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(21) International Application Number: PCT/US96/12302 (22) International Filing Date: 26 July 1996 (26.07.96) (30) Priority Data: 08/507,569 26 July 1995 (26.07.95) US Not furnished 8 July 1996 (08.07.96) US (71) Applicant: LOCKHEED MARTIN ENERGY SYSTEMS, INC. [US/US]; P.O. Box 2009, Oak Ridge, TN 37831-8243 (US). (72) Inventors: JANKE, Christopher, J.; 250 Walls Hollow Road, Oliver Springs, TN 37840 (US). LOPATA, Vincent, J.; 8 McGregor Crescent, Pinawa, Manitoba R0E 1L0 (CA). HAVENS, Stephen, J.; 9125-C Cedar Park Lane, Knoxville, TN 37923 (US). DORSEY, George, F.; 12036 S. Fox Den Drive, Farragut, TN 37922 (US). MOULTON, Richard, J.; 18 Westwind Road, Lafayette, CA 94549 (US). (74) Agent: SMIRMAN, Preston, H.; Lockheed Martin Energy Systems, Inc., P.O. Box 2009, Oak Ridge, TN 37831-8243 (US).	(81) Designated States: AL, AU, BB, BG, BR, CA, CH, CN, CU, CZ, EE, GB, GE, HU, IL, IS, JP, KP, KR, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: IONIZING RADIATION CURING OF EPOXY RESIN SYSTEMS INCORPORATING CATIONIC PHOTOINITIATORS		
(57) Abstract Mixtures of toughened epoxy resins with cationic initiators are curable under high energy ionizing radiation such as electron beam radiation, X-ray radiation, and gamma radiation. The composition of this process consists of an epoxy resin, a cationic initiator such as a diaryliodonium or triarylsulfonium salt of specific anions, and a toughening agent such as a thermoplastic, hydroxy-containing thermoplastic oligomer, epoxy-containing thermoplastic oligomer, reactive flexibilizer, rubber, elastomer, or mixture thereof. Cured compositions have high glass transition temperatures, good mechanical properties, and good toughness. These properties are comparable to those of similar thermally cured epoxies. A mixture of epoxy resins such as a semi-solid triglycidyl ether of tris (hydroxyphenyl) methane and a low viscosity bisphenol A glycidyl ether and a cationic photoinitiator such as a diaryliodonium salt is cured by irradiating with a dosage of electron beams from about 50 to about 150 kGy forming a cross-linked epoxy resin polymer.		

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1 **IONIZING RADIATION CURING OF EPOXY RESIN SYSTEMS INCORPORATING**
2 **CATIONIC PHOTOINITIATORS**

3
4 This invention was made with Government support under contract DE-AC05-
5 84OR21400 awarded by the U.S. Department of Energy to Lockheed Martin Energy
6 Systems, Inc. and the Government has certain rights in this Invention.

7
8 **CROSS REFERENCE TO RELATED APPLICATION**

9 This application is a continuation-in-part application under 37 C.F.R. § 1.53 of
10 U.S. Patent Application Serial No. 08/507,569, filed July 26, 1995, the entire disclosure
11 of which is incorporated herein by reference.

12
13 **FIELD OF THE INVENTION**

14 The present invention relates to a epoxy resin system and a method of curing
15 epoxy resins, more particularly, to a toughened epoxy resin system and a method of
16 curing epoxy resin systems containing cationic photoinitiators.

17
18 **BACKGROUND OF THE INVENTION**

19 For the most part the polymerization or curing of monomers to high molecular
20 weight or highly cross linked polymers by means of high energy electron beam
21 radiation has been limited to a few general types of monomers. Monomers containing
22 acrylate and methacrylate groups have been extensively used as electron beam
23 curable coatings and adhesives. Monomers containing carbon-carbon double bonds,

1 such as vinyls, allenes, and dienes, are also known to be electron beam curable.
2 These monomers react by means of free radical mechanisms and under high energy
3 ionizing radiation such as electron beam require no free radical initiators. However,
4 these monomers tend to be toxic and expensive. Of greater concern is the fact that the
5 polymers produced by cross linking these materials are of limited value for many
6 applications. Such drawbacks include low glass transition temperature (or low service
7 temperature), low mechanical properties such as toughness, strength, and modulus,
8 and high shrinkage when cured.

9 What is desired is a means by which higher performance resins can be
10 processed and cured by means of electron beam radiation, and still achieve the same
11 thermal and mechanical properties as when thermally cured. A recent patent by
12 Aerospatiale (Eur. Pat. Appl EP 499,542) described a process by which bismaleimides
13 can be cured at ambient temperature by electron beam radiation to yield materials with
14 good mechanical properties and glass transition temperatures in excess of 300°C.
15 Coreactive diluents were added to the bismaleimides to make them processable at
16 lower temperatures.

17 Epoxy resins are much more widely used than bismaleimides although their
18 thermal properties are not quite as high. Epoxies are produced in hundreds of millions
19 of pounds annually and are widely used in a variety of applications (L.V. McAdams and
20 J. A. Gannon, "Epoxy Resin", Encyclopedia of Polymer Science and Technology, John
21 Wiley & Sons). A method of curing epoxy resins by means of electron beam radiation
22 would therefore be of considerable value. Visible-ultraviolet curing of thin films of
23 cycloaliphatic epoxies using a cationic initiator is well known (J.V. Crivello, Advances in

1 Polymer Science, Vol. 61, p.1, 1984).

2 However, these processes are limited to thin coatings due to the low penetration
3 of visible-ultraviolet radiation. Thermal and mechanical properties of these materials
4 are low and curing is incomplete. There has been little reported success with the
5 electron beam curing of epoxies. Crivello (J. V. Crivello, M. Fan, and D. Bi., Journal of
6 Applied Polymer Science, Vol. 44, p.9, 1992; U.S. Pat. 5,260,349) has recently
7 disclosed a series of highly reactive cycloaliphatic silicone epoxies which are electron
8 beam curable in the presence of certain cationic photoinitiators (diaryliodonium and
9 triarylsulfonium salts). Crivello further reported that cycloaliphatic epoxies and
10 conventional bisphenol A based epoxies cured poorly under the same conditions.
11 Massive doses of electron beam radiation were required. Others (R.S Davidson and S.
12 A. Wilkinson, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 58,
13 p.123, 1991 and T. Okada, T. Asano, M. Hatada, J. Takezaki, and K. Ochi, Kobunshi
14 Ronbunshu, Vol. 44, p. 761, 1987) have also reported that examples of these same
15 types of photoinitiators do not lead to complete electron beam curing of certain
16 cycloaliphatic epoxies and bisphenol A based glycidyl ethers. Thermal postcuring is
17 required to achieve a more complete degree of cure.

18 The U.S. Patent Application, parent to this application, disclosed that
19 conventional epoxy resins can be fully cured at ambient temperature to high glass
20 transition temperatures (essentially the same or higher as with thermal curing).
21 Cationic initiators are also required for this process. The process also requires ionizing
22 radiation produced by an electron beam accelerator. The main difficulty associated
23 with the cured epoxy resins is that they are brittle. While much research has been

1 devoted to the toughening of thermally cured epoxies, there are no reports in the
2 literature of any means to toughen epoxies which are radiation cured using cationic
3 initiators.

4 Radiation cured epoxy resins incorporating cationic photoinitiators tend to be
5 very brittle. Resins for many structural and non-structural applications including
6 composites, adhesives, and coatings for use in aircraft, aerospace, marine,
7 transportation, sporting goods, and other consumer products must have sufficient
8 toughness and impact resistance to endure many years of harsh service. What is
9 needed is a means by which radiation cured cationic epoxies can be toughened and
10 still retain the good thermal and mechanical properties of the original composition. This
11 invention describes a variety of toughening agents which can be incorporated into the
12 epoxy resin initiator mixture. These toughening agents include thermoplastics,
13 hydroxy-containing thermoplastic oligomers epoxy-containing thermoplastic oligomers,
14 reactive flexibilizers, elastomers, rubbers, and mixtures thereof. An additional
15 advantage obtained by the use of low viscosity reactive flexibilizers is reduction of the
16 overall viscosity of the uncured resin mixture. Incorporation of one or more of these
17 toughening agents has resulted in increases in toughness of more than 230% over that
18 of the untoughened epoxy resin.

19 20 OBJECTS OF THE INVENTION

21 Accordingly, it is an object of the present invention to provide a **method of curing**
22 **epoxy resin systems containing cationic photoinitiators** and to provide a toughened
23 epoxy resin composition. It is an additional object of the present invention to provide a

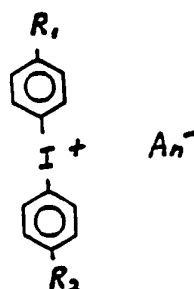
1 method for making a toughened epoxy resin system from the toughened epoxy resin
2 composition.

