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## (54) Title: TWO-PART EPOXY-BASED STRUCTURAL ADHESIVES

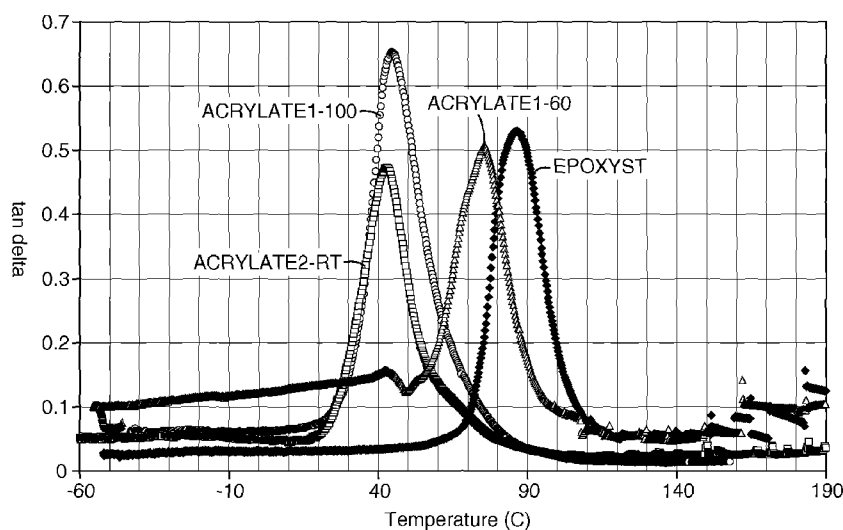


Fig. 1

(57) Abstract: A two-part structural adhesive composition comprising a curable epoxy resin, an amine curing agent, a toughening agent, and a reactive liquid modifier. The structural adhesive may also include secondary curatives, initiators, reactive diluents and combinations thereof. The structural adhesives may be used to replace or augment conventional joining means such as welds or mechanical fasteners in bonding parts together.

5

**TWO-PART EPOXY-BASED STRUCTURAL ADHESIVES**

10

**FIELD OF THE INVENTION**

The present invention relates to two-part epoxy-based structural adhesives, particularly epoxy-based adhesives that when cured exhibit properties useful in structural assembly. The present invention also relates to methods of making and using the two-part epoxy-based structural adhesives.

15

**BACKGROUND**

Structural adhesives can be defined as materials used to bond other high strength materials, such as wood, composites, or metal, so that the practical adhesive bond strength is in excess of 6.9 MPa (1,000 psi) at room temperature. Structural adhesives are used in a variety of applications that include general-use industrial applications, as well as high-performance applications in the automotive and aerospace industries. Structural adhesives may be used to replace or augment conventional joining techniques such as screws, bolts, nails, staples, rivets and metal fusion processes (e.g., welding, brazing and soldering). In particular, in the transportation industry (e.g., automotive, aircraft or watercraft), structural adhesives can present a light weight alternative to mechanical fasteners. To be suitable as structural adhesives, the adhesives should have high mechanical strength and impact resistance.

The inherent brittleness of heat-cured epoxy-based adhesives can be overcome by adding toughening agents to the adhesive compositions which impart greater impact resistance to the cured epoxy compositions. Typically, a rather large amount of toughening agent may have to be employed to achieve satisfying toughening and/or impact resistance. However, large amounts of toughening agents can lead to an increased viscosity of the adhesive composition and poor handling. Therefore, there is a need for providing compositions, in particular compositions suitable as structural adhesives, having the same or even improved toughening effect and/or impact resistance at a lower level of toughening agent.

**SUMMARY**

In one embodiment, the invention provides a two-part structural adhesive composition comprising a curable epoxy resin, an amine curing agent, a toughening

5 agent, and a reactive liquid modifier comprising an acrylate functionalized compound, an acrylamide functionalized compound, an oxalic amide functionalized compound, an acetoacetoxy functionalized urethane, an acetoacetoxy functionalized polyalkene, or a combination thereof.

10 In another embodiment, the invention provides a method of making a composite article, the method comprising applying the two-part adhesive to a surface, and curing the two-part adhesive in contact with the surface to form a composite article.

15 In a further embodiment, the invention provides a method of forming a bonded joint between members, the method comprising applying the two-part adhesive to a surface of at least one of two or more members, joining the members so that the two-part adhesive is sandwiched between the two or more members, and curing the two-part adhesive to form a bonded joint between the two or more members.

Other features and aspects of the invention will become apparent by consideration of the detailed description and accompanying drawings.

20

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a DMA plot of tangent delta versus temperature for various acrylate-epoxy adhesives described in Example 1.

25 FIG. 2 is a DMA plot of tangent delta versus temperature for various oxalic amide-epoxy adhesives described in Example 2.

FIG. 3 is a DMA plot of tangent delta versus temperature for various AcAcUD-epoxy adhesives described in Example 3.

FIG. 4 is a DMA plot of tangent delta versus temperature for various AcAcXM-epoxy adhesives described in Example 3.

30 FIG. 5 is a DMA plot of tangent delta versus temperature for various AcAc1K-epoxy adhesives described in Example 4.

FIG. 6 is a DMA plot of tangent delta versus temperature for various AcAc2K-epoxy adhesives described in Example 4.

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#### DETAILED DESCRIPTION

Before any embodiments of the invention are explained in detail, it is to be understood that the invention is not limited in its application to the details of construction and the arrangement of components set forth in the following description

5 or illustrated in the following drawings. The invention is capable of other  
embodiments and of being practiced or of being carried out in various ways. Also, it  
is to be understood that the phraseology and terminology used herein is for the  
purpose of description and should not be regarded as limiting. The use of  
“including,” “comprising,” or “having” and variations thereof herein is meant to  
10 encompass the items listed thereafter and equivalents thereof as well as additional  
items. Any numerical range recited herein includes all values from the lower value to  
the upper value. For example, if a concentration range is stated as 1% to 50%, it is  
intended that values such as 2% to 40%, 10% to 30%, or 1% to 3%, etc., are expressly  
enumerated in this specification. These are only examples of what is specifically  
15 intended, and all possible combinations of numerical values between and including  
the lowest value and the highest value enumerated are to be considered to be  
expressly stated in this application.

The present invention relates to two-part epoxy-based structural adhesives  
comprising a curable epoxy resin, an amine curing agent, a toughening agent and a  
20 reactive liquid modifier. Without wishing to be bound by theory, it is believed that  
the reactive liquid modifier polymerizes to form an interpenetrating polymer network  
and/or semi-interpenetrating polymer network (referred to collectively as “IPNs”)  
with the epoxy resin. As used herein, interpenetrating polymer network refers to an  
intimate combination of two polymers both in network form, at least one of which is  
25 synthesized and/or cross-linked in the immediate presence of the other. Semi-  
interpenetrating polymer network refers to a combination of two polymers, one cross-  
linked and one linear, at least one of which is synthesized and/or cross-linked in the  
immediate presence of the other. The IPNs are believed to enhance the performance  
of the structural adhesives.

30 Structural adhesives of the present invention may also include secondary  
curatives, radical initiators, reactive diluents, and combinations thereof, as well as  
other ingredients known to those skilled in the art (e.g., fillers and pigments).

The structural adhesives may be used to replace or augment conventional  
joining means such as welds or mechanical fasteners in bonding parts together.

### 35 Curable Epoxy Resins

Structural adhesives of the present invention comprise at least one curable  
epoxy resin. The epoxy resins may be monomeric, dimeric, oligomeric or

- 5 polymeric epoxy materials containing at least one epoxy functional group per molecule. Such resins may be aromatic or aliphatic, cyclic or acyclic, monofunctional or polyfunctional. The backbone of the resin may be of any type, and substituent groups thereon can be any group not having a nucleophilic group or electrophilic group (such as an active hydrogen atom) which is reactive with an oxirane ring. Exemplary
- 10 substituent groups include halogens, ester groups, ethers, sulfonate groups, siloxane groups, nitro groups, amide groups, nitrile groups, and phosphate groups.

The molecular weights of the epoxy resins may range from about 100 g/mole for monomeric or oligomeric resins to 50,000 g/mole or more for polymeric resins. Suitable epoxy resins are typically a liquid at room temperature. However, soluble

15 solid epoxy resins may also be used. Epoxy resins may be used alone or in combination. In some embodiments, the epoxy component comprises a mixture of two or more epoxy resins in order to modify and adapt the mechanical properties of the cross-linked structural adhesive with respect to specific requirements.

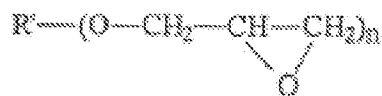
Types of epoxy resins that can be used include, for example, the reaction

20 product of bisphenol A and epichlorohydrin, the reaction product of phenol and formaldehyde (novolac resin) and epichlorohydrin, peracid epoxies, glycidyl esters, glycidyl ethers, the reaction product of epichlorohydrin and p-amino phenol, the reaction product of epichlorohydrin and glyoxal tetraphenol and the like.

Epoxides that are particularly useful in the present invention are of the

25 glycidyl ether type. Suitable glycidyl ether epoxides may include those in general formula (I):

(I)



- 30 wherein R' is an n valent organic residue that may include, for example, an alkyl group, an alkyl ether group, or an aryl group; and n is at least 1. In some

- 5     embodiments R' is a poly(alkylene oxide). In some embodiments, n ranges from 1 to 4.

      Suitable glycidyl ether epoxides of formula (I) include glycidyl ethers of bisphenol A and F, aliphatic diols and cycloaliphatic diols. In some embodiments, the glycidyl ether epoxides of formula (I) have a molecular weight in the range of from about 170 g/mol to about 10,000 g/mol. In other embodiments, the glycidyl ether epoxides of formula (I) have a molecular weight in the range of from about 200 g/mol to about 3,000 g/mol .

      Useful glycidyl ether epoxides of formula (I) include linear polymeric epoxides having terminal epoxy groups (e.g., a diglycidyl ether of polyoxyalkylene glycol) and aromatic glycidyl ethers (e.g., those prepared by reacting a dihydric phenol with an excess of epichlorohydrin). Examples of useful dihydric phenols include resorcinol, catechol, hydroquinone, and the polynuclear phenols including p,p'-dihydroxydibenzyl, p,p'-dihydroxyphenylsulfone, p,p'-dihydroxybenzophenone, 2,2'-dihydroxyphenyl sulfone, p,p'-dihydroxybenzophenone, 2,2-dihydroxy-1,1-dinaphthylmethane, and the 2,2', 2,3', 2,4', 3,3', 3,4', and 4,4' isomers of dihydroxydiphenylmethane, dihydroxydiphenyldimethylmethane, dihydroxydiphenylethylmethylmethane, dihydroxydiphenylmethylpropylmethane, dihydroxydiphenylethylphenylmethane, dihydroxydiphenylpropylphenylmethane, dihydroxydiphenylbutylphenylmethane, dihydroxydiphenyltolylethane, dihydroxydiphenyltolylmethylmethane, dihydroxydiphenyldicyclohexylmethane, and dihydroxydiphenylcyclohexane.

      Suitable commercially available aromatic and aliphatic epoxides include diglycidylether of bisphenol A (e.g., EPON 828, EPON 872, EPON 1001, EPON 1310 and EPONEX 1510 available from Hexion Specialty Chemicals GmbH in Rosbach, Germany), DER-331, DER-332, and DER-334 (available from Dow Chemical Co. in Midland, MI, USA); diglycidyl ether of bisphenol F (e.g., EPICLON 830 available from Dainippon Ink and Chemicals, Inc.); PEG<sub>1000</sub>DGE (available from Polysciences, Inc. in Warrington, PA, USA); silicone resins containing diglycidyl epoxy functionality; flame retardant epoxy resins (e.g., DER 580, a brominated bisphenol type epoxy resin available from Dow Chemical Co. in Midland, MI, USA); 1,4-dimethanol cyclohexyl diglycidyl ether; and 1,4-butanediol diglycidyl ether. Other epoxy resins based on bisphenols are commercially available under the tradenames D.E.N., EPALLOY and EPILOX.

5 In some embodiments of the present invention, the structural adhesives comprise at least about 20% by weight curable epoxy resin, in some embodiments at least about 40% by weight curable epoxy resin, and in some embodiments at least about 50% by weight curable epoxy resin. In some embodiments of the present invention, the structural adhesives comprise less than about 90% by weight curable epoxy resin, in some embodiments less than about 80% by weight curable epoxy resin, and in some embodiments less than about 70% by weight curable epoxy resin. Percent weight is based upon the total weight of the two-part structural adhesive (i.e., the combined weights of Parts A and B).

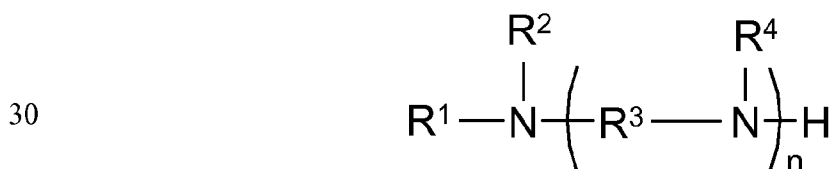
15 In some embodiments of the present invention, the structural adhesives comprise from about 20% to about 90% by weight curable epoxy resin. In other embodiments, the structural adhesives comprise from about 40% to about 70% by weight curable epoxy resin. In yet other embodiments, the structural adhesives comprise from about 50% to about 70% by weight curable epoxy resin.

#### Amine Curing Agents

20 Structural adhesives of the present invention also comprise at least one curing agent capable of cross-linking the curable epoxy resin. The amine curing agent may also be used to cross-link some types of reactive liquid modifiers. Typically these agents are primary or secondary amines. The amines may be aliphatic, cycloaliphatic, aromatic, or aromatic structures having one or more amino moieties.

25 Suitable amine curing agents include those amines having the general formula (II):

(II)



wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are each independently hydrogen or a hydrocarbon containing from about 1 to 15 carbon atoms, wherein the hydrocarbons include polyethers; and the value for  $n$  ranges from about 1 to 10. In some embodiments, the curing agent is a primary amine. In the same, or other, embodiments,  $R^3$  is a polyetheralkyl.

5 Exemplary amine curing agents include ethylene diamine, diethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, tetraethylene pentamine, hexaethylene heptamine, hexamethylene diamine, 2-methyl-1,5-pentamethylene-diamine, 4,7,10-trioxatridecan-1,13-diamine, aminoethylpiperazine and the like.

10 In some embodiments, the amine curing agent is a polyether amine having one or more amine moieties, including those polyether amines that can be derived from polypropylene oxide or polyethylene oxide. Commercially available polyether amines include the JEFFAMINE<sup>TM</sup> series of polyether polyamines (available from Huntsman Corporation in The Woodlands, TX, USA) and 4,7,10-trioxatridecane-  
15 1,13-diamine (TTD) (available from TCI America in Portland, OR, USA).

The primary or secondary amine hydrogens on the amine curing agent will react stoichiometrically with the epoxy moieties on the curable epoxy resin to form a cross-linked epoxy network. The molar ratio of epoxy moieties to primary or secondary amine hydrogens can be adjusted to achieve desired performance. In some  
20 embodiments, the structural adhesives of the present invention have a molar ratio of epoxy moieties on the curable epoxy resin to amine hydrogens on the amine curing agent ranging from about 0.5:1 to about 3:1. This includes embodiments where the molar ratio is about 2:1 or about 1:1. If other ingredients within the structural adhesive also react with the amine curing agent (e.g., some types of reactive liquid  
25 modifiers), the amount of amine curing agent in the structural adhesive may be increased accordingly.

In some embodiments of the present invention, the structural adhesives comprise at least about 3% by weight amine curing agent, in some embodiments at least about 5% by weight amine curing agent, and in some embodiments at least about  
30 10% by weight amine curing agent. In some embodiments of the present invention, the structural adhesives comprise less than about 30% by weight amine curing agent, in some embodiments less than about 20% by weight amine curing agent, and in some embodiments less than about 15% by weight amine curing agent.

