2. A curable adhesive of claim 1 which comprises an expanding agent to expand the adhesive during curing.

3. A curable adhesive of claim 2 wherein the expanding agent comprises expanded or expandable hollow plastic microspheres.

4. A curable adhesive of claim 1 in which the acrylate-terminated urethane resin comprises the reaction product of an isocyanate terminated urethane prepolymer and an isocyanate reactive acrylate or methacrylate.

5. A curable adhesive of claim 4 in which the isocyanate terminated prepolymer is prepared by reacting a polyfunctional isocyanate with a polyol.

6. A curable adhesive of claim 5 in which the polyfunctional isocyanate is an aromatic diisocyanate.

7. The curable adhesive of claim 5 in which the number average molecular weight of the polyol is from about 400 to about 4000.

8. The curable adhesive of claim 5 in which the number average molecular weight of the polyol is from about 700 to about 2000.

9. The curable adhesive of claim 4 in which the isocyanate terminated urethane prepolymer is prepared by reacting polypropylene glycol or polytetramethylene glycol and an isocyanate selected from the group consisting of 2,4 toluenediisocyanate, 2,6-toluenediisocyanate, 2,6 -toluenediisocyanate, 2,4 -toluenediisocyanate, methylenediphenyldiisocyanate, isophoronediisocyanate, hexamethylenediisocyanate, paraphenylenediisocyanate and mixtures thereof.

10. The curable adhesive of claim 4 in which the isocyanate reactive acrylates and methacrylates are selected from the group consisting of hydroxy alkylacrylates and hydroxyalkyl methacrylates.

11. The curable adhesive of claim 4 in which the isocyanate reactive acrylate or methacrylate is derived from a C_2-C_8 alcohol.

12. A curable adhesive composition comprising :a prereacted reaction product of

A) a pre-reacted reaction product of

(a) about 0.5 to about 1 equivalent of an epoxy resin which is solid at room temperature prepared from bisphenol A or bisphenol F and epichlorohydrin having an epoxide equivalent weight of from about 400 to about 700;

(b) about 0.5 to about 1 equivalent of an epoxy resin which is liquid at room temperature prepared from bisphenol A or bisphenol F and epichlorohydrin having an epoxide equivalent weight of from about 150 to about 220; and

(c) about 0.125 to about 0.5 equivalent of an amino-terminated polyalkylene glycol selected from the group consisting of polyethylene and polypropylene glycols; wherein said epoxy resins (a) and (b) are present in an amount such that a stoichiometric excess of at least 1 equivalent of epoxy groups over the amino groups is provided, said amino-terminated polyalkylene glycol comprising

i) a linear amino-terminated polyethylene glycol, or

ii) a linear amino-terminated polypropylene glycol, or,

iii) a linear amino-terminated polyethylene glycol and a trifunctional amino-terminated polypropylene glycol;

wherein about 4 to about 40% of the epoxy equivalents of the total epoxy resin component are replaced by an adduct of dimeric fatty acides on epoxy resins prepared from diglycidyl ethers of bisphenol A or F, or by an adduct of carboxyl-terminated butadiene-nitrile rubber on epoxy resins prepared from diglycidyl ethers of bisphenol A or F;

B) an acrylate terminated urethane resin which comprises the reaction product of an isocyanate terminated urethane prepolymer and an isocyanate reactive acrylate or methacrylate;

C) a latent curing agent; and

D) an expanding agent comprising hollow plastic microspheres.

13. A curable adhesive composition which comprises:

A) a reaction product of a polyepoxide resin having at least two 1,2-epoxy groups per molecule with polyoxy alkylene amine and, optionally, an adduct of carboxy terminated butadiene-nitrile rubber (BNR);

B) an acrylate terminated urethane resin; and

C) a latent curing agent.

14. A curable adhesive which comprises:

A) a prepolymer reaction mixture of

(a) an epoxy resin, an epoxy resin which is solid at room temperature prepared from bisphenol A or bisphenol F and epichlorohydrin having an epoxide equivalent weight of from about 400 to about 700;

(b) an epoxy resin which is liquid at room temperature prepared from bisphenol A or bisphenol F and epichlorohydrin having an epoxide equivalent weight of from about 150 to about 220; and

(c) an amino-terminated polyalkylene glycol selected from the group consisting of polyethylene and polypropylene glycols, or a carboxyl terminated butadienenitrile resin, or mixtures thereof;

B) an acrylate-terminated urethane resin;

C) a latent curing agent; and

D) an expanding agent comprising hollow microspheres.

15. A method of making a composite article which comprises: contacting a surface with a curable adhesive which comprises:

A) a prepolymer reaction mixture of

(a) epoxy resin or resins prepared from bisphenol A or bisphenol F and epichlorohydrin having an epoxide equivalent weight of from about 150 to about 700;

(b) an amino-terminated polyalkylene glycol selected from the group consisting of polyethylene and polypropylene glycols, or a carboxyl terminated butadiene nitrile resin, or mixtures thereof,

B) an acrylate-terminated urethane resin; and

C) a latent curing agent; and curing the adhesive in contact with the surface to prepare a composite article.

16. The method of claim 15 in which the surface is metal or plastic.

17. The method of claim 15 in which at least two surfaces are contacted with the curable adhesive and cured in contact therewith.

18. The method of claim 15 in which the curable adhesive is flowed into contact with the surface at a temperature between about 10 and about 50 degrees C.

19. The method of claim 15 in which the curable adhesive is flowed into contact with the surface at a temperature between about 20 and about 40 degrees C.

20. The method of claim 15 in which the curable adhesive contains hollow plastic microspheres.

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