3 Further and other objects of the present invention will become apparent from the
4 description contained herein.

5 SUMMARY OF THE INVENTION

6 In accordance with one aspect of the present invention, a new and improved
7 method of curing an epoxy resin system comprises the following steps:

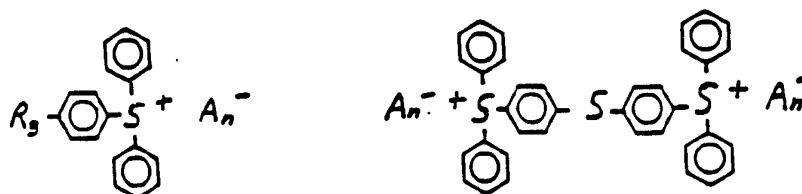
8 Step 1. Provide a blend of an epoxy resin system. The epoxy resin system
9 comprises an epoxy resin and a cationic photoinitiator. The epoxy resin is selected from
10 the group consisting of: glycidyl ethers of bisphenol A, epoxy phenolic novolacs, epoxy
11 cresol novolacs, bisphenol F epoxies, tetraglycidyl ether of tetrakis (4-hydroxyphenyl)
12 ethane, diglycidyl ether of 9, 9- bis (4-hydroxyphenyl) fluorene, glycidyl ether of the
13 condensation product of dicyclopentadiene and phenol, triglycidyl ether of tris
14 (hydroxyphenyl) methane, 3',4'-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate,
15 diglycidylester of hexahydrophthalic anhydride, bis (3,4-epoxycyclohexylmethyl) adipate,
16 isomeric mixture of bis (2,3-epoxycyclopentyl) ether, isomeric mixture of bis (2,3-
17 epoxycyclopentyl) ether reacted with ethylene glycol, isomeric mixture of bis (2,3-
18 epoxycyclopentyl) ether blended with a bisphenol A based glycidyl ether, and mixtures
19 thereof. The cationic photoinitiator is selected from the group consisting of:
20 diaryliodonium salts, triarylsulfonium salts, and mixtures thereof. The diaryliodonium
21 salts have the following formula:



where R_1 and R_2 are selected from the group consisting of: H, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, Cl, Br, OC_nH_{2n+1} , $OCH_2CH(CH_3)C_nH_{2n+1}$, $OCH_2CH(C_2H_5)C_nH_{2n+1}$, $OCH_2CH(OH)C_nH_{2n+1}$, $OCH_2CO_2C_nH_{2n+1}$, $OCH(CH_3)CO_2C_nH_{2n+1}$, $OCH(C_2H_5)CO_2C_nH_{2n+1}$, and mixtures thereof where n is an integer between 0 and 18.

An^- is an anion selected from the group consisting of: hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorophosphate (PF_6^-), boron tetrafluoride (BF_4^-), trifluoromethane sulfonate ($CF_3SO_3^-$), and tetrakis (pentafluorophenylborate) ($B[C_6F_5]_4^-$), and mixtures thereof.

The triarylsulfonium salts have the following formulas:



where R_1 is selected from the group consisting of: H, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, phenylsulfide (PhS), phenoxy (PhO), and mixtures thereof.

An^- is an anion selected from the group consisting of: hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorophosphate (PF_6^-), boron tetrafluoride (BF_4^-), trifluoromethane sulfonate ($CF_3SO_3^-$), and tetrakis (pentafluorophenylborate) ($B[C_6F_5]_4^-$), and mixtures thereof.

1 **Step 2. Irradiate the blend with ionizing radiation to form a cross-linked epoxy**
2 **resin polymer.**

3 **In accordance with another aspect of the present invention, a new and improved**
4 **method of curing an epoxy resin system comprises the following steps:**

5 **Step 1. Provide a blend of an epoxy resin system. The epoxy resin system**
6 **comprises epoxy resins and a cationic photoinitiator. The epoxy resins are a blend of a**
7 **semi-solid epoxy, triglycidyl ether of tris (hydroxyphenyl) methane, and a low viscosity**
8 **epoxy, glycidyl ether of bisphenol A. The cationic photoinitiator is (4-octyloxyphenyl)**
9 **phenyliodonium hexafluoroantimonate.**

10 **Step 2. Irradiate the blend of an epoxy resin system with ionizing radiation to**
11 **form a crosslinked epoxy resin polymer.**

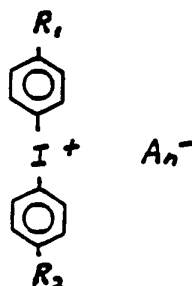
12 **In accordance with another aspect of the present invention, a new and improved**
13 **method of curing an epoxy resin system comprises the following steps:**

14 **Step 1. Provide a blend of an epoxy resin system. The epoxy resin system**
15 **comprises epoxy resins and a cationic photoinitiator. The epoxy resins are a blend of a**
16 **glycidyl ether of the condensation product of dicyclopentadiene and phenol, and a low**
17 **viscosity epoxy, glycidyl ether of bisphenol A. The cationic photoinitiator is**
18 **(4-octyloxyphenyl) phenyliodonium hexafluoroantimonate.**

19 **Step 2. Irradiate the blend of an epoxy resin system with ionizing radiation to**
20 **form a crosslinked epoxy resin polymer.**

21 **In accordance with another aspect of the present invention, a new and improved**
22 **epoxy resin system comprises a blend of an epoxy resin and a cationic photoinitiator.**
23 **The epoxy resin is selected from the group consisting of: glycidyl ethers of bisphenol A,**
24 **epoxy phenolic novolacs, epoxy cresol novolacs, bisphenol F epoxies, tetraglycidyl ether**
25 **of tetrakis (4-hydroxyphenyl) ethane, diglycidyl ether of 9, 9- bis (4-hydroxyphenyl)**
26 **fluorene, glycidyl ether of the condensation product of dicyclopentadiene and phenol,**
27 **triglycidyl ether of tris (hydroxyphenyl) methane, 3',4'-epoxycyclohexylmethyl 3,4-**

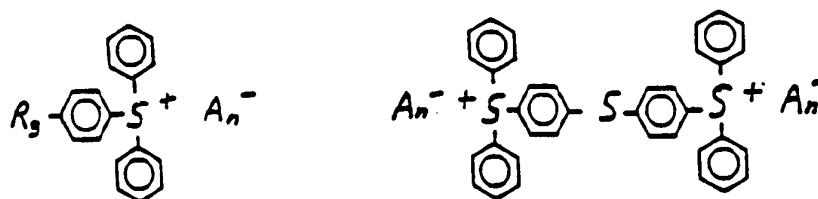
1 epoxycyclohexanecarboxylate, diglycidylester of hexahydrophthalic anhydride, bis (3,4-
 2 epoxycyclohexylmethyl) adipate, isomeric mixture of bis (2,3-epoxycyclopentyl) ether,
 3 isomeric mixture of bis (2,3-epoxycyclopentyl) ether reacted with ethylene glycol, isomeric
 4 mixture of bis (2,3-epoxycyclopentyl) ether blended with a bisphenol A based glycidyl
 5 ether, and mixtures thereof. The cationic photoinitiator is selected from the group
 6 consisting of: diaryliodonium salts, triarylsulfonium salts, and mixtures thereof. The
 7 diaryliodonium salts have the following formula:



18 where R_1 and R_2 are selected from the group consisting of: H, methyl, ethyl, n-
 19 propyl, isopropyl, n-butyl, tert-butyl, Cl, Br, $\text{OC}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CH}(\text{CH}_3)\text{C}_n\text{H}_{2n+1}$,
 20 $\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CH}(\text{OH})\text{C}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CO}_2\text{C}_n\text{H}_{2n+1}$,
 21 $\text{OCH}(\text{CH}_3)\text{CO}_2\text{C}_n\text{H}_{2n+1}$, $\text{OCH}(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_n\text{H}_{2n+1}$, and mixtures thereof where n is
 22 an integer between 0 and 18.

23 An^- is an anion selected from the group consisting of: hexafluoroarsenate (AsF_6^-),
 24 hexafluoroantimonate (SbF_6^-), hexafluorophosphate (PF_6^-), boron tetrafluoride
 25 (BF_4^-), trifluoromethane sulfonate (CF_3SO_3^-), and tetrakis
 26 (pentafluorophenylborate) ($\text{B}[\text{C}_6\text{F}_5]_4^-$), and mixtures thereof.

The triarylsulfonium salts have the following formulas:



where R_3 is selected from the group consisting of: H, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, phenylsulfide (PhS), phenoxy (PhO), and mixtures thereof.

A_n^- is an anion selected from the group consisting of: hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorophosphate (PF_6^-), boron tetrafluoride (BF_4^-), trifluoromethane sulfonate (CF_3SO_3^-), and tetrakis (pentafluorophenylborate) ($\text{B}[\text{C}_6\text{F}_5]_4^-$), and mixtures thereof.

In accordance with another aspect of the present invention, a new and improved toughened epoxy resin system mixture composition comprises an epoxy resin, a cationic initiator, and a toughening agent. The cationic initiator is selected from the group consisting of a diaryliodonium salt of a specific anion, a triarylsulfonium salt of a specific anion and combination thereof. The toughening agent is selected from the group consisting of a thermoplastic, hydroxy-containing thermoplastic oligomer, epoxy-containing thermoplastic oligomer, reactive flexibilizer, rubber, elastomer, and mixtures thereof.

In accordance with another aspect of the present invention, a new and improved

1 method for making a toughened epoxy resin system comprises the following steps:

2 Step 1. A toughened epoxy resin system mixture composition is provided. The
3 toughened epoxy resin system mixture composition comprises an epoxy resin, a
4 cationic initiator, and a toughening agent. The cationic initiator is selected from the
5 group consisting of a diaryliodonium salt of a specific anion, a triarylsulfonium salt of a
6 specific anion and combination thereof.

7 Step 2. The toughened epoxy resin system mixture composition is exposed to
8 high energy ionizing radiation for a period of time sufficient to cure the epoxy resin
9 system forming a cured toughened epoxy resin system.

10 In accordance with another aspect of the present invention, a new and improved
11 method for making a toughened epoxy resin system mixture comprises the following
12 steps:

13 Step 1. A toughened epoxy resin system mixture composition is provided. The
14 toughened epoxy resin system mixture composition comprises an epoxy resin, a
15 cationic initiator, and a toughening agent. The cationic initiator is selected from the
16 group consisting of a diaryliodonium salt of a specific anion, a triarylsulfonium salt of a
17 specific anion and combination thereof.