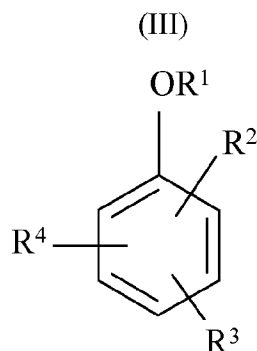
In some embodiments of the present invention, the structural adhesives  
35 comprise from about 3% to about 30% by weight amine curing agent. In other embodiments, the structural adhesives comprise from about 5% to about 15% by weight amine curing agent.



## 5 Secondary Curatives

Structural adhesives of the present invention may optionally comprise a secondary curative. Secondary curatives according to the invention include imidazoles, imidazole-salts, imidazolines or aromatic tertiary amines including those having the structure of formula (III):

10



wherein

R<sup>1</sup> is H or alkyl (e.g., methyl or ethyl);

15 

R<sup>2</sup> is CHNR<sup>5</sup>R<sup>6</sup>;

R<sup>3</sup> and R<sup>4</sup> may be, independently from each other, present or absent and when present R<sup>3</sup> and R<sup>4</sup> are CHNR<sup>5</sup>R<sup>6</sup>; and

R<sup>5</sup> and R<sup>6</sup> are, independent from each other, alkyl (e.g., CH<sub>3</sub> or CH<sub>2</sub>CH<sub>3</sub>).

An exemplary secondary curative is tris-2,4,6-(dimethylaminomethyl)phenol  
20 (available as ANCAMINE K54 from Air Products Chemicals in Europe B.V).

## Toughening Agents

Toughening agents are polymers, other than the curable epoxy resins or the reactive liquid modifiers (described below), capable of increasing the toughness of cured epoxy resins. The toughness can be measured by the peel strength of the cured  
25 compositions. Typical toughening agents include core/shell polymers, butadiene-nitrile rubbers, acrylic polymers and copolymers, etc. Commercially available toughening agents include a polyether diamine (available as Dynamar<sup>TM</sup> Polyetherdiamine HC 1101 from 3M Corporation in St. Paul, MN, USA) and carboxyl-terminated butadiene acrylonitrile (available from Emerald Chemical in  
30 Alfred, ME, USA).

In some embodiments, the structural adhesives of the present invention comprise from about 5% to about 55% by weight toughening agent. In other

5       embodiments, the structural adhesives comprise from about 5% to about 30% by weight toughening agent. In yet other embodiments, the structural adhesives comprise from about 5% to about 15% by weight toughening agent.

          Suitable toughening agents include core/shell polymers. A core/shell polymer is understood to mean a graft polymer having a core comprising a graftable elastomer, 10       which means an elastomer on which the shell can be grafted. The elastomer may have a glass transition temperature lower than 0°C. Typically the core comprises or consists of a polymer selected from the group consisting of a butadiene polymer or copolymer, an acrylonitrile polymer or copolymer, an acrylate polymer or copolymer and combinations thereof. The polymers or copolymers may be cross-linked or not 15       cross-linked. In some embodiments, the core polymers are cross-linked.

          Onto the core is grafted one or more polymers, the “shell”. The shell polymer typically has a high glass transition temperature, i.e. a glass transition temperature greater than 26°C. The glass transition temperature may be determined by dynamic mechanical thermo analysis (DMTA) (“Polymer Chemistry, The Basic Concepts, Paul 20       C. Hiemenz, Marcel Dekker 1984).

          The “shell” polymer may be selected from the group consisting of a styrene polymer or copolymer, a methacrylate polymer or copolymer, an acrylonitrile polymer or copolymer, or combinations thereof. The thus created “shell” may be further functionalized with epoxy groups or acid groups. Functionalization of the 25       “shell” may be achieved, for example, by copolymerization with glycidylmethacrylate or acrylic acid. In particular, the shell may comprise acetoacetoxy moieties in which case the amount of acetoacetoxy-functionalized polymer may be reduced, or it may be completely replaced by the acetoacetoxy-functionalized core/shell polymer.

          The shell of suitable core/shell polymers may comprise a polyacrylate polymer 30       or copolymer shell such as, for example, a polymethylmethacrylate shell. The polyacrylate shell, such as the polymethylmethacrylate shell, may not be cross-linked.

          The core of suitable core/shell polymers may comprise a butadiene polymer or copolymer, a styrene polymer or copolymer, or a butadiene-styrene copolymer. The polymers or copolymers making up the core, such as a butadiene-styrene core, may be 35       cross-linked.

          In some embodiments, the core/shell polymer according to the present invention may have a particle size from about 10 nm to about 1,000 nm. In other

5     embodiments, the core/shell polymer may have a particle size from about 150 nm to about 500 nm.

        Suitable core/shell polymers and their preparation are for example described in US 4,778,851. Commercially available core/shell polymers may include, for example, PARALOID EXL 2600 and 2691 (available from Rohm & Haas Company  
10    in Philadelphia, PA, USA) and KANE ACE MX120 (available from Kaneka in Belgium).

#### Reactive Liquid Modifiers

        Suitable reactive liquid modifiers have a molecular weight less than about 4,000 g/mole. Reactive liquid modifiers having larger molecular weights are typically  
15    incompatible with the epoxy resins, resulting in phase separation and diminished adhesive strength. In some embodiments of the present invention, the reactive liquid modifier has a molecular weight of less than about 4,000 g/mole, in some embodiments a molecular weight of less than about 3,500 g/mole, and in some embodiments a molecular weight of less than about 2,000 g/mole. In some  
20    embodiments of the present invention, the reactive liquid modifier has a molecular weight of at least about 100 g/mole, in some embodiments a molecular weight of at least about 200 g/mole, and in some embodiments a molecular weight of at least about 500 g/mole.

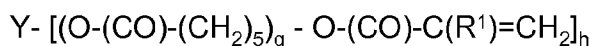
        In some embodiments of the present invention, the reactive liquid modifier has  
25    a molecular weight of from about 100 g/mole to about 4,000 g/mol. In other embodiments, the reactive liquid modifier has a molecular weight of from about 200 g/mole to about 3,500 g/mole. In further embodiments, the reactive liquid modifier has a molecular weight of from about 500 g/mole to about 2,000 g/mole.

        The reactive liquid modifiers of the present invention may be polymerized by  
30    chain-initiated homopolymerization or by condensation reactions with amine curing agents to form IPNs. Reactive liquid modifiers that undergo chain initiated homopolymerization include acrylate functionalized compounds and acrylamide functionalized compounds. Reactive liquid modifiers that undergo condensation reactions include oxalic amide functionalized compounds, acetoacetox  
35    functionalized urethanes, and acetoacetox functionalized polyalkenes.

*Acrylate Functionalized Compounds.* Acrylate functionalized compounds may be mono-, di- or poly-functionalized compounds. Suitable acrylate

- 5 functionalized compounds include caprolactone derivatives having general formula (IV):

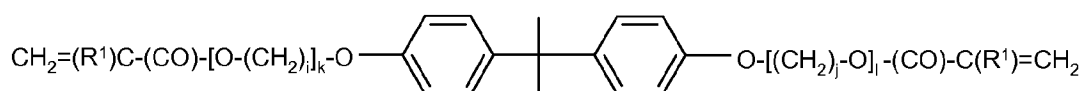
(IV)



- where Y represents a branched or linear alkyl chain having from about 1 to 10 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, etc.) or a heteroalkyl chain having from about 1 to 10 carbon atoms (e.g., alkyl ethers, alkyl sulfides, etc.); each  $R^1$  is, independently, H or a  $C_1$ - $C_4$  alkyl (e.g., methyl, ethyl, etc.); each g is, independently, an integer value ranging from about 1 to 35; and h is an integer value ranging from about 1 to 22.

- 15 Other suitable acrylate functionalized compounds include bisphenol A derivatives having the general formula (V):

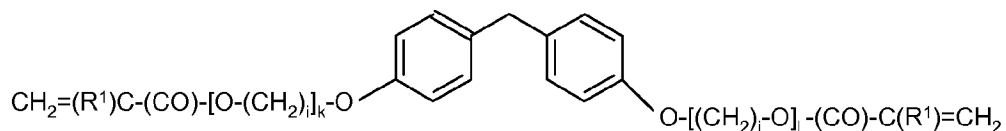
(V)



- 20 where each  $R^1$  is, independently, H or a  $C_1$ - $C_4$  alkyl (e.g., methyl, ethyl, etc.); i and j are each, independently, integer values ranging from about 1 to 10; and k and l are each, independently, integer values of at least 1 whose combined sum (i.e.,  $k + l$ ) ranges from about 2 to 135. In some embodiments, the combined sum of i and j (i.e.,  $i + j$ ) ranges from about 2 to 10. In some embodiments, i and j are each 2.

- 25 Yet other suitable acrylate functionalized compounds include bisphenol F derivatives having the general formula (VI):

(VI)



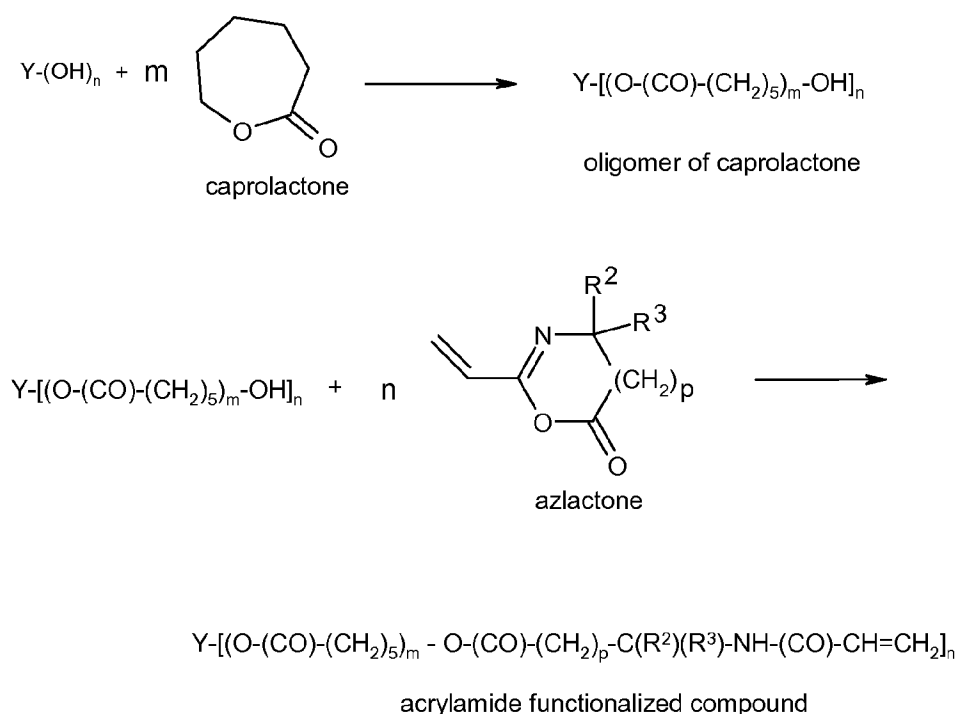
- where each  $R^1$  is, independently, H or a  $C_1$ - $C_4$  alkyl (e.g., methyl, ethyl, etc.); i and j are each, independently, integer values ranging from about 1 to 10; and k and l are each, independently, integer values of at least 1 whose combined sum (i.e.,  $k + l$ )

- 5 ranges from about 2 to 135. In some embodiments, the combined sum of i and j (i.e., i + j) ranges from about 2 to 10. In some embodiments, i and j are each 2.

Commercially available acrylate functionalized reactive liquid modifiers include SR602 (an ethoxylated (10) bisphenol A diacrylate available from Sartomer Company, Inc. in Exton, PA, USA).

- 10 *Acrylamide Functionalized Compounds.* Acrylamide functionalized compounds may be mono-, di- or poly-functionalized compounds. Suitable acrylamide functionalized compounds may be derived from the reaction of an oligomer of caprolactone with an azlactone as shown below (Scheme I).

Scheme I



- 15 Y represents a branched or linear alkyl chain having from about 1 to 10 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, etc.) or a heteroalkyl chain having from about 1 to 10 carbon atoms (e.g., alkyl ethers, alkyl sulfides, etc.). Each m is, independently, an integer value ranging from about 1 to 20. n is an integer value ranging from about 1 to 5.

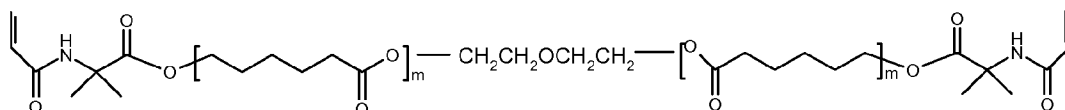
20  $R^2$  and  $R^3$  are each, independently, an alkyl group having from about 1 to 14 carbon atoms, a cycloalkyl group having from about 3 to 14 carbon atoms, an aryl group having from about 5 to 12 ring atoms, and arenyl group having from about 6 to

- 5 26 carbon atoms and about 0 to 3 S, N, or nonperoxidic O atoms, or R<sup>2</sup> and R<sup>3</sup> taken together with the carbon to which they are both joined form a carbocyclic ring having about 4 to 12 carbon atoms. Each p is, independently, 0 or 1.

In some embodiments, the azlactone is 2-vinyl-4,4-dimethylazlactone.

- 10 In some embodiments, the acrylamide functionalized compound is a bisacrylamide (VII) where Y is an alkyl ether (-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-), m is 5, n is 2, p is 0 and R<sup>2</sup> and R<sup>3</sup> are each a methyl group (synthesis provided in Examples section).

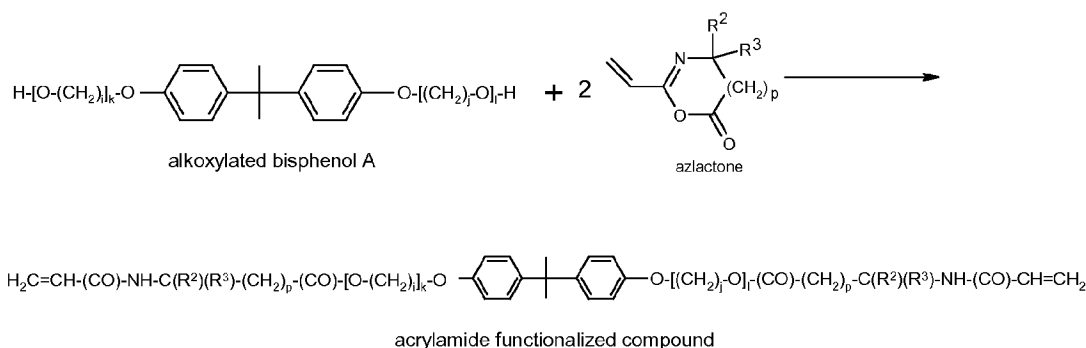
(VII)



- 15 bisacrylamide

Other suitable acrylamide functionalized compounds may be derived from the reaction of an alkoxyated bisphenol A with an azlactone as shown below (Scheme II).

Scheme II



- 20

i and j are each, independently, integer values ranging from about 1 to 10. In some embodiments, the combined sum of i and j (i.e., i + j) ranges from about 2 to 10. In some embodiments, i and j are each 2.

- 25 k and l are each, independently, integer values of at least 1 whose combined sum (i.e., k + l) ranges from about 2 to 120.

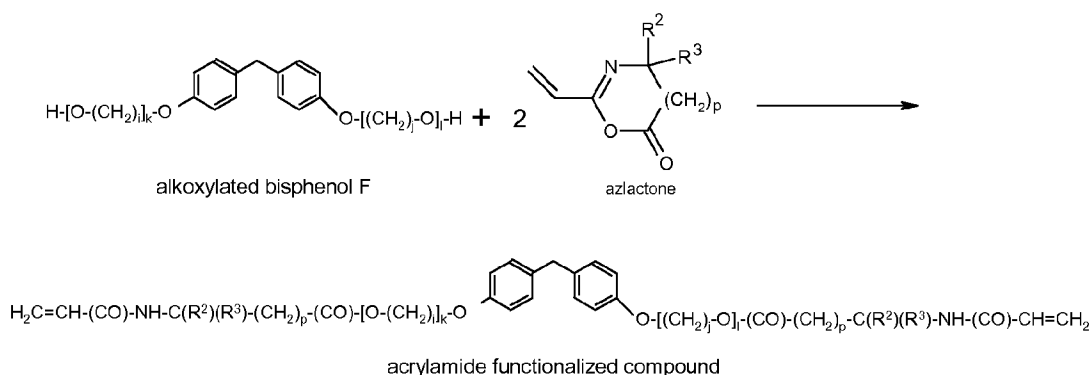
R<sup>2</sup> and R<sup>3</sup> are each, independently, an alkyl group having from about 1 to 14 carbon atoms, a cycloalkyl group having from about 3 to 14 carbon atoms, an aryl

- 5 group having from about 5 to 12 ring atoms, and arenyl group having from about 6 to 26 carbon atoms and about 0 to 3 S, N, or nonperoxidic O atoms, or  $R^2$  and  $R^3$  taken together with the carbon to which they are both joined form a carbocyclic ring having about 4 to 12 carbon atoms. Each p is, independently, 0 or 1.

In some embodiments, the azlactone is 2-vinyl-4,4-dimethylazlactone.

- 10 Yet other suitable acrylamide functionalized compounds may be derived from the reaction of an alkoxyated bisphenol F with an azlactone as shown below (Scheme III).

Scheme III



15

i and j are each, independently, integer values ranging from about 1 to 10. In some embodiments, the combined sum of i and j (i.e.,  $i + j$ ) ranges from about 2 to 10. In some embodiments, i and j are each 2.

- 20 k and l are each, independently, integer values of at least 1 whose combined sum (i.e.,  $k + l$ ) ranges from about 2 to 120.

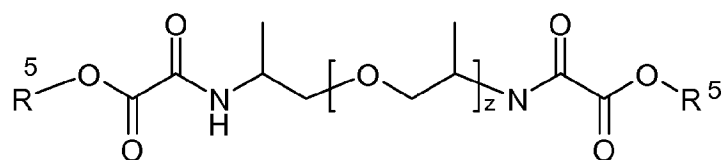
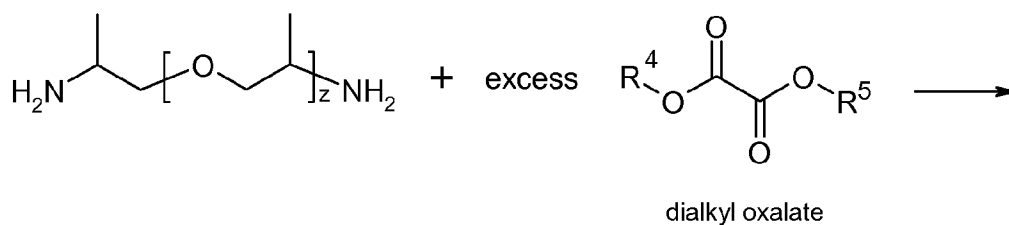
- 25  $R^2$  and  $R^3$  are each, independently, an alkyl group having from about 1 to 14 carbon atoms, a cycloalkyl group having from about 3 to 14 carbon atoms, an aryl group having from about 5 to 12 ring atoms, and arenyl group having from about 6 to 26 carbon atoms and about 0 to 3 S, N, or nonperoxidic O atoms, or  $R^2$  and  $R^3$  taken together with the carbon to which they are both joined form a carbocyclic ring having about 4 to 12 carbon atoms. Each p is, independently, 0 or 1.

In some embodiments, the azlactone is 2-vinyl-4,4-dimethylazlactone.

- 30 *Oxalic Amide Functionalized Compounds.* Oxalic amide compounds may be functionalized di- or poly-functionalized compounds. Suitable oxalic amide functionalized compounds may be derived from the reaction of a diamine with a dialkyl oxalate as shown below (Scheme IV).

5

Scheme IV



oxalic amide functionalized compound

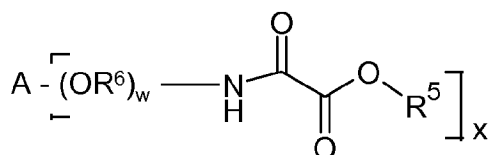
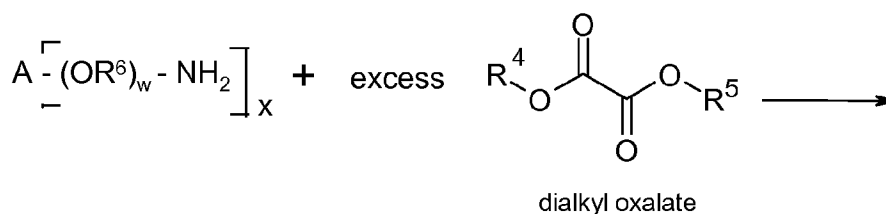
$z$  is an integer value ranging from about 1 to 75. In some embodiments,  $z$  is 6.

$\text{R}^4$  and  $\text{R}^5$  are each, independently, an alkyl group having from about 1 to 4 carbon atoms, a cycloalkyl group having from about 3 to 12 carbon atoms, or an aromatic group having from about 6 to 12 carbon atoms. In some embodiments,  $\text{R}^4$  and  $\text{R}^5$  are each an ethyl group.

In some embodiments, the oxalic amide functionalized compound is DEO-400 (synthesis provided in Examples section) where  $z$  is 5-6 and  $\text{R}^4$  and  $\text{R}^5$  are each ethyl groups.

15 Another suitable oxalic amide functionalized compound may be derived from the reaction of a polyamine with a dialkyl oxalate as shown below (Scheme V).

Scheme V



oxalic amide functionalized compound



5 A represents a branched or linear alkyl chain having from about 1 to 10 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, etc.). R<sup>6</sup> is a branched or linear alkyl chain having from about 1 to 5 carbon atoms. Each w is, independently, an integer value ranging from about 1 to 130. x is an integer value ranging from about 1 to 40.

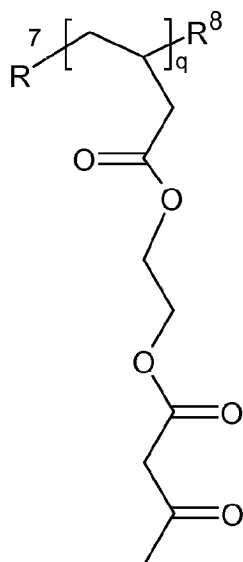
10 R<sup>4</sup> and R<sup>5</sup> are each, independently, an alkyl group having from about 1 to 4 carbon atoms, a cycloalkyl group having from about 3 to 12 carbon atoms, or an aromatic group having from about 6 to 12 carbon atoms. In some embodiments, R<sup>4</sup> and R<sup>5</sup> are each an ethyl group.

*Acetoacetoxy Functionalized Urethanes.* Acetoacetoxy functionalized urethanes may be mono-, di- or poly-functionalized compounds prepared by capping one or more hydroxyl groups of oligourethane polyols with acetoacetoxy functional groups. Preferably acetoacetoxy functionalized urethanes are isocyanate free. In some embodiments, the acetoacetoxy functionalized urethanes are di-functionalized.

Exemplary acetoacetoxy functionalized urethanes include AcAcUD and  
20 AcAcXM (synthesis provided in the Examples section below).

*Acetoacetoxy Functionalized Polyalkenes.* Acetoacetoxy functionalized polyalkenes may be mono-, di- or poly-functionalized compounds. Suitable acetoacetoxy functionalized polyalkenes include those having general formula (VIII).

(VIII)



25

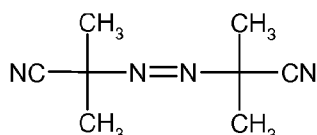
q represents the average number of acetoacetoxy groups per molecule and is an integer or non-integer number ranging from about 1 to about 10. For example, in

- 5 some embodiments, n ranges from about 2 to about 5. This includes embodiments where n is about 4.6. In other embodiments, n ranges from about 7 to about 10. This includes embodiments where n is about 9.

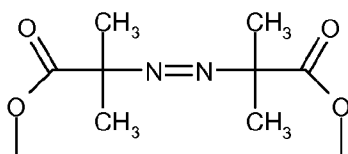
$R^7$  is H or an initiator fragment from a thermally decomposing initiator.

- Thermally decomposing initiators generally fall into two classes of compounds: azo- and peroxy-type compounds. Azo-type compounds are a widely used class of thermally decomposing initiators that generate both carbon- and oxygen-centered radicals by either C-N (dialkyl diazenes) or O-N (dialkyl hyponitrites) bond scission driven by the expulsion of a stable nitrogen molecule. Most of the azo-type compounds generate two identical radical species upon fragmentation. Exemplary azo-type compounds are provided below.

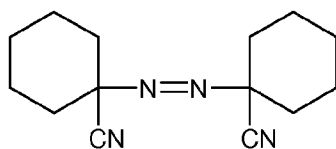
#### Azo-Type Compounds



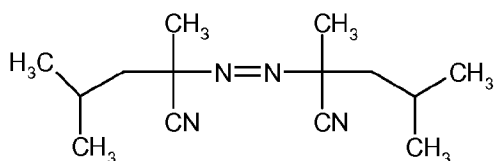
2,2'-azobisisobutyronitrile



dimethyl 2,2'-azobisisobutyrate

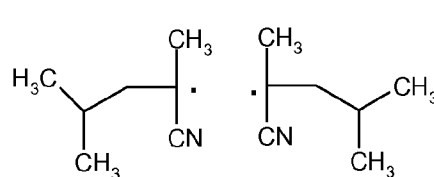
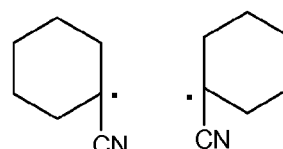
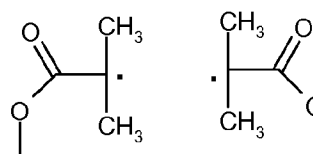
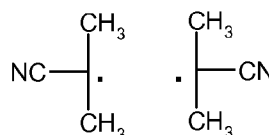


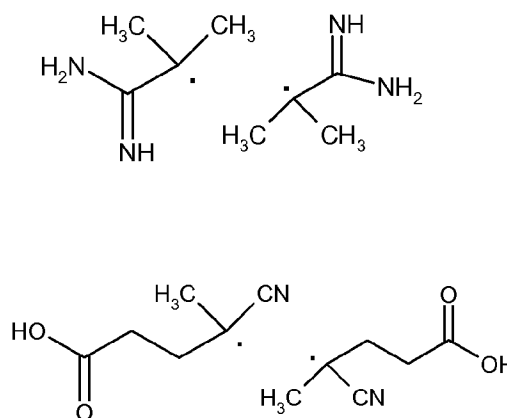
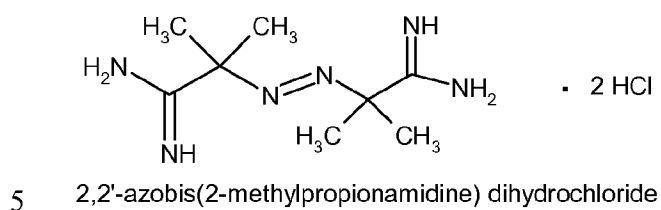
20 1,1'-azobis(1-cyclohexanecarbonitrile)



2,2'-azobis-2,4-dimethylvaleronitrile

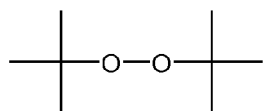
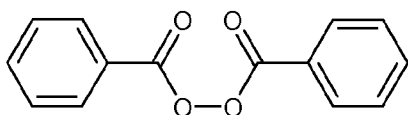
#### Initiator Fragments



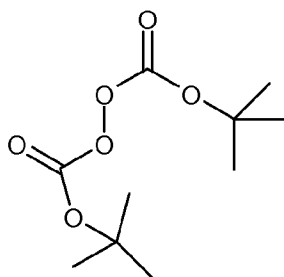
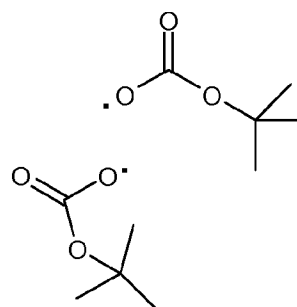
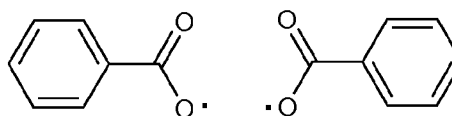
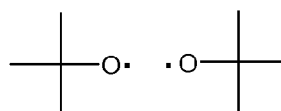


4,4'-azobis(4-cyanovaleric acid)

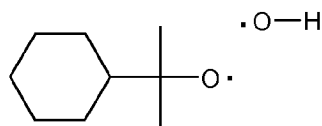
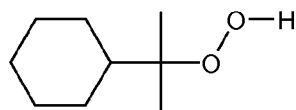
- 10      Peroxy-type compounds are thermally decomposing initiators that generate oxygen-centered radicals by O-O bond scission. Exemplary peroxy-type compounds are provided below.

Peroxy-type Compoundsdi-*tert*-butyl peroxide

benzoyl peroxide

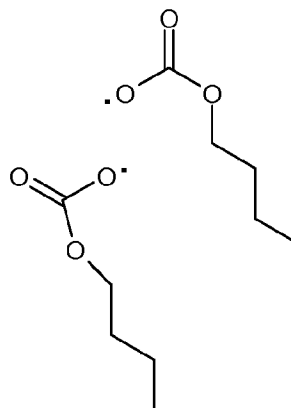
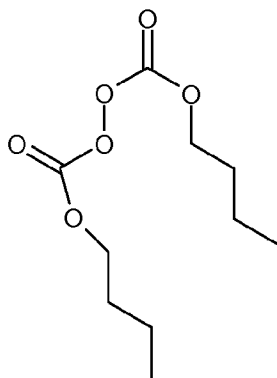
di-*tert*-butyl peroxalateInitiator Fragments

15



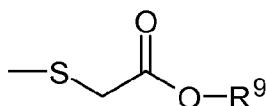
5

cumene hydroperoxide

di-*n*-propyl peroxydicarbonate

- Other suitable peroxy-type compounds include 1,1-bis(*tert*-amylperoxy)cyclohexane, 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(*tert*-butylperoxy)cyclohexane, 2,2-bis(*tert*-butylperoxy)butane, 2,4-pentandione peroxide, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane, 2-butanone peroxide, di-*tert*-amyl peroxide, dicumyl peroxide, lauroyl peroxide, *tert*-butyl hydroperoxide, *tert*-butyl peracetate, *tert*-butyl peroxide, *tert*-butyl peroxybenzoate, and *tert*-butylperoxy 2-ethylhexyl carbonate.
- 15  $R^8$  is H, an initiator fragment from a thermally decomposing initiator, or a thioester represented by formula (IX):

(IX)



- where  $R^9$  is a  $C_1$ - $C_{12}$  linear alkyl, a  $C_1$ - $C_{12}$  branched alkyl or a  $C_1$ - $C_{12}$  cyclic alkyl (e.g., methyl, ethyl, propyl, butyl, sec-butyl, *tert*-butyl, isooctyl, etc.). This includes embodiments where  $R^9$  is isooctyl.
- 20

In some embodiments, the reactive liquid modifier of the present invention is MaAcAc 1000 MW Oligomer (synthesis provided in Examples section) where  $q$  is about 4.6,  $R^7$  is a *tert*-butyl group,  $R^8$  is general formula (IX) and  $R^9$  is isooctyl.

5           In some embodiments, the reactive liquid modifier of the present invention is MaAcAc 2000 MW Oligomer (synthesis provided in Examples section) where q is about 9, R<sup>7</sup> is a tert-butyl group, R<sup>8</sup> is general formula (IX) and R<sup>9</sup> is isooctyl.

          In some embodiments of the present invention, the structural adhesives comprise at least about 5% by weight reactive liquid modifier, in some embodiments  
10   at least about 8% by weight reactive liquid modifier, and in some embodiments at least about 10% by weight reactive liquid modifier. In some embodiments of the present invention, the structural adhesives comprise less than about 20% by weight reactive liquid modifier, in some embodiments less than about 15% by weight reactive liquid modifier, and in some embodiments less than about 12% by weight  
15   reactive liquid modifier.