18 Step 2. The toughened epoxy resin system mixture composition is exposed to
19 high energy radiation from the sun for a period of time sufficient to cure the epoxy resin
20 system forming a cured toughened epoxy resin system.

21
22 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

23 This invention describes toughened epoxy resins and a method thereof which

1 are cured or cross linked by means of radiation induced cationic polymerization. It was
2 found that conventional epoxy resins can be cured at, below, or above ambient
3 temperatures to high glass transition temperatures (essentially the same or higher as
4 with thermal curing), while still exhibiting the same mechanical properties. A cationic
5 initiator at a concentration of 0.25 to 10 parts per hundred of the epoxy resin is required
6 for this process. Upon irradiation by ionizing radiation the initiator produces a cationic
7 species (positively charged ion) which initiates the cationic cure of the epoxy resins.
8 The mechanism of the cationic curing of epoxies is well known (L. V. McAdams and J.
9 A. Gannnon, "Epoxy Resins", Encyclopedia of polymer Science and Engineering, John
10 Wiley and Sons). Ionizing radiation refers to high energy radiation such as X-rays,
11 gamma rays, and electron beam (e-beam) radiation. E-beam radiation as produced by
12 an accelerator is particularly useful. In addition, high energy radiation from the sun
13 and high energy ultraviolet radiation can be used.

14 Additional advantages obtained from this process are the lack of mechanical
15 stresses, which result from thermal curing, and reduced manufacturing expenses
16 related to faster curing times, lower energy requirements, and the elimination of
17 expensive thermal processing equipment.

18 Uses of the process of this invention include coatings, encapsulants for
19 electronic devices, adhesives, molded and cast parts, and laminates and composites
20 with fiber reinforcement. Unlike the cationic curing of epoxy resins with visible or
21 ultraviolet light, the use of a penetrating high energy electron beam to initiate the curing
22 reaction means that thick sections of material can be completely and uniformly cured.
23 Thus, thick composite parts can now be fabricated and cured at any temperature at or

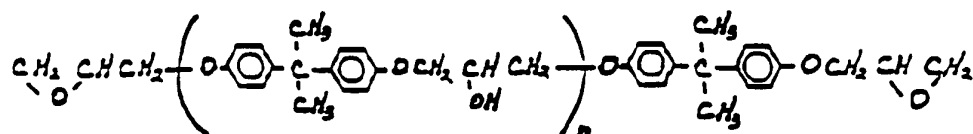
1 above the glass transition temperature of the epoxy monomers in relatively short
2 periods of time with minimal residual mechanical stresses.

3 The primary problem associated with epoxy resins cured by this process is that
4 they are too brittle to be used for many applications. What is needed is a toughening
5 agent which can be added to the epoxy resin/initiator blend. Requirements of this
6 toughening agent are: that it be miscible with or form a stable suspension with the
7 epoxy resin/initiator composition; that it not interfere with the cationic curing
8 mechanism; and, that it not significantly reduce the thermal and mechanical properties
9 of the cured resin. There is no mention in the literature of any tougheners for use with
10 epoxy resins which are cured by means of ionizing radiation induced cationic
11 polymerization. A variety of toughening agents and flexibilizers have been used with
12 thermally cured epoxy resins, which typically use an amine coreactant or hardener for
13 cross linking. These tougheners include: rubbers or elastomers, either as discrete
14 particles or reacted with epoxy resin, epoxy functionalized flexibilizers, engineering
15 thermoplastics, and amine or hydroxy-terminated thermoplastic oligomers. However,
16 the utility of these materials in toughening epoxy resins cured by the previously
17 described process cannot be predicted.

18 Specifically, this invention relates to the radiation curing of an epoxy resin or
19 mixtures of epoxy resins (Part A) which contains an initiator (Part B), and a toughener
20 (Part C).

21 The epoxy resin (Part A) may be virtually any of a variety of commercially
22 available materials. The glycidyl ethers of various phenolic compounds are particularly
23 important. These include the glycidyl ethers of bisphenol A as given by the following

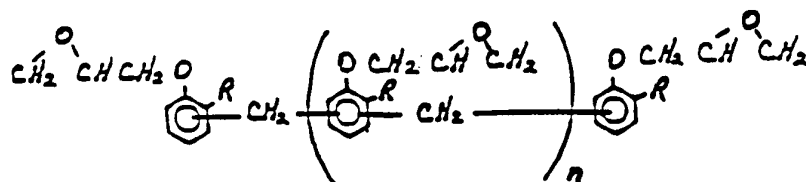
formula where n ranges from 0 to 12:



These resins are widely available from a number of manufacturers such as Shell Chemical Company, DOW Chemical Company, and Ciba-Geigy Corporation in a variety of molecular weights and viscosities. Examples include: D.E.R. 332, D.E.R. 330, D.E.R. 331, D.E.R. 383, D.E.R. 661, Tactix 123, Tactix 138, and Tactix 177 (DOW trademarks); Epon 825, Epon 826, and Epon 828 (Shell trademarks); and, Araldite GY 6008, Araldite GY 6010, and Araldite GY2600 (Ciba-Geigy trademarks).

Additionally, flame retardant epoxy resins can be used including fluorinated or brominated bisphenol type epoxy resins, such as D.E.R. 542 and D.E.R. 566-A80 from DOW Chemical Company.

Another important class of glycidyl ethers are those of phenolic novolac and cresol novolac resins as given by the following formula where n ranges from 0 to 8:



For epoxy phenolic novolacs, R=H, and for epoxy cresol novolacs, R=CH₃. For bisphenol F epoxy resins R=H and the value of n is low (0 to 0.15). These materials

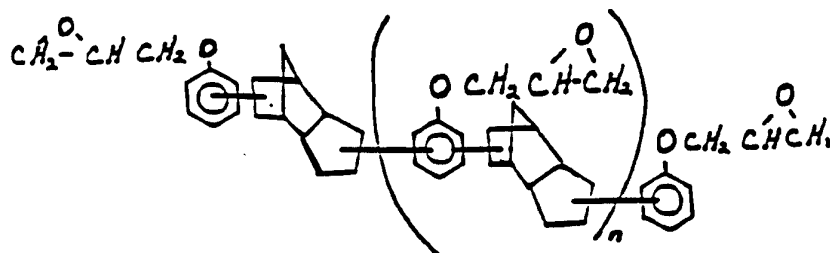
are also widely available from a number of manufacturers in a variety of molecular weights and viscosities. Examples include Epon 862, Epon 155, SU-8 (Shell trademarks); D.E.R. 354, D.E.N. 431, D.E.N. 438, and D.E.N. 439 (DOW trademarks); and Araldite PY 306, Araldite EPN 1139, Araldite EPN 1138, Araldite GY 281, Araldite GY 285, Araldite GY 302-2, Araldite LY 9703, Araldite XD 4955, and Araldite ECN 9511 (Ciba-Geigy trademarks).

Several other polyfunctional glycidyl ethers are of significant importance for high performance applications i.e. heavy mechanical loads under conditions of high temperature and harsh environment. The materials include:

The tetraglycidyl ether of tetrakis (4-hydroxyphenyl) ethane, which is commercially available as Epon 1031 (Shell Chemical trademark) and Araldite MT 0163 (Ciba-Geigy trademark).

The diglycidyl ether of 9, 9- bis (4-hydroxyphenyl) fluorene is available as Epon HPT 1079 (Shell Chemical trademark).

A glycidyl ether of the condensation product of dicyclopentadiene and phenol is available as Tactix 556 (DOW Chemical trademark) as given by the following formula where n is approximately 0.2:



1
2 The triglycidyl ether of tris (hydroxyphenyl) methane is available as Tactix 742
3 (DOW Chemical trademark) or as XD9053.

4 These latter materials, Epon 1031, Epon HPT 1079, Tactix 556, Tactix 742 and
5 XD9053, are either high viscosity liquids or solids at room temperature. Therefore it is
6 advantageous to blend these materials with a low viscosity bisphenol A or bisphenol F
7 based diglycidyl ether or reactive diluents. The resulting blends are less viscous at
8 ambient temperatures and are more easily processed. Some heating may be required
9 for adequate flow, but not temperatures high enough to cause thermal curing of the
10 epoxy group. Specific blends were found to have a good overall combination of low
11 viscosity in the uncured state and high glass transition temperature, flexural strength,
12 and modulus when cured. It was found to be particularly advantageous to blend a high
13 performance semi-solid epoxy such as Tactix 556, Tactix 742 or Epon HPT 1079 with a
14 low viscosity bisphenol A or bisphenol F based glycidyl ether epoxy such as Epon 862,
15 Tactix 123, or a reactive diluent.

16 Cycloaliphatic epoxies represent another group of epoxies useful in the present
17 invention. They are usually low viscosity liquids at room temperature and can either be
18 used alone or as reactive diluents in blends with the semi-solid glycidyl ether epoxies.
19 These materials include 3',4'-epoxycyclohexylmethyl 3,4-
20 epoxycyclohexanecarboxylate, which is available as ERL-4221 (Union Carbide
21 Corporation trademark) and Araldite CY-179 (Ciba-Geigy trademark); diglycidylester of
22 hexahydrophthalic anhydride which is available as CY 184 (Ciba-Geigy trademark); bis
23 (3,4-epoxycyclohexylmethyl) adipate, which is available as ERL-4299 (Union Carbide

1 trademark); the isomeric mixture of bis (2,3-epoxycyclopentyl) ether, which was once
2 available as ERL-4205 (Union Carbide trademark); ERL-4205 reacted with ethylene
3 glycol or blended with a bisphenol A based diglycidyl ether, which were once available
4 from Union Carbide as ERLB-4617 and ERL-2258(Union Carbide trademarks),
5 respectively.