          In some embodiments of the present invention, the structural adhesives comprise from about 5% to about 20% by weight reactive liquid modifier. In other embodiments, the structural adhesives comprise from about 6% to about 12% by weight reactive liquid modifier. In yet other embodiments, the structural adhesives  
20   comprise from about 6% to about 10% by weight reactive liquid modifier.

#### Radical Initiators

          Compositions of the present invention that comprise an acrylate functionalized reactive liquid modifier or an acrylamide functionalized reactive liquid modifier also include one or more radical initiators that polymerize the ethylenically unsaturated  
25   acrylate or acrylamide moieties. Radical initiators may include thermal initiators, such as peroxides and azo compounds. Exemplary peroxide thermal initiators may include acyl peroxides (e.g., acetyl peroxide and benzoyl peroxide), alkyl peroxides (e.g., cumyl peroxides and t-butyl peroxides), hydroperoxides (e.g., cumyl hydroperoxides and t-butyl hydroperoxides) and peresters (e.g., t-butyl perbenzoate).  
30   Exemplary azo thermal initiators may include 2,2'-azobisisobutyronitrile and VAZO-52 and VAZO-67 (available from DuPont Chemicals in Wilmington, DE, USA).

          Radical initiators may also include redox initiators comprising at least one oxidant and at least one reductant. Various redox systems may optionally include microencapsulated reducing and/or oxidizing agents. The oxidizing agent reacts with,  
35   or otherwise cooperates with, the reducing agent to produce free radicals. The free radicals are capable of initiating polymerization of the ethylenically unsaturated acrylate or acrylamide moieties.

5           Suitable oxidizing agents may include: persulfates (e.g., sodium, potassium, ammonium, and alkyl ammonium persulfates); peroxides or peroxide salts (e.g., hydrogen peroxide, benzoyl peroxide, and hydroperoxides including, for example, cumene hydroperoxide, tert-butyl hydroperoxide, tert-amyl hydroperoxide, and 2,5-dihydroperoxy-2,5-dimethylhexane); salts of cobalt(III) and iron(III); perboric acid  
10 and its salts; salts of a permanganate anion, and combinations thereof.

          Suitable reducing agents may include: amines (e.g., aromatic amines); ascorbic acid; metal complexed ascorbic acid; cobalt(II) chloride; ferrous chloride; ferrous sulfate; hydrazine; hydroxylamine; oxalic acid; thiourea; and salts of dithionite, thiosulfate, benzene sulfinate, or sulfite anions.

15           Exemplary redox initiators may include the benzoyl peroxide/N,N-dialkylaniline initiator system and the benzoyl peroxide/N,N-bis(2-hydroxyethyl)-p-toluidine initiator system.

          In some embodiments, the radical initiator comprises at least one of VAZO-52, VAZO-67, and combinations thereof. In other embodiments, the radical initiator  
20 comprises the benzoyl peroxide/N,N-bis(2-hydroxyethyl)-p-toluidine redox initiator system.

          The amount of free radical initiator can be sufficient to cause polymerization of the adhesive composition and form an IPN. In some embodiments, the structural adhesives of the present invention comprise from about 0.01% to about 5% by  
25 weight initiator. This includes embodiments where the structural adhesives comprise from about 0.1% to about 2% by weight initiator.

#### Reactive Diluents

          Reactive diluents may optionally be added to control the flow characteristics of the adhesive composition. Suitable diluents can have at least one reactive terminal  
30 end portion and, preferably, a saturated or unsaturated cyclic backbone. Reactive terminal end portions include glycidyl ether. Examples of suitable diluents include the diglycidyl ether of resorcinol, diglycidyl ether of cyclohexane dimethanol, diglycidyl ether of neopentyl glycol, and triglycidyl ether of trimethylolpropane. Commercially available reactive diluents are, for example, Reactive Diluent 107  
35 (available from Hexion Specialty Chemical in Houston, TX, USA) and EPODIL 757 (available from Air Products and Chemical Inc. in Allentown, PA, USA).

5           In some embodiments, the structural adhesives of the present invention comprise from about 0.001% to 25% by weight reactive diluent.

#### Structural Adhesive Compositions

          Two-part compositions according to the present invention comprise a Part A and, separate therefrom, a Part B. Part A comprises an amine curing agent and Part B  
10       comprises a curable epoxy resin. Part A may also comprise curable epoxy resin in addition to that in Part B. As for any remaining ingredients (e.g., toughening agents, reactive liquid modifiers, secondary curatives, radical initiators, reactive diluents, etc.), compounds with epoxy reactive groups are added to Part A, compounds with amine reactive groups are added to Part B, and compounds that do not contain either  
15       an epoxy reactive group or an amine reactive group may be added to Part A, Part B or a combination thereof. Alternatively, a separate part for one or more of these ingredients may be contemplated.

          The amounts of Part A and Part B combined to make the adhesive will depend upon the desired molar ratio of epoxy to amine curing agent in the cross-linked epoxy  
20       network. In some embodiments, the structural adhesives of the present invention have a molar ratio of epoxy moieties on the curable epoxy resin to amine hydrogens on the amine curing agent ranging from about 0.5:1 to about 3:1. This includes embodiments where the molar ratio is about 2:1 or about 1:1. If other ingredients within the structural adhesive also react with the amine curing agent, the amount of  
25       amine curing agent in the structural adhesive may be increased accordingly. The respective amounts of Part A and Part B are preferably mixed together immediately prior to use.

          In some embodiments, the structural adhesives of the present invention comprise a curable epoxy resin, an amine curing agent, a toughening agent and a  
30       reactive liquid modifier. In other embodiments, the structural adhesives comprise a curable epoxy resin, an amine curing agent, a secondary curative, a toughening agent, and a reactive liquid modifier. In yet other embodiments, the structural adhesives comprise a curable epoxy resin, an amine curing agent, a secondary curative, a toughening agent, a reactive liquid modifier, and a reactive diluent.

35       The ingredients used to make up the compositions of the present invention should create morphologies marked by co-continuous phases. In other words, the reactive liquid modifiers should be compatible with the epoxy resins in order to create

5 the IPNs. From a chemical standpoint, IPNs are whole unit structures formed of two entirely different types of polymers that exhibit physical properties of both polymers. If the reactive liquid modifier is compatible with the epoxy resin, the glass transition temperature of the epoxy-rich phase will lie somewhere in-between the Tg of the epoxy resin and the Tg of the polymerized liquid modifier, where the amount of  
10 change is determined by the amount of reactive liquid modifier in the composition. If, on the other hand, the reactive liquid modifier is incompatible with the epoxy resin, phase separation will occur, and the glass transition temperature of the epoxy-rich phase will remain largely unchanged by the amount of reactive liquid modifier present. Therefore, compositions of the present invention will typically exhibit glass  
15 transition temperatures either lower or higher than corresponding compositions without the reactive liquid modifier. In some embodiments, the compositions of the present invention will exhibit a Tg lower than that of corresponding compositions without the reactive liquid modifier.

#### Curing

20 To produce an IPN in accordance with this invention, the cure rate of the reactive liquid modifier is preferably greater than that of the epoxy resin. If the epoxy resin cures before the reactive liquid modifier, “domaining” may occur, causing unacceptable discontinuities in the adhesive. Thus, the chemical and physical properties of the final IPN are strongly affected by the relative rates of epoxy resin  
25 and reactive liquid modifier curing.

Generally, when the reactive liquid modifier is an oxalic amide functionalized compound, an acetoacetoxy functionalized urethane or an acetoacetoxy functionalized polyalkene, the amine curing agent will substantially polymerize the reactive liquid  
30 modifier prior to curing the epoxy resin (see Examples 2-4). When the reactive liquid modifier is an acrylate functionalized compound or an acrylamide functionalized compound, radical initiators and/or polymerization temperatures should be selected such that the reactive liquid modifiers polymerize before substantial curing of the epoxy resin (see Example 1).

Example 1 illustrates how polymerization rate of the reactive liquid modifier  
35 can effect the formation of an IPN and ultimately the quality of the structural adhesive. The acrylate functionalized reactive liquid modifier in ACRYLATE1 was polymerized as separate samples at 60°C (ACRYLATE1-60) and 100°C



5 (ACRYLATE1-100) prior to curing of the epoxy resin. Polymerization rate of the reactive liquid modifier increases with temperature. Therefore, polymerization of the reactive liquid modifier will proceed further in the sample cured at 100°C than in the sample cured at 60°C during the same time period. As illustrated in Fig. 1, the glass transition temperature of ACRYLATE1-60 is similar to EPOXYST (a 1:1 epoxy  
10 adhesive without reactive liquid modifier). At 60°C, the reactive liquid modifier was unable to substantially polymerize prior to curing of the epoxy resin, resulting in phase separation between the reactive liquid modifier and the epoxy resin. Hence, the glass transition temperature is similar to that of cured epoxy resin. In contrast, ACRYLATE1-100 has a glass transition temperature significantly lower than  
15 EPOXYST. At 100°C, the reactive liquid modifier substantially polymerizes prior to curing of the epoxy resin, resulting in an IPN with properties of both the cured epoxy resin and polymerized reactive liquid modifier. Therefore, in some embodiments of the present invention, the reactive liquid modifier is polymerized prior to curing of the epoxy resin.

20 The structural adhesives of the present invention are typically cured in a two step process. In the first step (first cure), the primary reaction is the polymerization of the reactive liquid modifier. In the second step (second cure), the primary reaction is the cross-linking of the epoxy resin.

The conditions of the primary cure will depend to some extent upon the nature  
25 of the reactive liquid modifiers. In some embodiments, the primary cure is carried out at room temperature for at least 3 hours. This includes embodiments where the primary cure is carried out at room temperature for at least 24 hours. This also includes embodiments where the primary cure is carried out at room temperature for at least 72 hours. In other embodiments, the primary cure may be conducted at  
30 temperatures greater than room temperature. This includes embodiments where the primary cure is conducted at about 110°C for about 30 minutes, or at about 110°C for about 1 hour.

The secondary cure is typically carried out at elevated temperatures ranging from about 80°C to about 200°C. The length of time over which the adhesive is cured  
35 will vary with the desired properties. In some embodiments, the secondary cure is carried out for 30 minutes at 180°C.

In some embodiments of the present invention, the structural adhesives are cured for 30 minutes at 110°C followed by 30 minutes at 180°C.

5           In further embodiments, the adhesive may reach a desirable cohesive strength after short heat curing periods. Since the cohesive strength can still increase when curing the composition at the same conditions for longer periods, this kind of curing is referred to herein as partial curing. In principle, partial curing can be carried out by any kind of heating. In some embodiments, induction curing (e.g., spot induction  
10   curing or ring induction curing) may be used for partial curing. Induction curing is a non-contact method of heating using electric power to generate heat in conducting materials by placing an inductor coil through which an alternating current is passed in proximity to the material. The alternating current in the work coil sets up an electromagnetic field that creates a circulating current in the work piece. This  
15   circulating current in the work piece flows against the resistivity of the material and generates heat. Induction curing equipment can be commercially obtained, for example, EWS from IFF-GmbH in Ismaning, Germany.

          In yet further embodiments, adhesives of the present invention may undergo an induction cure, followed by a room temperature cure and a higher temperature post  
20   cure.

#### Bond Strength

          It is desirable for the two-part epoxy-based adhesive to build a strong, robust bond to one or more substrates upon curing. A bond is considered robust if the bond breaks apart cohesively at high shear values when tested in an overlap shear test and  
25   high T-peel values when tested in a T-peel test. The bonds may break in three different modes: (1) the adhesive splits apart, leaving portions of the adhesive adhered to both metal surfaces in a cohesive failure mode; (2) the adhesive pulls away from either metal surface in an adhesive failure mode; or (3) a combination of adhesive and cohesive failure. Structural adhesives of the present invention may  
30   exhibit a combination of adhesive and cohesive failure, more preferably cohesive failure during overlap shear testing and T-peel testing.

          In some embodiments, structural adhesives of the present invention may have a lap shear strength of at least 1,000 psi when cured for 30 minutes at 110°C followed by 30 minutes at 180°C. In other embodiments, the structural adhesives may have a  
35   lap shear strength of at least 2500 psi. In yet other embodiments, the structural adhesives may have a lap shear strength of at least 4000 psi.

5           In some embodiments, the structural adhesives of the present invention may have a T-peel strength of at least 30 lb<sub>f</sub>/in-width when cured for 30 minutes at 110°C followed by 30 minutes at 180°C. In other embodiments, the structural adhesives may have a T-peel strength of at least 50 lb<sub>f</sub>/in-width. In yet other embodiments, the structural adhesives may have a T-peel strength of at least 60 lb<sub>f</sub>/in-width.

10           Structural adhesives of the present invention may have a lap shear strength of at least 2500 psi and a T-peel strength of at least 30 lb<sub>f</sub>/in-width when cured for 30 minutes at 110°C followed by 30 minutes at 180°C. Additionally, structural adhesives of the present invention may have a lap shear strength of at least 2500 psi and a T-peel strength of at least 50 lb<sub>f</sub>/in-width when cured for 30 minutes at 110°C  
15 followed by 30 minutes at 180°C. Furthermore, structural adhesives of the present invention may have a lap shear strength of at least 4000 psi and a T-peel strength of at least 30 lb<sub>f</sub>/in-width when cured at room temperature for about 18 hours followed by 180° for 30 minutes.

#### Use of Adhesive Compositions

20           The present adhesive compositions may be used to supplement or completely eliminate a weld or mechanical fastener by applying the adhesive composition between two parts to be joined and curing the adhesive to form a bonded joint. Suitable substrates onto which the adhesive of the present invention may be applied include metals (e.g., steel, iron, copper, aluminum, etc., including alloys thereof),  
25 carbon fiber, glass fiber, glass, epoxy fiber composites, wood, and mixtures thereof. In some embodiments, at least one of the substrates is a metal. In other embodiments, both substrates are metal.

          In areas of adhesive bonding, the adhesive can be applied as liquid, paste, and semi-solid or solid that can be liquefied upon heating, or the adhesive may be applied  
30 as a spray. It can be applied as a continuous bead, in intermediate dots, stripes, diagonals or any other geometrical form that will conform to forming a useful bond. In some embodiments, the adhesive composition is in a liquid or paste form.

          The adhesive placement options may be augmented by welding or mechanical fastening. The welding can occur as spot welds, as continuous seam welds, or as any  
35 other welding technology that can cooperate with the adhesive composition to form a mechanically sound joint.

5           The compositions according to the present invention may be used as structural adhesives. In particular, they may be used as structural adhesives in vehicle assembly, such as the assembly of watercraft vehicles, aircraft vehicles or motorcraft vehicles, such as cars, motor bikes or bicycles. In particular, the adhesive compositions may be used as hem-flange adhesives. The adhesive may also be used  
10 in body frame construction. The compositions may also be used as structural adhesives in architecture or as structural adhesives in household and industrial appliances.

          In some embodiments, the present invention provides a method of making a composite article, the method comprising applying the two-part adhesive of the  
15 present invention to a surface, and curing the two-part adhesive in contact with the surface to form a composite article.

          In other embodiments, the present invention provides a method of forming a bonded joint between members, the method comprising applying the two-part adhesive of the present invention to a surface of at least one of two or more members,  
20 joining the members so that the two-part adhesive is sandwiched between the two or more members, and curing the two-part adhesive to form a bonded joint between the two or more members.

          The composition according to the invention may also be used as a welding additive.

25           The composition may be used as a metal - metal adhesive, metal - carbon fiber adhesive, carbon fiber - carbon fiber adhesive, metal-glass adhesive, and carbon fiber - glass adhesive.

          Exemplary embodiments of the present invention are provided in the following examples. The following examples are presented to illustrate the present  
30 invention and methods for applying the present invention and to assist one of ordinary skill in making and using the same. The examples are not intended in any way to otherwise limit the scope of the invention.

## EXAMPLES

### Materials Employed

35           ANCAMINE K54 (available from Air Products in Allentown, PA, USA) is a technical grade tris-2,4,6-dimethylaminomethyl-phenol catalytic tertiary amine additive.

5 BP (available from Aldrich Chemical Company in Milwaukee, WI, USA) is benzoyl peroxide.

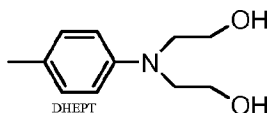
$\gamma$ -Butyrolactone (available from Aldrich Chemical Company in Milwaukee, WI, USA).

Polycaprolactone diol (available from Sigma-Aldrich Chemical Company in 10 Milwaukee, WI, USA - Catalog No. 18,941-3).

CPR-1250 Bisacrylamide (synthesis provided below) is an acrylamide reactive liquid modifier.

DBU (available from Aldrich Chemical Company in Milwaukee, WI, USA) is 1,8-diazabicyclo[5.4.0]undec-7-ene.

15 DHEPT (available from TCI America in Portland, OR, USA) is N,N-Bis(2-hydroxyethyl)-p-toluidine.



DEO-400 (synthesis provided below) is an oxamido ester terminated polypropylene oxide.

20 DER 331 (available from Dow Chemical Co. in Midland, MI, USA) is the diglycidyl ether of bis-phenol A having an approximate epoxy equivalent weight of 187.5.

Diethyloxalate (available from Alfa Aesar in Ward Hill, MA, USA).

EPODIL 757 (available from Air Products and Chemicals Inc. in Allentown, 25 PA, USA) is a reactive diluent based on 1,4-cyclohexandimethanoldiglycidylether.

EPON 828 (available from Hexion Specialty Chemicals in Houston, TX, USA) is the diglycidyl ether of bis-phenol A having an approximate epoxy equivalent weight of 187.5.

Ethyl acetate (available from Alfa Aesar in Ward Hill, MA, USA).

30 IOTGA (available from TCI America in Portland, OR, USA) is an isooctyl ester of thioglycidic acid.

JEFFAMINE<sup>®</sup> D-400 Polyetheramine (available from Hunstman Corporation in The Woodlands, Texas, USA).

35 K-FLEX XM-311 (available from King Industries in Norwalk, CT, USA) is a polyurethane polyol.

5           K-FLEX UD-320-1000 (available from King Industries in Norwalk, CT, USA) is a polyurethane polyol.

          MaAcAc (available from Aldrich Chemical Company in Milwaukee, WI, USA) is 2-(methacryloyloxy)ethyl acetoacetate.

          MaAcAc 1000 MW Oligomer (synthesis provided below) is an acetoacetoxy-  
10 functionalized reactive liquid modifier having an oligomeric molecular weight of approximately 1000.

          MaAcAc 2000 MW Oligomer (synthesis provided below) is an acetoacetoxy-  
functionalized reactive liquid modifier having an oligomeric molecular weight of approximately 2000.

15           Music wire (0.005" and 0.010" in diameter) (available from Small Parts Inc. in Miramar, FL, USA).

          PARALOID EXL 2600 (available from Rohm and Haas Company in Philadelphia, PA, USA) is a methacrylate/butadiene/styrene polymer with a core/shell architecture (core crosslinked rubber comprising of a polybutadiene-co-polystyrene-  
20 copolymer; shell: polymethacrylate) with a particle size of approximately 250 nm.

          SR602 (available from Sartomer Company, Inc. in Exton, PA, USA) is an ethoxylated (10) bisphenol A diacrylate.

          t-butyl acetoacetate (available from Aldrich Chemical Company in Milwaukee, WI, USA).

25           TTD (available from TCI America in Portland, OR, USA) is 4,7,10-trioxa-1,13-tridecane diamine.

          Urethane diAcAc #1 (synthesis provided below) is an acetoacetoxy-terminated urethane reactive liquid modifier.

          Urethane diAcAc #2 (synthesis provided below) is an acetoacetoxy-terminated  
30 urethane reactive liquid modifier.

          VAZO-52 (available from DuPont Chemicals in Wilmington, DE, USA) is an azo free-radical initiator.

          VAZO-67 or AIBN (available from DuPont Chemicals in Wilmington, DE, USA) is azoisobutyronitrile.

35           VDM (synthesis provided below) is 2-vinyl-4,4-dimethylazlactone.

          Zeller-Gmelin KTL N16 (available from Zeller + Gmelin GmbH & Co. KG in Eislingen, Germany) is a deep-draw oil.

5 Z6040 (available from Alfa Aesar in Ward Hill, MA, USA) is an adhesion promoter identified as (3-glycidyloxypropyl)trimethoxysilane.

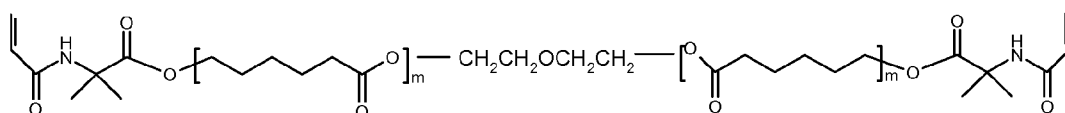
### Synthesis of 2-Vinyl-4,4-Dimethylazlactone

2-Vinyl-4,4-Dimethylazlactone (VDM) was prepared from *N*-acryloylmethylalanine (S. M. Heilmann and H. K. Smith II, *J. Appl. Polym. Sci.*, 24, 1551 (1979)) by the Taylor and Platt procedure (L. D. Taylor and T. E. Platt, *J. Polym. Sci. Polym. Lett. Ed.*, 7, 597 (1969)) with ethyl chloroformate as the dehydrating agent. A modified workup procedure was used in which, instead of cooling the filtrate to crystallize the product, the filtrate was concentrated on a rotary evaporator, and the crude product was distilled just above room temperature at 0.5 Torr. Receiving flasks were cooled to -78°C to collect the product. Typical distilled yields were approximately 80%.

### Synthesis of Acrylamide Functionalized Reactive Liquid Modifiers

*CPR-1250 Bisacrylamide (VII)*. A round bottom flask was charged with 31.12 grams polycaprolactone diol followed by 6.95 grams VDM added carefully via  
20 pipette. The mixture was then placed in a heated bath at 80°C and stirred as the polycaprolactone diol melted. When the melting was essentially complete, 0.4 grams DBU were added to the mixture by pipette. After about an hour at 80°C, approximately 80% of the VDM had reacted. After 24 hours at 80°C the reaction was essentially complete as evidenced by <sup>1</sup>H NMR.

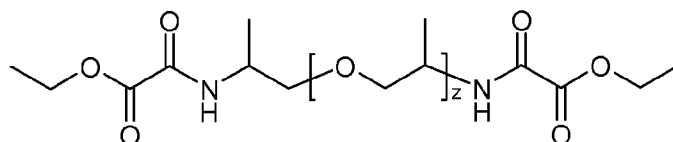
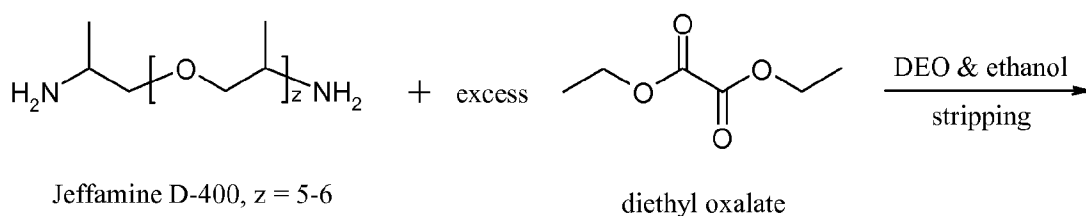
25 (VII)



m is 5

## 30 Synthesis of Oxalic Amide Functionalized Reactive Liquid Modifiers

*DEO-400.* The oxamido ester-terminated polypropylene oxide was prepared according to the below reaction scheme:



oxamido ester terminated polypropylene oxide

5

To a 2 L flask was added 730.70 grams sieve dried diethyloxalate and sufficient argon to purge the headspace. Using an addition funnel, 200.00 grams JEFFAMINE D-400 were added to the flask over the course of 90 minutes with vigorous stirring. Using a set up for distillation-argon sparge (sub-surface), the temperature of the contents in the flask was slowly increased to 150°C in order to distill out excess diethyloxalate and ethanol. The resultant product was a whisky brown, clear liquid weighing 273.2 grams and having a viscosity of 3,400 cP.

10

#### Synthesis of Acetoacetoxy Functionalized Urethane Reactive Liquid Modifiers

*Urethane diAcAc #1 (AcAcUD).* 35 grams t-butyl acetoacetate were added to 20 grams K-FLEX UD-320-100. The resultant mixture was heated to 120°C and refluxed overnight using a vigoreaux condenser. The reaction product was then distilled under vacuum to remove the excess t-butyl acetoacetate. <sup>1</sup>H NMR (in CDCl<sub>3</sub>) confirms essentially pure Urethane diAcAc #1.

15

*Urethane diAcAc #2 (AcAcXM).* 50 grams t-butyl acetoacetate were added to 20 grams K-FLEX XM-311. The resultant mixture was heated to 120°C and refluxed overnight using a vigoreaux condenser. The reaction product was then distilled under vacuum to remove the excess t-butyl acetoacetate. <sup>1</sup>H NMR (in CDCl<sub>3</sub>) confirms essentially pure Urethane diAcAc #2.

20



5     Synthesis of Acetoacetoxy Functionalized Polyalkene Reactive Liquid Modifiers

*MaAcAc 1000 MW Oligomer (AcAc1K)*. 20 grams MaAcAc, 4.75 grams  
IOTGA, 0.051 grams VAZO 67 and 30 grams ethyl acetate were charged to a 4 oz.  
glass polymerization bottle. The bottle was purged with nitrogen for five minutes,  
sealed, and placed in a water bath maintained at 60°C for 24 hours. The reaction  
10    mixture was then removed from the bath, and the solvent was stripped under vacuum.  
Peak ratio of the tail fragment protons to the backbone protons in <sup>1</sup>H NMR (in CDCl<sub>3</sub>)  
indicated approximately 4.65 repeat units per molecule, or an epoxide equivalent  
weight (EEW) of 270.

*MaAcAc 2000 MW Oligomer (AcAc2K)*. 20 grams of MaAcAc, 2.32 grams  
15    IOTGA, 0.051 grams VAZO 67 and 30 grams ethyl acetate were charged to a 4 oz.  
glass polymerization bottle. The bottle was purged with nitrogen for five minutes,  
sealed, and placed in a water bath maintained at 60°C for 24 hours. The reaction  
mixture was then removed from the bath, and the solvent was stripped under vacuum.  
Peak ratio of the tail fragment protons to the backbone protons in <sup>1</sup>H NMR (in CDCl<sub>3</sub>)  
20    indicated approximately 9 repeat units per molecule, or an EEW of 243.

Preparation of Epoxy Part B

          307 grams of epoxy resin (DER 331) and 81 grams of the reactive diluent  
(EPODIL 757) were mixed together at 23°C with stirring. The mixture was then  
heated in an oil bath to 80°C with mechanical stirring. 174 grams of core-shell  
25    polymer (PARALOID EXL 2600) were added to the mixture over a period of 1 hour  
in small portions with stirring. After stirring an additional 30 minutes, the mixture  
was heated to 100°C and held at that temperature for 4 hours. The mixture was then  
heated to 110°C and stirred for another hour. The mixture was cooled to room  
temperature. During cooling, 12 grams of the silane coupling agent (Z6040) were  
30    stirred into the mixture.

Preparation of Epoxy Part A

          99 grams of TTD (amine curative) were heated to 80°C. Then 58 grams of  
EPON 828 were added in small portions such that the temperature of the mixture did  
not rise above 100°C. 18 grams of ANCAMINE K54 were subsequently added to the  
35    mixture, and the mixture was stirred for an additional 5 minutes. The mixture was  
then cooled to room temperature.

5     Dynamic Mechanical Analysis (DMA)

Liquid reactive modifier was added to Epoxy Part B and vigorously stirred for 3-4 minutes until a uniform translucent mass was established. To that mixture Epoxy Part A was added, again with vigorous stirring for an additional 2-3 minutes until color uniformity of the yellowish mass was achieved.

10       The mixture was then deposited into a silicone rubber mold, which was placed atop a silicone coated PET liner. The mold was prepared earlier by stamping out parallel 5 mm wide by approximately 30 mm long rectangles and 10 mm x 10 mm squares in 1.5 mm thick silicone rubber. Once spread uniformly in the mold, the mixture was covered by another silicone-coated PET liner. Then the construct was  
15     clamped between 5 mm thick plates of glass and the adhesive was cured (as described in the examples). After curing, the adhesive samples were freed from the glass, liner and mold in that order and placed into Seiko Instruments Dynamic Mechanical Analyzer.

The 5 x 30 mm rectangles were evaluated in tension mode using the Seiko  
20     DMS110 dynamic mechanical analyzer console and in shear mode using Seiko DMS200 dynamic mechanical console. The samples were cooled to -60°C, allowed to equilibrate at that temperature for 15 minutes and then heated at the rate of 2°C/minute to 200°C. The resulting curves of loss tangent (tan d) curve versus temperature were measured.

25     Cohesive Strength Method (Lap Shear Strength Testing)

Lap shear specimens were made using 4" x 7" x 0.063" 2024-T3 bare aluminum that had been anodized according to Boeing Aircraft Company Specification BAC-5555. The anodization voltage was 22.5 volts. The specimen was generated as described in ASTM Specification D-1002. A strip of approximately ½"  
30     x 10 mils of adhesive was applied to one edge of each of the two adherends using a scraper. Three 5 mil diameter piano wires were used as spacers for bondline thickness control. The bond was closed and taped on the edge. The bond was placed between sheets of aluminum foil and pieces of cardboard. Two 14# steel plates were used to apply pressure to provide for adhesive spreading. After the adhesive had been  
35     allowed to cure (as described in the examples), the larger specimen was cut into 1" wide samples, providing a ½ square inch bonded area. Six lap shear samples were obtained from each larger specimen. The bonds were tested to failure at room

5 temperature on a Sintech Tensile Testing machine using a crosshead displacement rate of 0.1"/min. The failure load was recorded. The lap width was measured with a vernier caliper. The quoted lap shear strengths are calculated as (2 x failure load)/measured width. The average and standard deviation were calculated from the results of six tests.

#### 10 T-Peel Test Method

T-peel specimens were made using 3" x 8" x 0.025" 2024-T3 bare aluminum that had been anodized as described above. The specimen was generated as described in ASTM D-1876. A strip of approximately 2" x 5" x 10 mil of adhesive was applied to both of the two adherends. 10 mil thick spacers made from brass shims were  
15 applied to the edges of the bonded area for bondline thickness control. The bond was closed and adhesive tape was applied to hold the adherends together during the cure. The adhesive bonds were placed between sheets of aluminum foil and also between pieces of cardboard. Four 14# steel plates were used to apply pressure to provide for adhesive spreading. In those cases in which the adhesive was too viscous, the T-peel  
20 specimens were placed in a hydraulic press in order to provide more force for spreading. After the adhesive had been allowed to cure (as described in the examples), the larger specimen was cut into 1" wide samples, yielding two 1" wide specimens. The bonds were tested to failure at room temperature on a Sintech Tensile Testing machine using a crosshead displacement rate of 12"/min. The initial part of  
25 the loading data was ignored. The average load was measured after about 1" was peeled. The quoted T-peel strength is the average of two peel measurements.

#### EXAMPLE 1 - Acrylate/Acrylamide-Epoxy Adhesives

##### Formulations

ACRYLATE1. 0.075 grams VAZO-52 initiator were pre-dissolved in 1.59  
30 grams SR602. Then 10.94 grams Epoxy Part B were added to the solution with stirring followed by 2.47 grams Epoxy Part A with stirring.

ACRYLATE2. Part B' was made by mixing 0.218 grams BP in several drops of  $\gamma$ -butyrolactone. The mixture was then dissolved in 3.18 grams SR602 and stirred to dissolution. Then 12.32 grams Epoxy Part B were added to the mixture with  
35 vigorous stirring.