6 The epoxy resin (Part A) as just described may also be advantageously modified
7 by mixing with various additives. Such additives include glycols such as ethylene
8 glycol, propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, and other polyols.
9 Aromatic diphenols and polyphenolic compounds may also be used to modify the epoxy
10 resin. Other reactive diluents, which contain vinyl, acrylate, or methacrylate may be
11 employed to change reactivity, glass transition temperature, or mechanical properties.
12 In addition, reactive diluents based on monofunctional or polyfunctional glycidyl ethers
13 may also be used to reduce the viscosity or modify the resin systems. Additionally,
14 nonreactive diluents, such as acetone, have been found to be useful for reducing the
15 viscosity of the resin system which improves the processibility of the material before it is
16 cured for certain applications, such as solvent based prepreg.

17 The initiator (Part B) for the present invention is a material which produces a
18 positively charged species (cation) when subjected to ionizing radiation. This positively
19 charged species must then be capable of initiating the cationic polymerization of the
20 epoxy (Part A). Much research has been devoted to the development of cationic
21 photoinitiators (J.V. Crivello, Advances in Polymer Science, Vol. 62, p. 1, 1984).
22 Cationic initiators react when subjected to visible or ultraviolet light of a particular
23 wavelength to produce a cationic species, typically a Bronstead acid. It was previously

1 determined that some of these initiators also react to generate cations when subjected
 2 to ionizing radiation. The behavior of these materials when subjected to higher energy
 3 ionizing radiation, such as produced by an electron beam accelerator or a gamma cell,
 4 cannot be predicted. Diaryliodonium salts and triarylsulfonium salts of certain anions
 5 are particularly effective as initiators for the ionizing radiation induced cationic
 6 polymerization of epoxies. Many examples of each have been reported and some are
 7 commercially available. Almost all could be useful in the present invention.

8 Specific examples of diaryliodonium salts are given by the following formula,
 9 where R_1 and R_2 are radicals such as H, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-
 10 butyl, Cl, Br, C_nH_{2n+1} , OC_nH_{2n+1} , $OCH_2CH(CH_3)C_nH_{2n+1}$, $OCH_2CH(C_2H_5)C_nH_{2n+1}$,
 11 $OCH_2CH(OH)C_nH_{2n+1}$, $OCH_2CO_2C_nH_{2n+1}$, $OCH(CH_3)CO_2C_nH_{2n+1}$, $OCH(C_2H_5)CO_2C_nH_{2n+1}$,
 12 and mixtures thereof where n is an integer between 0 and 18:

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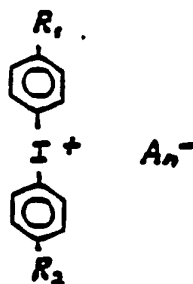
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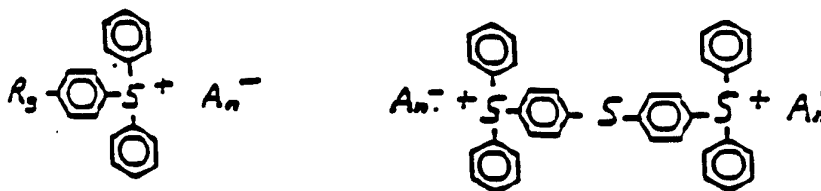
23



A_n^- denotes the anion which may be hexafluoroarsenate (AsF_6^-),
 hexafluoroantimonate (SbF_6^-), hexafluorophosphate (PF_6^-), boron tetrafluoride (BF_4^-),

1 trifluoromethane sulfonate (CF_3SO_3^-), tetrakis (pentafluorophenylborate), ($\text{B}[\text{C}_6\text{F}_5]_4^-$), or
 2 tetrakis [3,5-bis(trifluoromethyl) phenyl]borate ($\text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4^-$). For example, OPPI of
 3 Tables 1-4 denotes (4-octyloxyphenyl) phenyliodonium hexafluoroantimonate ($\text{R}_1 = \text{H}$,
 4 $\text{R}_2 = \text{OC}_8\text{H}_{17}$, $\text{An}^- = \text{SbF}_6^-$). This initiator, which was obtained from General Electric
 5 Corporation as Aryl Fluoroantimonate Product 479-2092 as well as CD-1012 from the
 6 Sartomer Company were found to be particularly effective with certain epoxy resins.
 7 However, initiators with other R_1 and R_2 substituents would be expected to exhibit
 8 similar reactivities.

9 Specific examples of triarylsulfonium salts are given by the following formulas,
 10 where R_3 is H, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, phenylsulfide (PhS),
 11 phenoxy (PhO) and An^- denotes the anion, which may be the same as those of the
 12 diaryliodonium salts:



18 Examples of commercially available triarylsulfonium salts are Cyracure UVI-6974
 19 and Cyracure UVI-6990 which are available from Union Carbide Corporation. These
 20 are mixtures of the triarylsulfonium salts given by the formulas where R_3 is
 21 phenylsulfide and An^- are the hexafluoroantimonate and hexafluorophosphate anions,
 22 respectively. Degussa Corporation Degacure KI-85 and 3M Corporation FX-512 are
 23 both mixtures of triarylsulfonium hexafluorophosphate salts.

1 The toughener or flexibilizer (Part C) may be any of a variety of materials. High
2 molecular weight engineering thermoplastics are particularly effective in increasing the
3 toughness of the radiation cured epoxy mixture as measured by fracture toughness
4 (K_{Ic}). Polysulfones such as Udel and Radel (Amoco Performance Products, Inc.) can
5 be dissolved in the epoxy resin/initiator composition to form a viscous homogeneous
6 mixture. Toughness of the cured composition is significantly improved in comparison
7 with the untoughened epoxy resin (Examples 1 and 2, Table 1). Similar results were
8 obtained with a polyetherimide such as Ultem (General Electric Company) as given by
9 Example 3. It is not necessary for the thermoplastic to be miscible with the epoxy
10 resin/initiator composition. The addition of Nylon 12 and Nylon 6/12 particles, Elf
11 Atochem Orgasol 2001 and Orgasol 3501, respectively, resulted in improved fracture
12 toughness even though these materials were insoluble in the epoxy resin mixture.
13 Similar results were obtained using insoluble polyimide particles, Imitac X-902. Other
14 thermoplastics such as polyamideimides, poly(arylene ethers), polyesters, polyarylates,
15 polycarbonates, polyurethanes, and others are potentially useful as Part C of the
16 present invention. Examples can be found in "Engineering Plastics," D. C. Clagett,
17 Encyclopedia of Polymer Science and Engineering, John Wiley and Sons.

18 Engineering thermoplastics are typically endcapped with nonreactive functional
19 groups. It may also be advantageous for the toughening agent of Part C to be a low
20 molecular weight segment or oligomer of a previously described engineering
21 thermoplastic, which contains functional groups that are capable of reaction with the
22 epoxy resin during radiation induced cationic polymerization. To this end hydroxy-
23 terminated polysulfone oligomers based on the Udel P-1700 polymer backbone were

1 synthesized at various molecular weights (Example 4 and Table 1). These materials
2 are more easily blended with the epoxy resin/initiator mixture and the resulting
3 compositions are less viscous than with the same percentage of high molecular weight
4 polymer of similar backbone. These materials were also found to be very effective in
5 increasing fracture toughness. Oligomers with other backbones could also be used,
6 particularly those of poly(arylene ethers), polyarylates, and polyester. Conceivably, the
7 oligomer backbone could be that of any of the previously referenced thermoplastics.
8 Reactive groups are limited to those which react with the epoxy resin during cationic
9 polymerization. These groups include hydroxy, epoxy, and carboxylate.

10 Flexible molecules which contain two or more epoxy groups represent a class of
11 material which is also useful as Part C of this invention. These compounds typically
12 contain long aliphatic groups which act to reduce crosslink density in the cured epoxy
13 resin. In addition to increasing the fracture toughness of the cured epoxy resin, the
14 addition of low viscosity flexibilizers can also significantly reduce the overall viscosity of
15 the uncured epoxy resin/initiator/flexibilizer mixture. Specific examples are given in
16 Examples 5 and 6, and in Table 2. Useful flexibilizers include but are not limited to:
17 1,4-butanediol diglycidyl ether (Shell Heloxy Modifier 67), neopentylglycol diglycidyl
18 ether (Shell Heloxy Modifier 68), cyclohexane dimethanol diglycidyl ether (Shell Heloxy
19 Modifier 107), trimethylol ethane triglycidyl ether (Shell Heloxy Modifier 44),
20 dibromoneopentyl glycol glycidyl ether (Shell Heloxy Modifier 56), propoxylated glycerol
21 polyglycidyl ether (Shell Heloxy Modifier 84), polypropylene glycol glycidyl ether (Shell
22 Heloxy Modifier 32), polyglycidyl ether of castor oil (Shell Heloxy Modifier 505), dimer
23 acid diglycidyl ester (Shell Heloxy Modifier 71), resorcinol diglycidyl ether (Rhône-

1 Poulenc Heloxy 69), epoxidized soybean oil (Elf Atochem Vikoflex 7170), epoxidized
2 linseed oil (Elf Atochem Vikoflex 7190, methyl epoxy soyate (Elf Atochem Vikoflex
3 7010), epoxidized propylene glycol dioleate (Elf Atochem Vikoflex 5075), epoxy ester
4 (Elf Atochem Vikoflex 4050), 1,2-tetradecane oxide (Elf Atochem Vikolox 14), internally
5 epoxidized 1,3-butadiene homopolymer (Elf Atochem Poly bd 600 and Poly bd 605),
6 diglycidyl ether, glycidyl glycidate, bis(2,3-epoxy-2-methylpropyl)ether, and
7 polyglycoldiepoxides (Dow Chemical DER 732 and DER 736). Flexible molecules
8 which contain two or more hydroxy groups are also useful as Part C of this invention.
9 These compounds also contain long aliphatic groups. Useful polyols include E-
10 caprolactone triol (Union Carbide Tone 0301, 0305, 0310).

11 Elastomers or rubbers may also be used as Part C. Examples of these materials
12 include, but are not limited to, the copolymers of styrene, butadiene, and ethylene or
13 styrene, butylene, and ethylene (Shell Kraton rubber), butadiene, styrene copolymers,
14 the copolymer of butadiene and styrene, butyl rubber, neoprene rubber, and poly
15 (siloxanes). Functionalized versions of these materials such as carboxyl terminated
16 poly (α - butylacrylate) rubber are particularly useful. Epoxy resins of Part A may be
17 reacted with these materials to form an epoxy terminated elastomer which is useful as
18 Part C. Maleic anhydride terminated Kraton rubber (Shell Chemical - FG 1901X), and
19 epoxy functionalized liquid Kraton rubbers (Shell Chemical - EXP-206 and EKP-207)
20 are especially useful as Part C. Specific examples are given in Examples 7 - 9 and in
21 Table 3.

22 It is also advantageous to blend the various types of tougheners or flexibilizers in
23 order to achieve toughness through different toughening mechanisms and to adjust the

1 overall viscosity of the uncured epoxy resin/initiator/toughener composition i.e. Parts A,
2 B, and C combined. A flexibilizer may be added to a mixture of a thermoplastic or
3 thermoplastic oligomer dissolved in an epoxy resin. Overall viscosity may be reduced
4 and toughness may be improved compared with using toughener or flexibilizer alone.
5 The thermoplastic may separate from the radiation cured epoxy to form a two phase
6 morphology while the flexibilizer provides long flexible groups to connect crosslink sites
7 in the epoxy network. Specific examples are given in Table 4.

8 The following examples illustrate the formulation and curing of the toughened
9 epoxy mixtures. The invention is not limited to these examples.

10 Example 1 - 10% Udel P-1700 NT with Tactix 123

11 Amoco Udel P-1700 NT Polysulfone (30 g) in pellet form was added to 270 g of
12 Dow Tactix 123 (high purity bisphenol A based glycidyl ether) in a three neck flask
13 equipped with a mechanical stirrer, nitrogen inlet, and a thermocouple probe. The
14 mixture was stirred under nitrogen at approximately 150°C until the thermoplastic
15 dissolved to form a high viscosity solution (24 h). The temperature of the solution was
16 reduced to approximately 90°C and 9.00 g of (4-octyloxyphenyl)phenyliodonium
17 hexafluoroantimonate, OPPI, was added to the stirred mixture. Mixing was complete
18 after 0.5 h. At 60°C the viscosity of the mixture was 7300 cp. The mixture was
19 degassed under vacuum at approximately 80°C, poured hot into aluminum molds, and
20 the specimens irradiated using an electron beam accelerator (Energy, 10 MeV; Power,
21 1 kW). Specimens were irradiated in three passes of 50 kGy per pass for a total
22 dosage of 150 kGy. Fracture toughness (K_{Ic}) as determined according to ASTM E399
23 was 0.680 MPa m^{1/2} at 25°C and 0.899 MPa m^{1/2} at -100°C. Glass transition

1 temperature (Tg) as determined by Dynamic Mechanical Analysis (DMA) was 168°C
2 (peak, Tan delta curve) and 156°C (peak, loss modulus curve, G"). Flexural modulus
3 was estimated by DMA to be 2.94 GPa at 25°C. The temperature at which the
4 modulus was 50% of the 25°C value was 132°C (initial service temperature). After 48 h
5 in boiling water the specimens absorbed 1.25% moisture.

6 **Example 2 - 20% Radel A-200NT with Tactix 123**

7 Amoco Radel A-200 NT (60 g) in pellet form was dissolved in approximately 300
8 mL of methylene chloride. The Radel solution was mixed at room temperature with 240
9 g of Dow Tactix 123 (mixture complete in 1-2 h with stirring) and the methylene chloride
10 removed under vacuum at 90°C (approximately 0.5 h). OPPI (9 g) was added and
11 dissolved in the stirred mixture at 90°C (approximately 0.5 h). Viscosity of the mixture
12 at 60°C was 24,000 cp. Specimens were cured as described in Example 1. Fracture
13 toughness was determined to be 0.494 and 0.612 Mpa m^{1/2} at 25°C and -100°C,
14 respectively. Glass transition temperature was 168°C (Tan delta) and 143°C (G").
15 Flexural modulus was 2.68 GPa at 25°C with an initial service temperature of 129°C.
16 Water absorption after 48 h water boil was 1.37%.

17 **Example 3 - 10% Ultem 1000 with Tactix 123**

18 General Electric Ultem 1000-1000 polyetherimide (60 g) in pellet form was
19 dissolved in approximately 300 mL of methylene chloride. The Ultem solution was
20 mixed at room temperature with 540 g of Dow Tactix 123 (mixture complete in 1-2 h
21 with stirring) and the methylene chloride removed under vacuum at 90°C. OPPI (18 g)
22 was added and dissolved in the stirred mixture at 90°C (approximately 0.5 h).
23 Specimens were cured as described in Example 1. Fracture toughness was 0.696 and

1 0.877 MPa m^{1/2} at 25°C and -100°C, respectively. Glass transition temperature was
2 175°C (Tan delta) and 157°C (G*). Flexural modulus was 3.07 GPa at 25°C with an
3 initial service temperature of 136°C. Water absorption after 48 h water boil was 1.37%.

4 Example 4 -30% Hydroxy-Terminated Polysulfone Oligomer (Mn, 6000 g/mole)
5 with Tactix 123

6 Hydroxy-terminated polysulfone oligomers were prepared according to a method
7 described in the literature [J. E. McGrath, T. C. Ward, E. Shehori, and A. J. Wnuk,
8 Polym. Eng. Sci. 17, 647 (1977)]. The following example illustrates the preparation of a
9 hydroxy-terminated polysulfone oligomer with a calculated molecular weight (Mn) of
10 6000 g/mole, based on a stoichiometric imbalance ($r=0.929$) using excess hydroxy-
11 containing monomer. This example further illustrates the use of this material to
12 toughen a bisphenol A based glycidyl ether mixture which was cured by means of
13 electron beam radiation. 2,2-Bis (4-hydroxyphenyl) propane, (bisphenol A), (228.29 g,
14 1.000 mole), bis (4-chlorophenyl) sulfone (266.78, 0.929 mole), powdered anhydrous
15 potassium carbonate (282.5 g, 2.044 mole), N,N-dimethylacetamide (1173 mL), and
16 toluene (125 mL) were added to a 2 L three necked flask equipped with a
17 thermocouple, nitrogen inlet, mechanical stirrer, and a Dean-Stark trap topped by a
18 reflux condenser. With heating provided by a heating mantle the stirred mixture was
19 slowly heated to approximately 140°C under an atmosphere of flowing nitrogen. Water
20 was removed over a period of several hours, then the toluene was removed through the
21 Dean-Stark trap and the temperature of the reaction mixture allowed to reach 155°C.
22 The reaction mixture was maintained at 155°C overnight (20 h), cooled to
23 approximately 100°C, and filtered through a fritted glass funnel. The filtrate was

1 acidified by the addition of glacial acetic acid (57 mL, 1.00 mole) mixed with 200 mL of
2 N,N-dimethylacetamide and precipitated into a total of 4-5 L of water in a blender. The
3 precipitated polymer was collected by filtration, washed with water, and dried in air at
4 105°C and under vacuum at 90°C. Yield of hydroxy-terminated polysulfone oligomer
5 was 423.8 g (99.2% yield). Glass transition temperature as determined by Differential
6 Scanning Calorimetry was 169°C and inherent viscosity was 0.13 dL/g at 0.5%
7 concentration in chloroform at 25°C. The hydroxy-terminated polysulfone oligomer (90
8 g) was added to 210 g of Dow Tactix 123 and the mechanically stirred mixture heated
9 at 120-130°C until the polysulfone oligomer dissolved (1-2 h). The temperature of the
10 solution was reduced to approximately 90°C and OPPI (9 g) added to the stirred
11 mixture. After 0.5 h mixing was complete. Viscosity of the solution was 29,000 cp at
12 60°C. Specimens were cured as described in Example 1. Fracture toughness was
13 0.705 and 1.114 MPa m^{1/2} at 25 and -100°C, respectively. Glass transition temperature
14 was 161°C (Tan delta) and 149°C (G"). Flexural modulus was 3.02 GPa at 25°C with
15 an initial service temperature of 134°C. The percent weight gain after 48 hour water
16 boil was 1.64%.

17 **Example 5** 10% Vikoflex 7170 with Tactix 123

18 Elf Atochem ATO Vikoflex 7170 (epoxidized soybean oil), (60 g), OPPI (18 g),
19 and Dow Tactix 123 (540 g) was mixed at approximately 80°C. Viscosity of the solution
20 was 3600 cp at 24°C. Specimens were cured as described in Example 1. Fracture
21 toughness was 0.598 and 0.752 MPa m^{1/2} at 25 and -100°C, respectively. Glass
22 transition temperature was 151°C (Tan delta) and 133°C (G"). Flexural modulus was
23 2.79 GPa at 25°C with an initial service temperature of 117°C. Water absorption after

1 48 h water boil was 2.02%.