5 Part A' was prepared by mixing 0.195 grams DHEPT with several drops of  $\gamma$ -butyrolactone. The mixture was then dissolved in 5.56 grams of Epoxy Part A.

Part A' was then added to Part B'. To compensate for incomplete transfer of Part A', an additional 0.4 grams Epoxy Part A were added into the reaction mixture. The resultant reaction mixture was vigorously stirred.

10 ACRYLAMIDE1 (5%). Part B' was made by first dissolving 0.200 grams DHEPT in a couple of drops of  $\gamma$ -butyrolactone. The solution was then added to 1 gram CPR-1250 bisacrylamide that had been gently heated to melt (80°C). To the resulting mixture was added 15.51 grams Epoxy Part B.

15 Part A' was made by first dissolving 0.2 grams BP in a couple of drops of  $\gamma$ -butyrolactone. The solution was then added to 4.3 grams Epoxy Part A. The amount of Epoxy Part A was sufficient to obtain transfer of approximately 3.50 grams Epoxy Part B for the adhesive sample lay up, with minimal left over in the parent container.

Part A' was then added to Part B'.

20 ACRYLAMIDE2 (7%). Part B' was made by mixing 0.218 grams BP in several drops of  $\gamma$ -butyrolactone. The solution was then dissolved in 3.18 grams CPR-1250 bisacrylamide and stirred to dissolution. Then 12.32 grams Epoxy Part B were added to the mixture with vigorous stirring.

Part A' was prepared by mixing 0.195 grams DHEPT with several drops of  $\gamma$ -butyrolactone. The mixture was then dissolved in 5.56 grams Epoxy Part A.

25 Part A' was then added to Part B'. To compensate for incomplete transfer of Part A', an additional 0.4 grams Epoxy Part A were added into the reaction mixture. The resultant reaction mixture was vigorously stirred.

EPOXYST. 1.841 grams Part A were added to 8.159 grams Part B, and the mixture was stirred vigorously for 2-3 minutes until homogeneous.

### 30 DMA

DMA was conducted on the following acrylate-epoxy adhesives.

35 ACRYLATE1-60. A sufficient amount of ACRYLATE1 was added to the silicone rubber mold and analyzed according to the DMA procedure described above. Curing was conducted for 1 hour at 60°C followed by 30 minutes at 180°C. After cooling to room temperature, the cured samples were freed from the mold and analyzed. A plot of tangent delta versus temperature for ACRYLATE1-60 is shown in Fig. 1.

5           ACRYLATE1-100. A sufficient amount of ACRYLATE1 was added to the silicone rubber mold and analyzed according to the DMA procedure described above. Curing was conducted for 1 hour at 100°C followed by 30 minutes at 180°C. After cooling to room temperature, the cured samples were freed from the mold and analyzed. A plot of tangent delta versus temperature for ACRYLATE1-100 is shown  
10 in Fig. 1.

          ACRYLATE2-RT. A sufficient amount of ACRYLATE2 was added to the silicone rubber mold and analyzed according to the DMA procedure described above. Curing was conducted overnight at room temperature. The cured samples were freed from the mold and analyzed. A plot of tangent delta versus temperature for  
15 ACRYLATE2-RT is shown in Fig. 1.

          EPOXYST. A sufficient amount of EPOXYST was added to the silicone rubber mold and analyzed according to the DMA procedure described above. Curing was conducted over night at room temperature followed by 30 minutes at 180°C. The samples were then allowed to cool to room temperature. The samples were removed  
20 from the mold and analyzed. A plot of tangent delta versus temperature for EPOXYST is shown in Fig. 1.

#### Strength Tests

          The adhesive strength of the acrylate-epoxy and acrylamide-epoxy adhesives were determined by the lap shear and T-peel strength tests described above. All tests  
25 were conducted on etched aluminum and cured under the following conditions.

          ACRYLATE1-110-180. ACRYLATE1 was cured for 30 minutes at 110°C followed by 30 minutes at 180°C. The lap shear measurement was 3976 lb/in<sup>2</sup>. The T-peel measurement was 63 lb<sub>f</sub>/in-width.

          ACRYLATE1-RT-180. ACRYLATE1 was cured at room temperature  
30 overnight and then placed in an oven for 30 minutes at 180°C. The lap shear measurement was 2867 lb/in<sup>2</sup>. The T-peel measurement was 37 lb<sub>f</sub>/in-width.

          ACRYLATE1-110. ACRYLATE1 was prepared using a hot press that was preset to 110°C and approximately 3.5 psi (1000 lbs over 2 ft<sup>2</sup> pressure). The samples were kept in the press for approximately 1 hour. The lap shear measurement was  
35 4276 lb/in<sup>2</sup>. The T-peel measurement was 51 lb<sub>f</sub>/in-width.

          ACRYLATE1-110-180. ACRYLATE1 was prepared using a hot press that was preset to 110°C and approximately 3.5 psi (1000 lbs over 2 ft<sup>2</sup> pressure). The

- 5 samples were kept in the press for approximately 1 hour followed by 30 minutes at 180°C. The lap shear measurement was 4152 lb/in<sup>2</sup>. The T-peel measurement was 44 lb<sub>f</sub>/in-width.

ACRYLAMIDE1-110-180. ACRYLAMIDE1 was cured for 30 minutes at 110°C followed by 30 minutes at 180°C. The lap shear measurement was 3880 lb/in<sup>2</sup>.

- 10 The T-peel measurement was 61 lb<sub>f</sub>/in-width.

ACRYLAMIDE2-110-180. ACRYLAMIDE2 was cured for 30 minutes at 110°C followed by 30 minutes at 180°C. The lap shear measurement was 4898 lb/in<sup>2</sup>. The T-peel measurement was 49 lb<sub>f</sub>/in-width.

#### EXAMPLE 2 - Oxalic Amide-Epoxy Adhesives

- 15 Oxalic amide-epoxy formulations were prepared by mixing together Epoxy Part B, Epoxy Part A and DEO-400 in the amounts shown in Table 1. Specifically, DEO-400 was added to Part B and stirred for 2-3 minutes to obtain a uniform mixture. Then, Part A was added to the mixture and the mixture was stirred for an additional 2-3 minutes until uniform.

20 **TABLE 1**

Adhesive	Wt% DEO-400	Part B (g)	DEO-400 (g)	Part A (g)
DEO5.3	5.3%	7.56	0.53	1.91
DEO7	7%	11.05	1.05	2.90
DEO10.6	10.6%	6.96	1.06	1.98
DEO19.7	19.7%	5.93	1.97	2.10
DEO25.3	25.3%	5.30	2.53	2.17

#### DMA

- A sufficient amount of adhesive was added to the silicone rubber mold and analyzed according to the DMA procedure described above. Curing was conducted  
25 for 18 hours at room temperature followed by 2 hours at 80°C. After cooling to room temperature, the cured samples were freed from the mold and analyzed. DMA plots of tangent delta versus temperature for various adhesives are shown in Fig. 2.

#### Strength Tests

- The adhesive strength of DEO7 was determined by the lap shear and T-peel  
30 strength tests described above. Both tests were conducted on etched aluminum and the adhesive was cured for 30 minutes at 110°C followed by 30 minutes at 180°C.

- 5 The lap shear measurement was 5214 lb/in<sup>2</sup>. The T-peel measurement was 70 lb/in-width.

### EXAMPLE 3 - PolyurethaneAcAc-Epoxy Adhesives

- AcAcUD-epoxy formulations were prepared by mixing together Epoxy Part B, Epoxy Part A and AcAcUD in the amounts shown in Table 2. Specifically, AcAcUD  
10 was added to Part B and stirred for 2-3 minutes to obtain a uniform mixture. Then, Part A was added to the mixture and the mixture was stirred for an additional 2-3 minutes until uniform.

**TABLE 2**

<b>Adhesive</b>	<b>Wt% AcAcUD</b>	<b>Part B (g)</b>	<b>AcAcUD (g)</b>	<b>Part A (g)</b>
AcAcUD5.3	5.3%	7.52	0.53	1.95
AcAcUD7	7%	10.97	1.05	2.99
AcAcUD10.6	10.6%	6.88	1.06	2.06
AcAcUD19.7	19.7%	5.77	1.97	2.25
AcAcUD25.3	25.3%	5.09	2.53	2.36

- 15 AcAcXM-epoxy formulations were prepared by mixing together Epoxy Part B, Epoxy Part A and AcAcXM in the amounts shown in Table 3. Specifically, AcAcXM was added to Part B and stirred for 2-3 minutes to obtain a uniform mixture. Then, Part A was added to the mixture and the mixture was stirred for an additional 2-3 minutes until uniform.

20 **TABLE 3**

<b>Adhesive</b>	<b>Wt% AcAcXM</b>	<b>Part B (g)</b>	<b>AcAcXM (g)</b>	<b>Part A (g)</b>
AcAcXM5.3	5.3%	7.65	0.53	1.82
AcAcXM7	7%	11.24	1.05	2.72
AcAcXM10.6	10.6%	7.15	1.06	1.79
AcAcXM19.7	19.7%	6.28	1.97	1.75
AcAcXM25.3	25.3%	5.74	2.53	1.73

### DMA

- A sufficient amount of adhesive was added to the silicone rubber mold and analyzed according to the DMA procedure described above. Curing was conducted  
25 for 18 hours at room temperature followed by 30 minutes at 180°C. After cooling to room temperature, the cured samples were freed from the mold and analyzed. Plots of

- 5 tangent delta versus temperature for various adhesives are shown in Fig. 3 (AcAcUD samples) and Fig. 4 (AcAcXM samples).

#### Strength Tests

- The adhesive strengths of AcAcUD7 and AcAcXM7 were determined by the lap shear and T-peel strength tests described above. Both tests were conducted on  
 10 etched aluminum and the adhesives were cured for 30 minutes at 110°C followed by 30 minutes at 180°C. AcAcUD7 exhibited a lap shear strength of 4505 lb/in<sup>2</sup> and a T-peel strength of 64 lb<sub>f</sub>/in-width. AcAcXM7 exhibited a lap shear strength of 5186 lb/in<sup>2</sup> and a T-peel strength of 57 lb<sub>f</sub>/in-width.

#### EXAMPLE 4- AcAcPolyalkene-Epoxy Adhesives

- 15 AcAc1K-epoxy formulations were prepared by mixing together Epoxy Part B, Epoxy Part A and AcAc1K in the amounts shown in Table 4. Specifically, AcAc1K was added to Part B and stirred for 2-3 minutes to obtain a uniform mixture. Then, Part A was added to the mixture and the mixture was stirred for an additional 2-3 minutes until uniform.

20 **TABLE 4**

Adhesive	Wt% AcAc1K	Part B (g)	AcAc1K (g)	Part A (g)
AcAc1K5.3	5.3%	7.54	0.53	1.93
AcAc1K7	7%	11.01	1.05	2.94
AcAc1K10.6	10.6%	6.92	1.06	2.02
AcAc1K19.7	19.7%	5.85	1.97	2.18
AcAc1K25.3	25.3%	5.20	2.53	2.27

- AcAc2K-epoxy formulations were prepared by mixing together Epoxy Part B, Epoxy Part A and AcAc2K in the amounts shown in Table 5. Specifically, AcAc2K  
 25 Part A was added to the mixture and the mixture was stirred for an additional 2-3 minutes until uniform.

**TABLE 5**

Adhesive	Wt% AcAc2K	Part B (g)	AcAc2K (g)	Part A (g)
AcAc2K5.3	5.3%	7.52	0.53	1.95
AcAc2K7	7%	10.97	1.05	2.98
AcAc2K10.6	10.6%	6.88	1.06	2.06
AcAc2K19.7	19.7%	5.77	1.97	2.26
AcAc2K25.3	25.3%	5.10	2.53	2.37



5

DMA

A sufficient amount of adhesive was added to the silicone rubber mold and analyzed according to the DMA procedure described above. Curing was conducted for 18 hours at room temperature followed by 30 minutes at 180°C. After cooling to  
10 room temperature, the cured samples were freed from the mold and analyzed. Plots of tangent delta versus temperature for various adhesives are shown in Fig. 5 (AcAc1K samples) and Fig. 6 (AcAc2K samples).

Strength Tests

The adhesive strengths of AcAc1K7 and AcAc2K7 were determined by the  
15 lap shear and T-peel strength tests described above. Both tests were conducted on etched aluminum and the adhesives were cured for 30 minutes at 110°C followed by 30 minutes at 180°C. AcAc1K7 exhibited a lap shear strength of 4524 lb/in<sup>2</sup> and a T-peel strength of 64 lb<sub>f</sub>/in-width. AcAc2K7 exhibited a lap shear strength of 3836 lb/in<sup>2</sup> and a T-peel strength of 38 lb<sub>f</sub>/in-width.

20 The embodiments described above and illustrated in the figures are presented by way of example only and are not intended as a limitation upon the concepts and principles of the present invention. As such, it will be appreciated by one having ordinary skill in the art that various changes in the elements and their configuration and arrangement are possible without departing from the spirit and scope of the  
25 present invention.

Thus, the invention provides, among other things, a two-part epoxy-based structural adhesive comprising a curable epoxy resin, an amine curing agent, a toughening agent and a reactive liquid modifier. Various features and advantages of the invention are set forth in the following claims.

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## CLAIMS

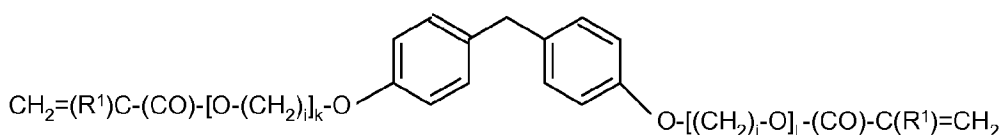
What is claimed is:

1. A two-part structural adhesive composition comprising:  
a curable epoxy resin;  
10 an amine curing agent;  
a toughening agent; and  
a reactive liquid modifier comprising an acrylate functionalized  
compound, an acrylamide functionalized compound, an oxalic amide functionalized  
compound, an acetoacetoxyl functionalized urethane, an acetoacetoxyl functionalized  
15 polyalkene, or combination thereof
  2. The composition of claim 1 wherein the curable epoxy resin comprises  
a diglycidylether of bisphenol A.
  - 20 3. The composition of claim 1 or claim 2 wherein the toughening agent  
comprises a core/shell polymer, an acrylic polymer, a butadiene nitrile rubber, a  
polyether diamine or combinations thereof.
  4. The composition of claim 1 or claim 2 wherein the toughening agent  
25 comprises a core/shell polymer having a core comprising a butadiene polymer, a  
butadiene copolymer, a styrene polymer, a styrene copolymer, or a butadiene-styrene  
copolymer and a shell comprising a polyacrylate polymer or a polyacrylate  
copolymer.
  - 30 5. The composition of any one of claims 1 to 4 wherein the reactive  
liquid modifier is an acrylate functionalized compound having the general formula
- $$Y-[(O-(CO)-(CH_2)_5)_g-O-(CO)-C(R^1)=CH_2]_h$$
- wherein Y is a branched or linear alkyl chain having from about 1 to 10  
carbon atoms or a heteroalkyl chain having from about 1 to 10 carbon atoms; each R<sub>1</sub>  
35 is, independently, H or a C<sub>1</sub>-C<sub>4</sub> alkyl; each g is, independently, an integer value  
ranging from about 1 to 35; and h is an integer value ranging from about 1 to 22.

- 5            6.        The composition of any one of claims 1 to 4 wherein the reactive liquid modifier is an acrylate functionalized compound having the general formula



OR



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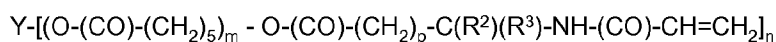
wherein

each  $\text{R}^1$  is, independently, H or a  $\text{C}_1$ - $\text{C}_4$  alkyl;

i and j are each, independently, integer values ranging from about 1 to 10; and

- 15            k and l are each, independently, integer values of at least 1 whose combined sum ranges from about 2 to 135.