2 Example 6 10% Elf Atochem ATO Poly bd 600 with Tactix 123

3 Elf Atochem ATO Poly bd 600 VM 312051 (internally epoxidized 1,3-butadiene
4 homopolymer), (60 g), OPPI (18 g), and Dow Tactix 123 (540 g) was mixed at
5 approximately 80°C. Viscosity of the solution was 6120 cp at 24°C. Specimens were
6 cured as described in Example 1. Fracture toughness was 0.594 MPa m^{1/2} and 0.463
7 MPa m^{1/2} at 25°C and -100°C, respectively. Glass transition temperature was 166°C
8 (Tan delta) and 151°C (G*). Flexural modulus was 2.68 GPa at 25°C with an initial
9 service temperature of 123°C. Water absorption after 48 h water boil was 1.28%.

10 Example 7 10% Paraloid EXL-2330 with Tactix 123

11 Rohm and Haas Paraloid EXL-2330 methacrylate-butadiene core shell rubber
12 (30 g) was stirred overnight with 30 g of acetone. The suspension was mixed with Dow
13 Tactix 123 (270 g) at room temperature and the acetone removed under vacuum at
14 approximately 80°C. OPPI (9 g) was added with mixing at 80°C until it was in solution
15 (0.5 h). Specimens were cured as described in Example 1. Fracture toughness was
16 0.585 MPa m^{1/2} at 25°C. Glass transition temperature was 132°C (Tan delta) and
17 132°C (G*). Flexural modulus was 2.69 GPa at 25°C with an initial service
18 temperature of 109°C. Water absorption after 48 h water boil was 2.59%.

19 Example 8 30% Dow XU 71790.04L with Tactix 123 and Tactix 556 (28:42)

20 Dow XU 71790.04L (bisphenol A based glycidyl ether reacted with acrylic
21 rubber), (90 g), Dow Tactix 123 (84 g), Dow Tactix 556 (126 g), and OPPI (9 g) was
22 mixed at approximately 90°C. Specimens were cured as described in Example 1.
23 Fracture toughness was 0.411 MPa m^{1/2} and 0.520 MPa m^{1/2} at 25 and -100°C,

1 respectively. Glass transition temperature was 176°C (Tan delta) and 161°C (G").
2 Flexural modulus was 2.48 GPa at 25°C with an initial service temperature of 137°C.
3 Water absorption after 48 h water boil was 2.22%.

4 Example 9 10% Kraton FG 1901X with Tactix 123

5 Shell Kraton FG 1901X, a styrene-ethylene/butylene-styrene block copolymer
6 terminated with maleic anhydride, (60g) was dissolved in 300 mL of toluene. The
7 Kraton solution was added to 540g of Dow Tactix 123 and the mixture stirred overnight
8 at approximately 60°C. Toluene was removed under vacuum at approximately 90°C.
9 OPPI (18g) was added and dissolved in the stirred mixture at 90°C (approximately 0.5
10 hour). The final mixture was a milky white suspension with a viscosity of 1100 cPs at
11 60°C. Specimens were cured as described in Example 1. Fracture toughness was
12 determined to be 0.92 MPa m^{1/2} at 25°C and 1.224 Mpa m^{1/2} at -100°C. Glass
13 transition temperature was 171°C (Tan delta). The temperature at which the flexural
14 modulus drops to one-half its value from 25°C was 131°C.

15 In addition to solvent mixing, Kraton FG 1901X was also mechanically blended
16 into the epoxy resin by using a Silverson high shear mixer/emulsifier. The solid rubber
17 was blended into the epoxy at approximately 7000 RPM for 0.5 hour at 190-200°C.

18 Additionally, it is expected that the toughened resin system may be reinforced
19 with fibers which may include carbon, graphite, glass, aramid, polyethylene, or other
20 reinforcement fibers to form a composite. Fillers such as clay, minerals, glass particles,
21 silica particles, alumina particles, aluminum powder and other inert materials may also
22 be added.

23 Mechanical, thermal, and physical properties for electron beam cured carbon-

1 fiber-reinforced composite laminates, incorporating some of the above described
2 toughened epoxy resin systems as well as examples of some untoughened epoxy resin
3 systems, are described in Table 5 and Table 6. These properties include those tested
4 at room temperature as well as those determined after cycling several times from low
5 temperatures (-194°C or -79°C) to elevated temperatures (121°C).

6 The impetus for developing Electron Beam (EB) curing of polymer matrix
7 composites (PMCs) that incorporate toughened epoxy resins is based primarily on
8 reducing the manufacturing costs and cycle times in comparison with traditional thermal
9 curing processes. One of the primary cost drivers in manufacturing with PMCs, and
10 one of the elements having the greatest effect on quality and performance, is the
11 standard thermal cure process. Thermal cure of PMCs requires relatively long cure
12 times and high-energy consumption, creates residual thermal stresses, produces
13 volatile toxic by-products during cure, requires the use of hardeners (curing agents)
14 which limit the shelf life of the resin system, requires resin systems to be stored and
15 transported under low temperature conditions before cure, and requires expensive
16 tooling that is tolerant to high temperatures (i.e., 250 to 750°F).

17 EB curing is a nonthermal curing method that uses high-energy, high-power
18 electrons to initiate polymerization and cross-linking reactions at controlled rates in EB
19 curable materials to enhance specific physical, mechanical, and chemical properties.
20 EB curing can eliminate or reduce many of the shortcomings of thermal curing and
21 facilitate technical developments that are presently unachievable utilizing thermal curing
22 technology.

23 Four advantages are offered by EB curing compared to traditional Thermal

1 Curing:

2 Lower Manufacturing Costs: resulting from faster cures, lower energy
3 consumption, the ability to use lighter and lower cost tooling, simplified transportation
4 and storage of resin systems, and easier waste cleanup after fabrication.

5 Simplified Processing: resulting from selectable cure temperatures, minimal part
6 and tool thermal mismatches, uniform and efficient cross-linking, unlimited resin pot life,
7 elimination of hardeners in the resin system, reduction in resin viscosity variations,
8 greater material integration flexibility, in-situ fabrication and curing capability, ability to
9 cure parts up to about 12-inches thick, no part size limitations, and its ability to be
10 retrofittable to traditional fabrication methods (i.e., automated tape and tow and fiber
11 placement, filament winding, pultrusion, resin transfer molding).

12 Environmentally Friendly: because it reduces toxic and volatile emissions and
13 minimizes the use of solvents normally required for waste clean-up operations.

14 Improved Product Performance: by lowering residual and internal stresses,
15 improving dimensional part quality, and the ability to tailor the material properties by
16 controlling the cure depth and the degree of cure.

17 This subject invention provides the user an almost unlimited number of epoxy
18 resin systems, incorporating epoxy resins, cationic initiators, and toughening materials
19 and combinations thereof, to choose from which meet the necessary performance
20 requirements for given applications.

21 The benefits of PMCs have long been recognized for high-performance
22 applications, but American industry has not capitalized on the advantages of these
23 materials because large-scale manufacturing of PMCs is cost prohibitive. One of the

1 primary cost drivers in manufacturing PMC parts and structures is the manufacturing
2 cycle times required to cure the materials. By utilizing these toughened EB-curable
3 materials discussed in this subject invention one can dramatically shorten the
4 manufacturing time for producing these materials, thereby greatly improving the
5 affordability and use of PMCs in many areas of the commercial sector, including
6 aircraft, aerospace, automotive, marine, sporting goods, infrastructure, and construction
7 industries.

8 Many companies involved in the manufacture of aircraft and aerospace
9 products, automobiles, chemicals, adhesives, polymer matrix composites, marine
10 products, reinforcement fibers, oil drilling platforms, and electron beam accelerators are
11 extremely interested in this technology area.

12 The toughened epoxy materials described in this invention also have enormous
13 potential for reducing the final cost and improving the performance for products used in
14 applications such as thick and thin coatings; tooling for manufacturing PMCs;
15 encapsulants for electronic devices; adhesives for bonding PMCs, metals, ceramics,
16 and other materials; and for manufacturing molded and cast parts.

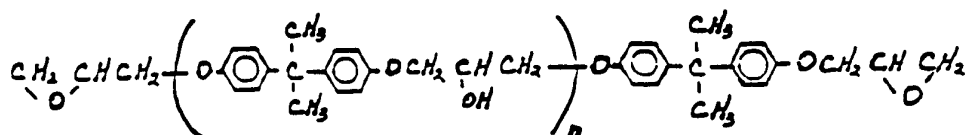
17 This invention describes a method or process by which conventional epoxy resins
18 can be cured (crosslinked) by the application of ionizing radiation. The currently used
19 thermal processes for curing epoxies with an amine, anhydride, or other coreactive
20 curing agent or with a catalyst require that the mixture be heated above its final glass
21 transition temperature. For many resin mixtures this may require a complex heating
22 cycle which may reach temperatures as high as 150 - 300°C. If not completely cured the
23 resin suffers from poor mechanical properties. The process of this invention allows the
24 epoxy resin to be rapidly cured to a high glass transition temperature (essentially the

1 same or higher in some cases as with thermal curing) at any temperature at or above the
 2 glass transition temperature of the epoxy monomers, while still exhibiting the same
 3 mechanical properties. Additional advantages obtained from this process are the lack of
 4 mechanical stresses, which result from thermal curing, and reduced manufacturing
 5 expenses related to faster curing times, lower energy requirements, and the elimination of
 6 expensive thermal processing equipment. This process is potentially useful in the
 7 manufacture and application of coatings, encapsulants, adhesives, and composite
 8 matrices.

9 Specifically, this invention relates to the radiation curing of an epoxy resin or
 10 mixtures of epoxy resins (Part A) which contains an initiator (Part B). When the initiator
 11 is subjected to ionizing radiation a cationic species (positively charged ion) is produced
 12 which initiates the cationic cure of the epoxy resin. The mechanism of the cationic curing
 13 of epoxies is well known (L.V. McAdams and J.A. Gannon, "Epoxy Resins",
 14 Encyclopedia of Polymer Science and Technology, John Wiley & Sons).

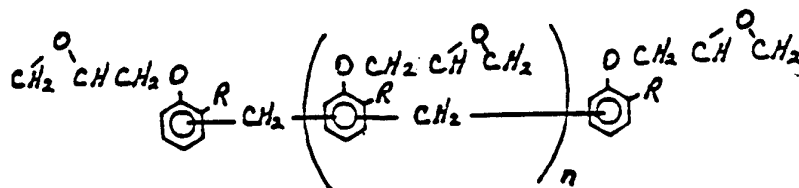
15 Ionizing radiation refers to high energy radiation such as x-rays, gamma rays, and
 16 electron beam (e-beam) radiation. Electron beam radiation as produced by an
 17 accelerator is particularly useful.

18 The epoxy resin (Part A) may be virtually any of a variety of commercially
 19 available materials. The glycidyl ethers of various phenolic compounds are particularly
 20 important. These include the glycidyl ethers of bisphenol A as given by the following
 21 formula where n ranges from 0 to 12:



1 These resins are widely available from a number of manufacturers such as Shell
 2 Chemical Company, DOW Chemical Company, and Ciba-Geigy Corporation in a variety
 3 of molecular weights and viscosities. Examples include: D.E.R. 332, D.E.R. 330, D.E.R.
 4 331, D.E.R. 383, Tactix 123, Tactix 138, and Tactix 177 (DOW trademarks); Epon 825,
 5 Epon 826, and Epon 828 (Shell trademarks); and, Araldite GY 6008, Araldite GY 6010,
 6 and Araldite GY 2600 (Ciba-Geigy trademarks).

7 Another important class of glycidyl ethers are those of phenolic novolac and cresol
 8 novolac resins as given by the following formula where n ranges from 0 to 5:



15 For epoxy phenolic novolacs, R=H, and for epoxy cresol novolacs, R=CH₃. For
 16 bisphenol F epoxy resins R=H and the value of n is low (0 to 0.15). These materials are
 17 also widely available from a number of manufacturers in a variety of molecular weights
 18 and viscosities. Examples include Epon 862, Epon 155 (Shell trademarks); D.E.R. 354,
 19 D.E.N. 431, D.E.N. 438, and D.E.N. 439 (DOW trademarks); and Araldite PY 306,
 20 Araldite EPN 1139, Araldite EPN 1138, Araldite GY 281, Araldite GY 285, Araldite GY
 21 302-2, Araldite LY 9703, Araldite XD 4955, and Araldite ECN 9511 (Ciba-Geigy
 22 trademarks).

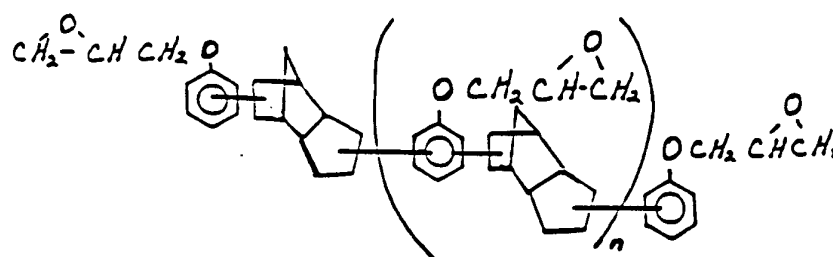
23 Several other polyfunctional glycidyl ethers are of significant importance for high
 24 performance applications i.e. heavy mechanical loads under conditions of high
 25 temperature and harsh environment. The materials include:

26 The tetraglycidyl ether of tetrakis (4-hydroxyphenyl) ethane, which is
 27 commercially available as Epon 1031 (Shell Chemical trademark) and Araldite MT 0163

(Ciba-Geigy trademark).

The diglycidyl ether of 9, 9- bis (4-hydroxyphenyl) fluorene is available as Epon HPT 1079 (Shell Chemical trademark).

A glycidyl ether of the condensation product of dicyclopentadiene and phenol is available as Tactix 556 (DOW Chemical trademark) as given by the following formula where n is approximately 0.2:



The triglycidyl ether of tris (hydroxyphenyl) methane is available as Tactix 742 (DOW Chemical trademark).

These latter materials, Epon 1031, Epon HPT 1079, Tactix 556, and Tactix 742, are either high viscosity liquids or solids at room temperature. Therefore it is advantageous to blend these materials with a low viscosity bisphenol A or bisphenol F based glycidyl ether. The resulting blends are less viscous at ambient temperatures and are more easily processed. Some heating may be required for adequate flow, but not temperatures high enough to cause thermal curing of the epoxy group.

Cycloaliphatic epoxies represent another group of epoxies useful in the present invention. They are usually low viscosity liquids at room temperature and can either be used alone or as reactive diluents in blends with the semi-solid glycidyl ether epoxies. These materials include 3',4'-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, which is available as ERL-4221 (Union Carbide Corporation trademark) and Araldite CY

1 179 (Ciba-Geigy trademark); diglycidylester of hexahydrophthalic anhydride which is
2 available as CY 184 (Ciba-Geigy trademark); bis(3,4-epoxycyclohexylmethyl) adipate,
3 which is available as ERL-4299 (Union Carbide trademark); the isomeric mixture of bis
4 (2,3-epoxycyclopentyl) ether, which was once available as ERL-4205 (Union Carbide
5 trademark); ERL-4205 reacted with ethylene glycol or blended with a bisphenol A based
6 glycidyl ether, which were once available from Union Carbide as ERLB-4617 and
7 ERL-2258 (Union Carbide trademarks), respectively.

8 The epoxy resin (Part A) as just described may also be advantageously modified by
9 mixing with ten percent or less of various additives. Such additives include glycols such as
10 ethylene glycol, propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, and other
11 polyols. Aromatic diphenols and polyphenolic compounds may also be used to modify the
12 epoxy resin. Other reactive diluents, which contain vinyl, acrylate, or methacrylate may
13 be employed to increase reactivity, glass transition temperature, or mechanical
14 properties. In addition, reactive diluents based on monofunctional or polyfunctional
15 glycidyl ethers may also be used to reduce the viscosity or modify the resin systems.

16 The most useful application of this invention lies in the blending of two or more of
17 the Part A epoxy resins in order to optimize overall resin viscosity for ease of processing.
18 Resin blending may also be used to enhance the thermal and mechanical properties of the
19 cured resin.

20 Specific blends were found to have a good overall combination of low viscosity in
21 the uncured state and high glass transition temperature, flexural strength, and modulus
22 when cured. It was found to be particularly advantageous to blend a high performance
23 semi-solid epoxy such as Tactix 556, Tactix 742 or Epon HPT 1079 with a low viscosity
24 bisphenol A or bisphenol F based glycidyl ether epoxy such as Epon 862. Specific
25 examples are listed in Tables 7-9. A description of the materials are listed in Table 10.
26 (4-Octyloxyphenyl) phenyliodonium hexafluoroantimonate (OPPI) at concentrations of
27 one and three parts per hundred of the epoxy blend was used as the initiator although

1 any of the initiators described as Part B could potentially be used at concentrations
2 ranging from 0.25 to 10 parts per hundred of active initiator. Ionizing radiation was
3 provided by an electron beam accelerator (Energy 10 MeV; Power, 1 kW). Specimens
4 were irradiated in single or multiple passes. Total dosage received by the specimens
5 ranged between 50 and 150 kGy, although possible curing dosages of between 10 and 500
6 kGy could be used. Accelerators with different energy and power levels could also be
7 used. X-ray or gamma sources could also be used as the source of ionizing radiation.

8 While the cured resins exhibit good thermal and mechanical properties they tend,
9 like most epoxies, to be somewhat brittle. It is envisioned that this short-coming will be
10 overcome by the addition of toughening agents to the resin system (Part A plus Part B).
11 Toughening agents such as elastomeric microspheres and thermoplastics (e.g. polyarylene
12 ethers, polysulfones and polyimides) may be added in concentrations ranging from 2 to
13 40 percent of the resin system. Three different resin systems containing three different
14 molecular weights of hydroxy-terminated polyether sulfone having molecular weights of
15 2650, 5360, or 8890 g/mole at 20% loading each were added to Dow's Tactix 123 resin
16 containing 3 phr of OPPI and electron beam cured at 150 kGy to toughen the resin
17 system. Results indicate that all three of these resin systems approximately doubled the
18 K_{IC} values compared to the control resin system (Control - Tactix 123 with 3 phr OPPI;
19 cured at 150 kGy with no added toughening agent) which had a value of $352 \text{ psi}\cdot\text{in}^{0.5}$
20 compared to values of 637, 665, and 672 $\text{psi}\cdot\text{in}^{0.5}$ for the 2650, 5360, and 8890 molecular
21 weights, respectively of the hydroxy-terminated thermoplastic material. Additionally, it
22 is expected that the resin system may be reinforced with fibers which may include
23 carbon, glass, aramid, polyethylene, or other reinforcement fibers to form a composite.
24 Fillers such as clay, minerals, and other inert materials may also be added.

25 Uses of the process of this invention include coatings, encapsulants for electronic
26 devices, adhesives, molded and cast parts, and laminates and composites with fiber
27 reinforcement. Unlike the cationic curing of epoxy resins with visible or ultraviolet light,

1 the use of a penetrating high energy electron beam to initiate the curing reaction means
2 that thick sections of material can be completely and uniformly cured. Thus, thick
3 composite parts can now be fabricated and cured at any temperature at or above the
4 glass transition temperature of the epoxy monomers in relatively short periods of time
5 with minimal residual mechanical stresses.