- 20            7.        The composition of any one of claims 1 to 4 wherein the reactive liquid modifier is an acrylamide functionalized compound having the general formula



wherein

Y is a branched or linear alkyl chain having from about 1 to 10 carbon atoms or a heteroalkyl chain having from about 1 to 10 carbon atoms;

- 25            each m is, independently, an integer value ranging from about 1 to 20;

n is an integer value ranging from about 1 to 5;

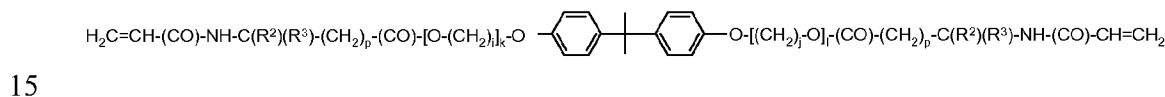
- 30             $\text{R}^2$  and  $\text{R}^3$  are each, independently, an alkyl group having from about 1 to 14 carbon atoms, a cycloalkyl group having from about 3 to 14 carbon atoms, an aryl group having from about 5 to 12 ring atoms, and arenyl group having from about 6 to 26 carbon atoms and about 0 to 3 S, N, or nonperoxidic O atoms, or  $\text{R}^2$  and  $\text{R}^3$  taken

5 together with the carbon to which they are both joined form a carbocyclic ring having from about 4 to 12 carbon atoms; and

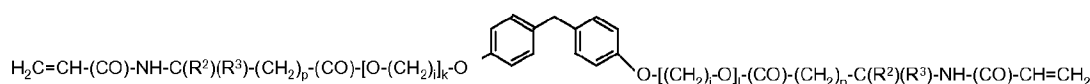
each p is, independently, 0 or 1.

8. The composition of claim 7 wherein Y is an alkyl ether, m is 5, n is 2,  
10 p is 0, and R<sup>2</sup> and R<sup>3</sup> are each a methyl group.

9. The composition of any one of claims 1 to 4 wherein the reactive liquid modifier is an acrylamide functionalized compound having the general formula



OR



wherein

20 i and j are each, independently, integer values ranging from about 1 to 10;

k and l are each, independently, integer values of at least 1 whose combined sum ranges from about 2 to 120;

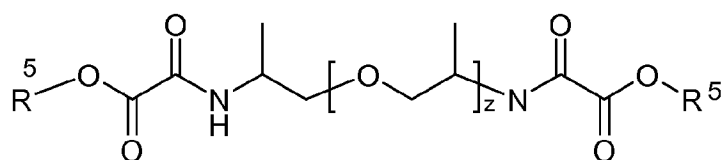
R<sup>2</sup> and R<sup>3</sup> are each, independently, an alkyl group having from about 1 to 14 carbon atoms, a cycloalkyl group having from about 3 to 14 carbon atoms, an aryl  
25 group having from about 5 to 12 ring atoms, and arenyl group having from about 6 to 26 carbon atoms and about 0 to 3 S, N, or nonperoxidic O atoms, or R<sup>2</sup> and R<sup>3</sup> taken together with the carbon to which they are both joined form a carbocyclic ring having from about 4 to 12 carbon atoms; and

each p is, independently, 0 or 1.

30

10. The composition of any one of claims 1 to 4 wherein the reactive liquid modifier is an oxalic amide having the formula

5



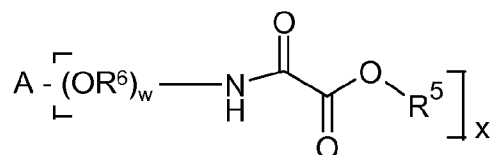
wherein

z is an integer value ranging from about 1 to 75; and

R<sup>5</sup> is an alkyl group having from about 1 to 4 carbon atoms, a cycloalkyl group having from about 3 to 12 carbon atoms, or an aromatic group having from  
10 about 6 to 12 carbon atoms.

11. The composition of claim 10 wherein z is 5-6 and R<sup>5</sup> is an ethyl group.

12. The composition of any one of claims 1 to 4 wherein the reactive  
15 liquid modifier is an oxalic amide having the general formula



wherein

A is a branched or linear alkyl chain having from about 1 to 10 carbon atoms;

R<sup>6</sup> is a branched or linear alkyl chain having from about 1 to 5 carbon atoms;

20 each w is, independently, an integer value ranging from about 1 to 130;

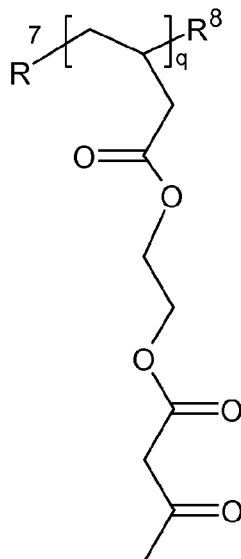
x is an integer value ranging from about 1 to 40; and

R<sup>5</sup> is an alkyl group having from about 1 to 4 carbon atoms, a cycloalkyl group having from about 3 to 12 carbon atoms, or an aromatic group having from about 6 to 12 carbon atoms.

25 13. The composition of any one of claims 1 to 4 wherein the reactive liquid modifier is an acetoacetoxy functionalized urethane comprising an oligourethane polyol capped with one or more acetoacetoxy functional compounds.

- 5            14.     The composition of claim 13 wherein the acetoacetoxy functionalized urethane is free of isocyanates.

- 10           15.     The composition of any one of claims 1 to 4 wherein the reactive liquid modifier is an acetoacetoxy functionalized polyalkene having the structure

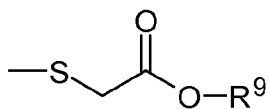


wherein

q is an integer or non-integer number ranging from about 1 to about 10;

R<sup>7</sup> is H or an initiator fragment from a thermally decomposing initiator; and

- 15           R<sup>8</sup> is H, an initiator fragment from a thermally decomposing initiator, or a thioester having the general formula



where R<sup>9</sup> is a C<sub>1</sub>-C<sub>12</sub> linear alkyl, a C<sub>1</sub>-C<sub>12</sub> branched alkyl or a C<sub>1</sub>-C<sub>12</sub> cyclic alkyl.

- 20           16.     The composition of claim 15 wherein R<sup>9</sup> is a methyl group, an ethyl group, a propyl group, a butyl group, a sec-butyl group, a tert-butyl group, or an isooctyl group.

5

17. The composition of claim 15 wherein q is about 4.6, R<sup>7</sup> is a tert-butyl group, and R<sup>9</sup> is isooctyl.

18. The composition of claim 15 wherein q is about 9, R<sup>7</sup> is a tert-butyl group, and R<sup>9</sup> is isooctyl.

19. The composition of any one of claims 1 to 18 wherein the adhesive composition comprises from about 5% to about 20% by weight reactive liquid modifier.

15

20. The composition of any one of claims 1 to 19 wherein the curable epoxy resin has one or more epoxy moieties and the amine curing agent has one or more amine hydrogens and the molar ratio of epoxy moieties on the curable epoxy resin to amine hydrogens on the amine curing agent ranges from about 0.5:1 to about 3:1.

20

21. The composition of any one of claims 1 to 20 wherein the adhesive composition cured for 30 minutes at 110°C followed by 30 minutes at 180°C has a lap shear measurement of at least 2500 psi.

25

22. The composition of any one of claims 1 to 21 wherein the adhesive composition cured for 30 minutes at 110°C followed by 30 minutes at 180°C has a T-peel measurement of at least 30 lb<sub>f</sub>/in-width.

23. The composition of any one of claims 1 to 22 further comprising a secondary curative.

30

24. A method of making a composite article, the method comprising:  
applying the two-part adhesive composition of any one of claims 1 to 23 to a surface; and

35

curing the two-part adhesive composition in contact with the surface to form a composite article.

5

25. The method of claim 24 wherein during curing the reactive liquid modifier polymerizes to form at least one of an interpenetrating polymer network and a semi-interpenetrating polymer network with the curable epoxy resin.

10

26. A method of forming a bonded joint between members, the method comprising:

applying the two-part adhesive composition of any one of claims 1 to 23 to a surface of at least one of two or more members;

15 joining the members so that the two-part adhesive composition is sandwiched between the two or more members; and

curing the two-part adhesive composition to form a bonded joint between the two or more members.

27. The method of claim 26 wherein during curing the reactive liquid  
20 modifier polymerizes to form at least one of an interpenetrating polymer network and a semi-interpenetrating polymer network with the curable epoxy resin.



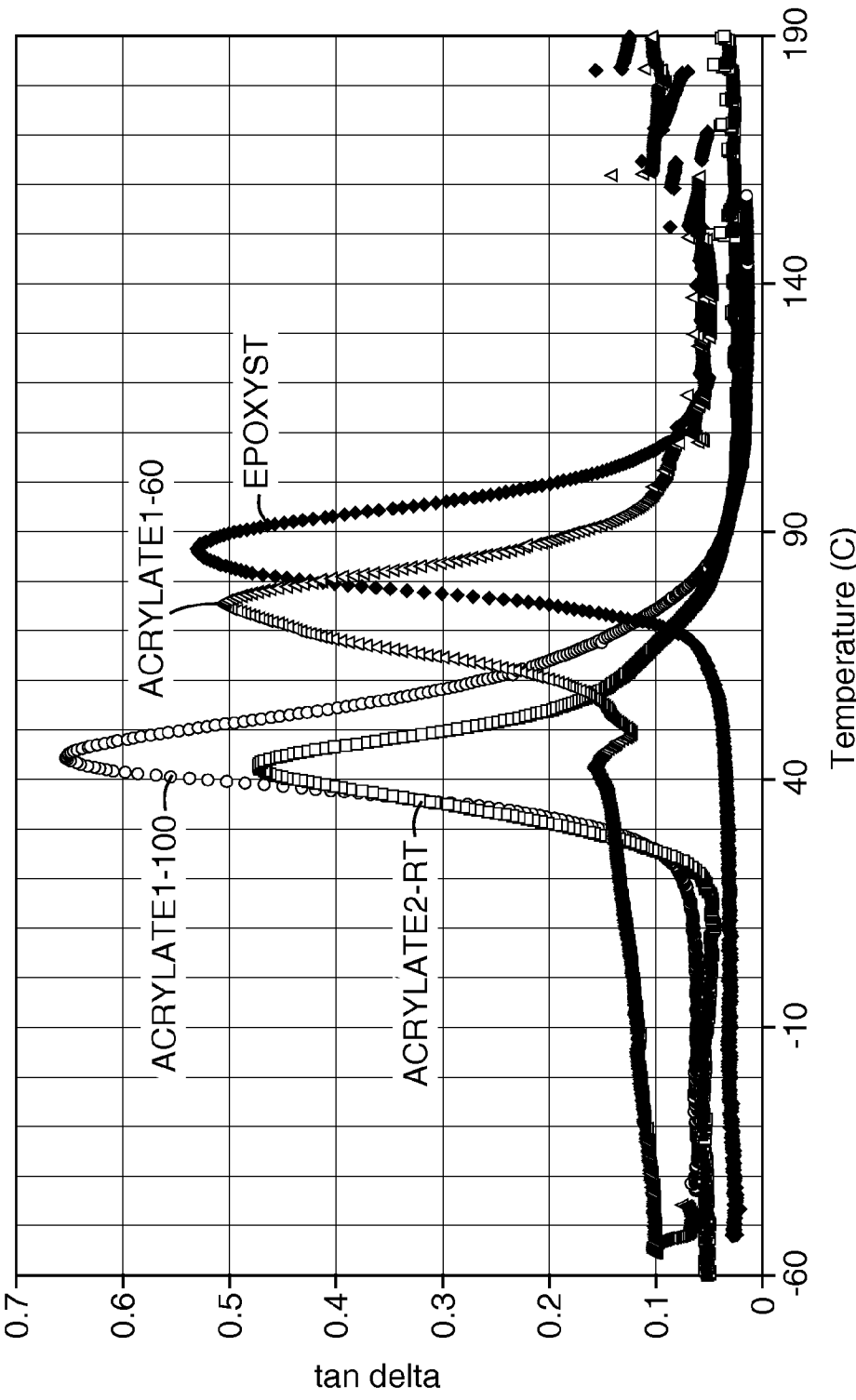


Fig. 1

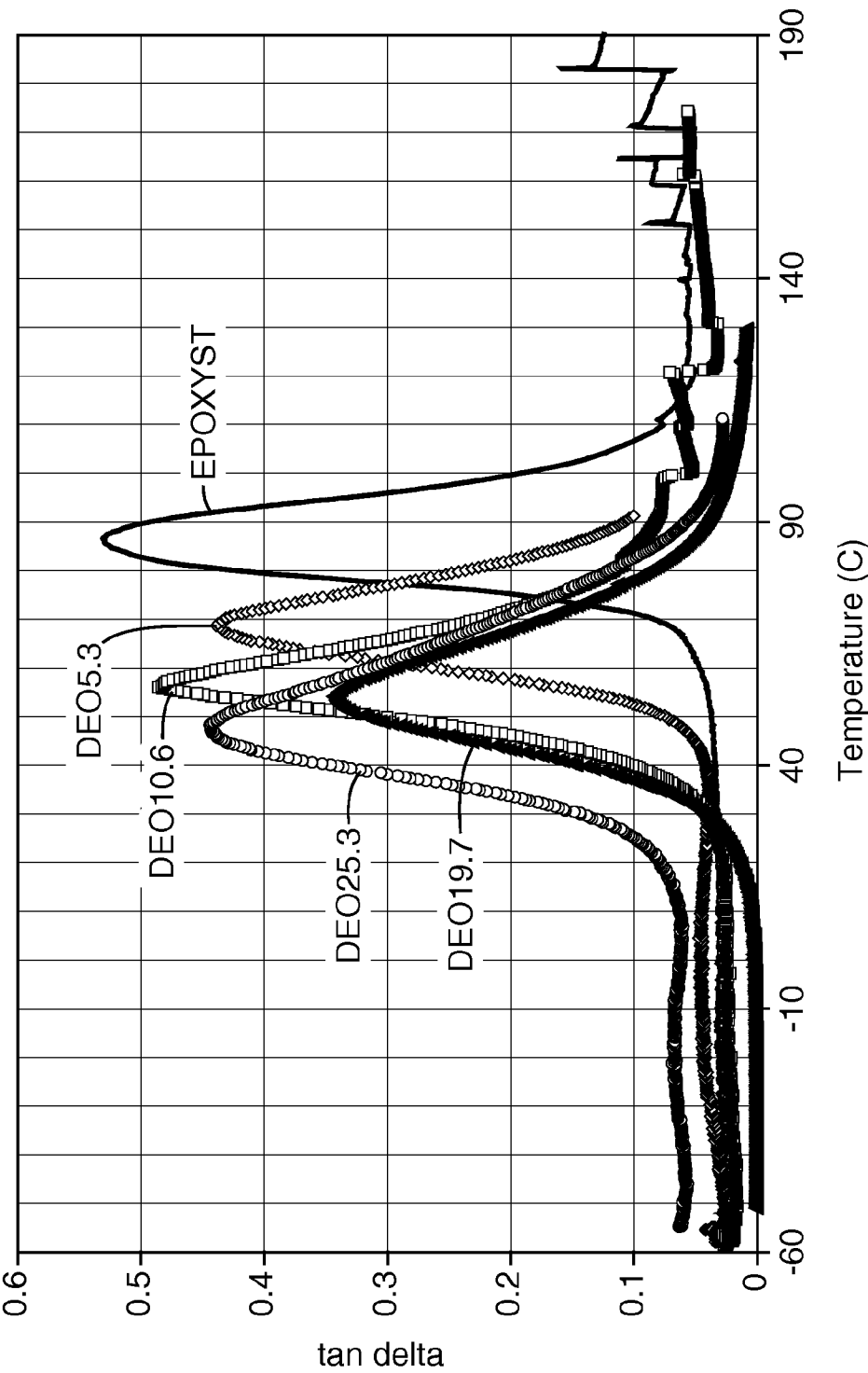
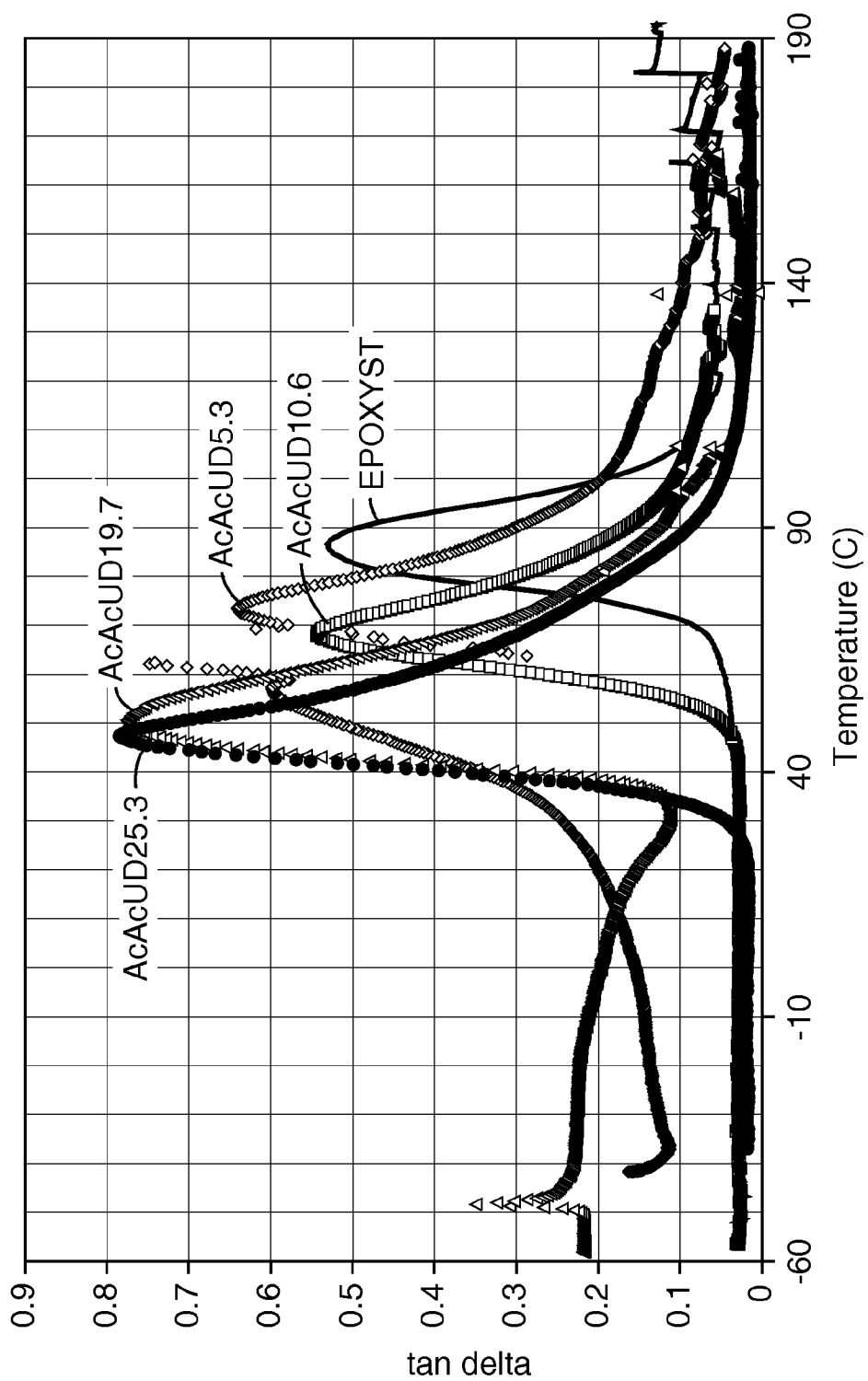


Fig. 2

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*Fig. 3*

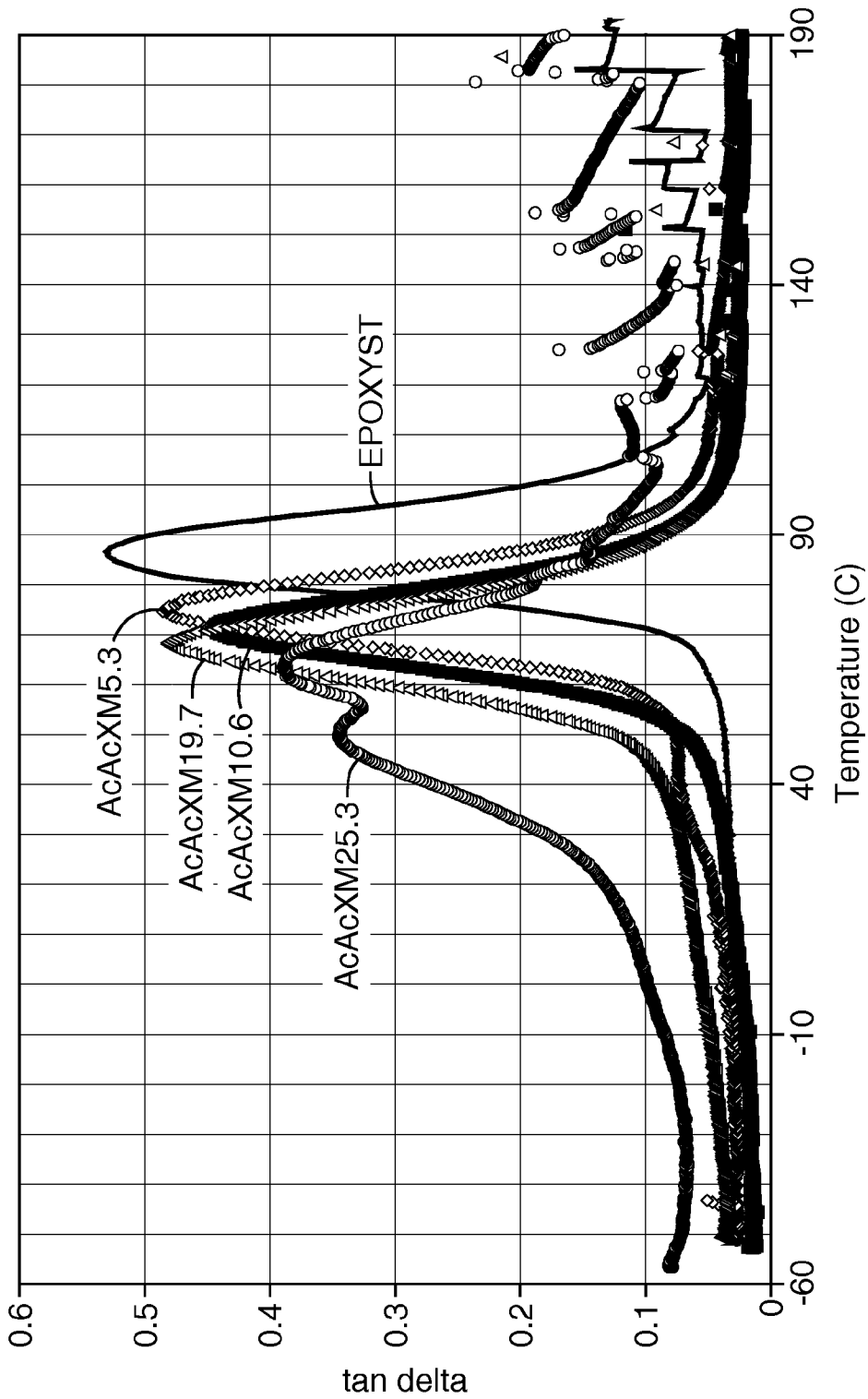


Fig. 4

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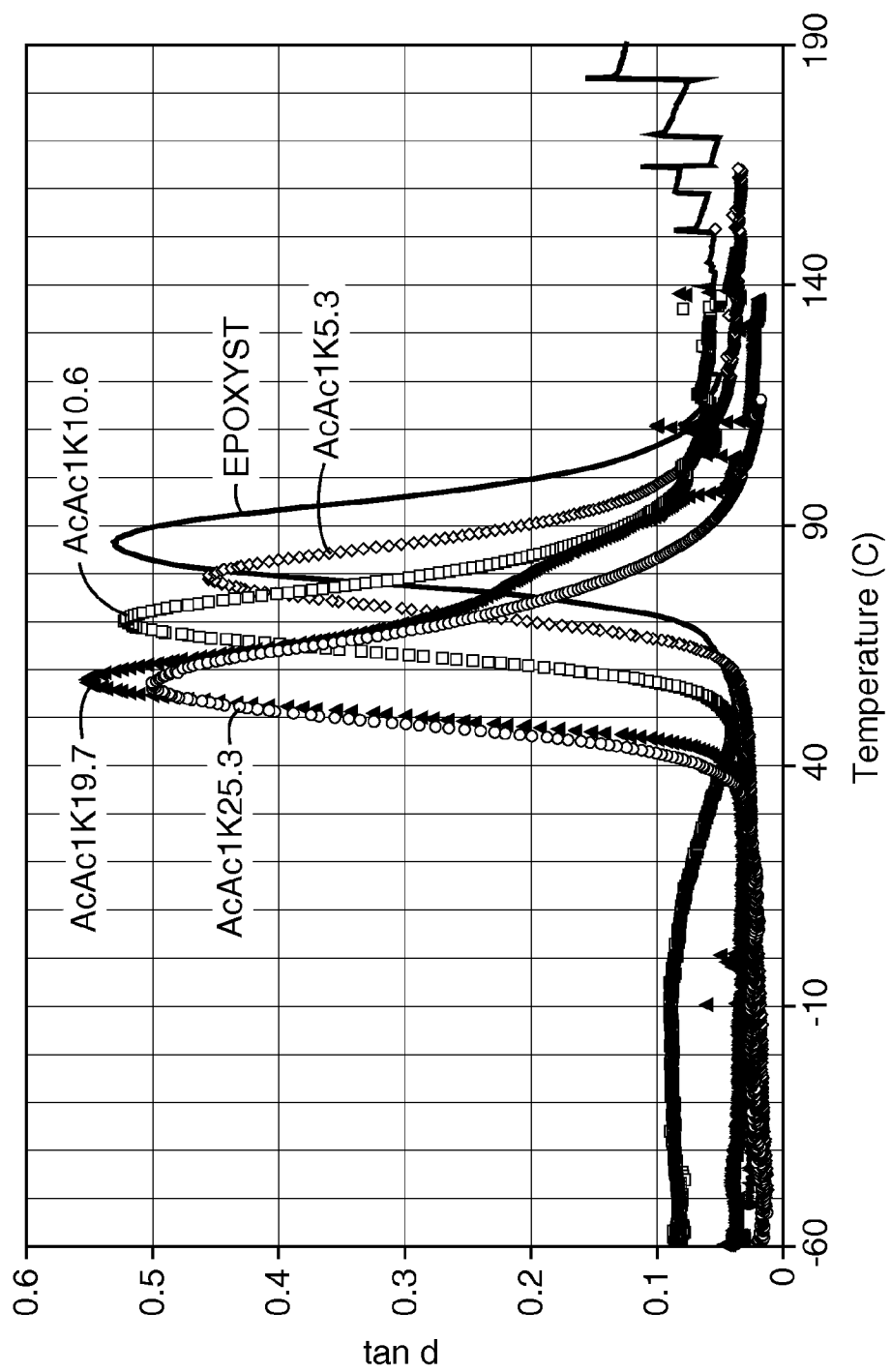


Fig. 5

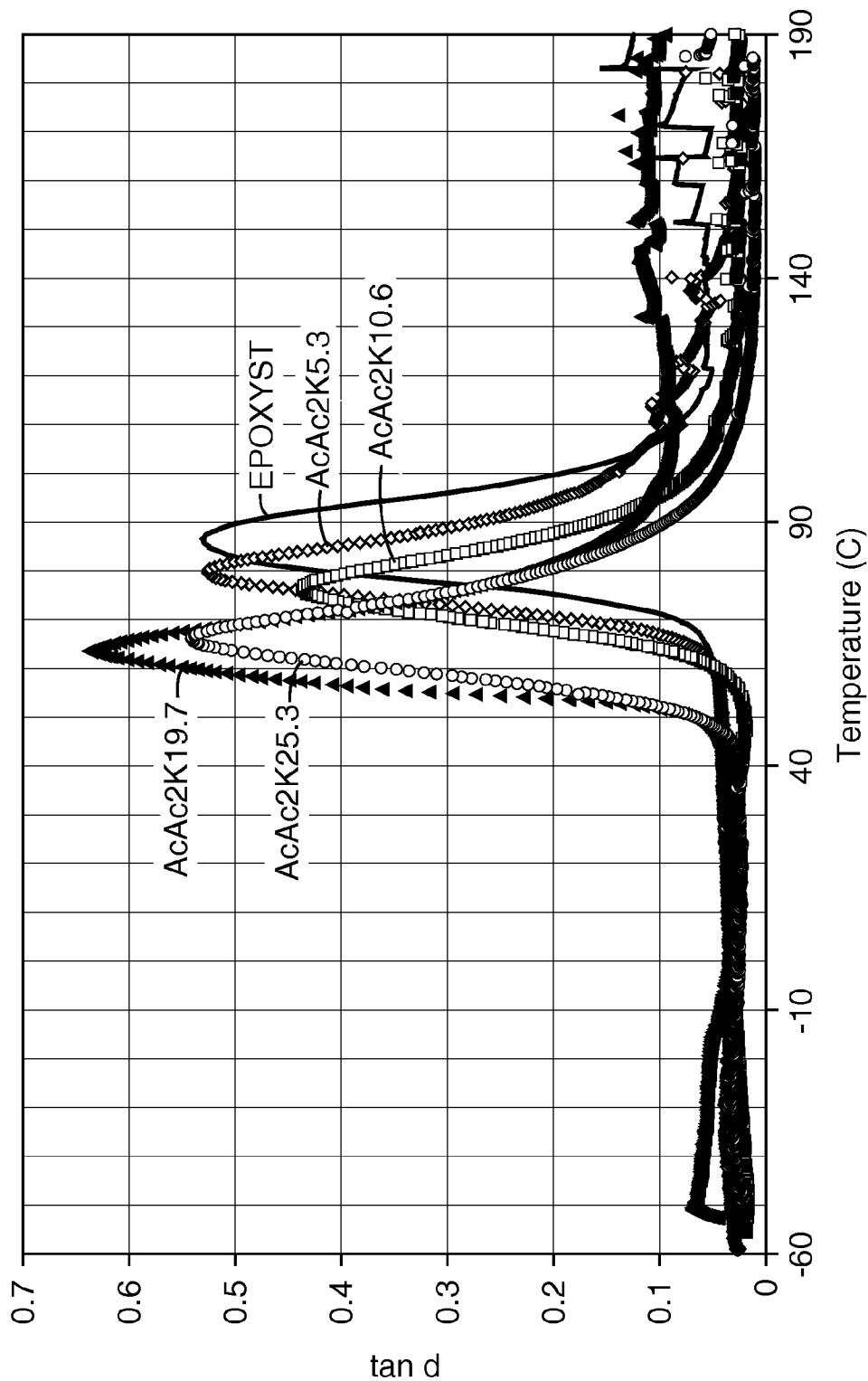


Fig. 6

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2009/051339

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C08L63/00 C08L63/02 C09J163/00 C09J163/02

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L C09J

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

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

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/078163 A1 (HENKEL KOMMANDITGESELLSCHAFT AU [DE]; SCHOENFELD RAINER [US]; HUBERT JA) 25 September 2003 (2003-09-25) page 1, lines 9-11 page 2, lines 3-15 examples 2-3 tables 1-2 claim 1	1-27
X	EP 0 301 720 A2 (LORD CORP [US]) 1 February 1989 (1989-02-01) page 2, lines 1-5 page 3, lines 28-39 example I claim 1	1-27

-/--

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

☒ See patent family annex.

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Date of the actual completion of the international search

3 November 2009

Date of mailing of the international search report

11/11/2009

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Authorized officer

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/051339

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International application No

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