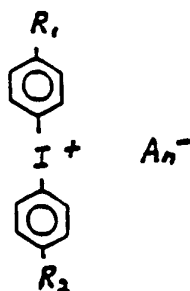
6 The initiator (Part B) for the present invention is a material which produces a
7 positively charged species (cation) when subjected to ionizing radiation. This positively
8 charged species must then be capable of initiating the cationic polymerization of the
9 epoxy (Part A). Much research has been devoted to the development of cationic
10 photoinitiators (J.V. Crivello, Advances in Polymer Science, Vol. 62, p. 1, 1984).

11 Cationic photoinitiators react when subjected to visible or ultraviolet light of a particular
12 wavelength to produce a cationic species, typically a Bronstead acid. The behavior of
13 these materials when subjected to higher energy ionizing radiation as produced by an
14 electron beam accelerator or a gamma cell cannot be predicted.

15 In order to determine which, if any, of the many commercially available and
16 noncommercially available cationic photoinitiators were effective when subjected to
17 ionizing radiation, a variety of cationic photoinitiators were evaluated using a ⁶⁰Co
18 gamma cell. The photoinitiator at a concentration of one part per hundred active
19 materials was mixed with each of a variety of epoxy resins. The mixture was then placed
20 in a gamma cell at a dose rate of 100 Gy per minute. The temperature increase
21 (exotherm of the curing reactions) of the sample versus that of an inert reference material
22 (water or cured resin) was measured (Tables 8 and 9). The dose at the exotherm peak
23 and the effect of gamma radiation (total dosage, up to approximately 25 kGy) on the
24 resins are listed. Some liquid resins in combination with certain initiators exhibited large
25 exotherms and crosslinked to form hard cured materials. Other combinations exhibited
26 little or no temperature increase and only small viscosity increases. This behavior could
27 not have been predicted.

From the Tables 7-10 it is clear that diaryliodonium salts and triarylsulfonium salts of certain anions are particularly effective as initiators for the ionizing radiation induced cationic polymerization of epoxies. Many examples of each have been reported and some are commercially available. Almost all could be useful in the present invention.

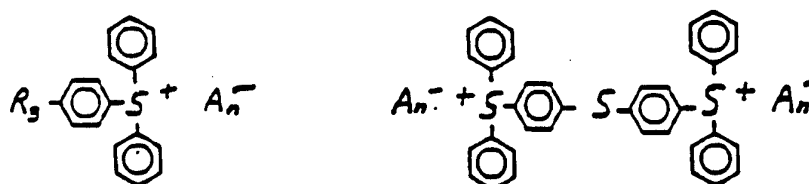
Specific examples of diaryliodonium salts are given by the following formula, where R_1 and R_2 are radicals such as H, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, Cl, Br, OC_nH_{2n+1} , $OCH_2CH(CH_3)C_nH_{2n+1}$, $OCH_2CH(C_2H_5)C_nH_{2n+1}$, $OCH_2CH(OH)C_nH_{2n+1}$, $OCH_2CO_2C_nH_{2n+1}$, $OCH(CH_3)CO_2C_nH_{2n+1}$, $OCH(C_2H_5)CO_2C_nH_{2n+1}$, and mixtures thereof where n is an integer between 0 and 18:



An^- denotes the anion which may be hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorophosphate (PF_6^-), boron tetrafluoride (BF_4^-), trifluoromethane sulfonate ($CF_3SO_3^-$), or tetrakis (pentafluorophenylborate), ($B[C_6F_5]_4^-$). For example, OPPI of Tables 7-10 denotes (4-octyloxyphenyl) phenyliodonium hexafluoroantimonate ($R_1 = H$, $R_2 = OC_8H_{17}$, $An^- = SbF_6^-$). This initiator, which was obtained from General Electric Corporation as Aryl Fluoroantimonate Product 479-2092 was found to be particularly effective with certain epoxy resins. However, initiators with other R_1 and R_2 substituents would be expected to exhibit similar reactivities.

Specific examples of triarylsulfonium salts are given by the following formulas, where R_3 is H, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, phenylsulfide (PhS), or phenoxy (PhO) and An^- denotes the anion, which may be the same as those of

the diaryliodonium salts:



In Table 10, 6974 and 6990 refer to Cyracure UVI-6974 and Cyracure UVI-6990, which were obtained from Union Carbide Corporation. These are mixtures of the triarylsulfonium salts given by the formulas where R₃ is phenylsulfide and An⁻ are the hexafluoroantimonate and hexafluorophosphate anions, respectively. KI-85 and FX-512 in Table 9 denote Degussa Corporation Degacure KI-85 and 3M Corporation FX-512, respectively. These materials are both mixtures of triarylsulfonium hexafluorophosphate salts.

Table 7 lists glass transition temperatures and flexural moduli for various resin systems (Part A plus Part B) after curing by electron beam radiation.

The impetus for developing Electron Beam (EB) curing of polymer matrix composites (PMCs) that incorporate epoxy resins is based primarily on reducing the manufacturing costs and cycle times in comparison with traditional thermal curing processes. One of the primary cost drivers in manufacturing with PMCs, and one of the elements having the greatest effect on quality and performance, is the standard thermal cure process. Thermal cure of PMCs requires relatively long cure times and high-energy consumption, creates residual thermal stresses, produces volatile toxic by-products during cure, requires the use of hardeners (curing agents) which limit the shelf life of the resin system, requires resin systems to be stored and transported under low temperature

1 conditons before cure, and requires expensive tooling that is tolerant to high
2 temperatures (i.e., 250 to 750°F).

3 EB curing is a nonthermal curing method that uses high-energy, high-power
4 electrons to initiate polymerization and cross-linking reactions at controlled rates in EB
5 curable materials to enhance specific physical, mechanical, and chemical properties. EB
6 curing can eliminate or reduce many of the shortcomings of thermal curing and facilitate
7 technical developments that are presently unachievable utilizing thermal curing
8 technology.

9 Four advantages are offered by EB curing compared to traditional Thermal
10 Curing:

11 Lower Manufacturing Costs: resulting from faster cures, lower energy
12 consumption, the ability to use lighter and lower cost tooling, simplified transportation
13 and storage of resin systems, and easier waste cleanup after fabrication.

14 Simplified Processing: resulting from selectable cure temperatures, minimal part
15 and tool thermal mismatches, uniform and efficient cross-linking, unlimited resin pot
16 life, elimination of hardeners in the resin system, reduction in resin viscosity variations,
17 greater material integration flexibility, in-situ fabrication and curing capability, ability to
18 cure parts up to about 12-inches thick, no part size limitations, and its ability to be
19 retrofittable to traditional fabrication methods (i.e., automated tape and tow and fiber
20 placement, filament winding, pultrusion, resin transfer molding), and the ability to be
21 cured in either on-line or batch operations.

22 Environmentally Friendly: because it reduces toxic and volatile emissions and
23 minimizes the use of solvents normally required for waste clean-up operations.

24 Improved Product Performance: by lowering residual and internal stresses,
25 improving dimensional part quality, and the ability to tailor the material properties by
26 controlling the cure depth and the degree of cure.

27 This subject invention provides the user an almost unlimited number of epoxy

1 resin systems to choose from which meet the necessary performance requirements for
2 given applications.

3 The benefits of PMCs have long been recognized for high-performance applications, but
4 American industry has not capitalized on the advantages of these materials because
5 large-scale manufacturing of PMCs is cost prohibitive. One of the primary cost drivers
6 in manufacturing PMC parts and structures is the manufacturing cycle times required to
7 cure the materials. By utilizing the radiation curable materials discussed in this subject
8 invention one can dramatically shorten the manufacturing time for producing these
9 materials, thereby greatly improving the affordability and use of PMCs in many areas of
10 the commercial sector, including aircraft, aerospace, automotive, marine, sporting goods,
11 infrastructure, and construction industries.

12 Many companies involved in the manufacture of aircraft and aerospace products,
13 automobiles, chemicals, adhesives, polymer matrix composites, marine products,
14 reinforcement fibers, oil drilling platforms, and electron beam accelerators are extremely
15 interested in this technology area.

16 The materials described in this invention also have enormous potential for
17 reducing the final cost for products used in applications such as thick and thin coatings;
18 tooling for manufacturing PMCs; encapsulants for electronic devices; adhesives for
19 bonding PMCs, metals, ceramics, and other materials; and for manufacturing molded
20 and cast parts.

21 While there has been shown and described what is at present considered the
22 preferred embodiments of the invention, it will be obvious to those skilled in the art that
23 various changes and modifications may be made therein without departing from the
24 scope of the invention as defined by the appended claims.

25

Table 1. Toughening of Radiation Cured Epoxy Resins with Engineering Thermoplastics and Hydroxy-Terminated Thermoplastic Oligomers^{1,2}

Toughening Agent	Toughening Agent Concentration (%)	Epoxy Resin	Glass Transition Temperature (°C)		Initial Service Temperature ³ (°C)	Flexural Modulus E' (estimated) 25°C (GPa)	Weight Gain (48h H ₂ O Boil) (%)	Fracture Toughness, K _{1c} (MPa m ^{1/2})
			Tan Delta	G"				
Control	None	Tactix 123	163	145	120	3.04	1.41	0.411 (25°C)
Udel P-1700 NT	10	Tactix 123	168	156	132	2.94	1.25	0.680 (25°C)
Udel P-1700 NT	20	Tactix 123	156	144	128	2.85	0.95	0.899 (-100°C)
Radel A-200 NT	10	Tactix 123	177	162	141	2.79	1.38	0.746 (25°C)
Radel A-200 NT	20	Tactix 123	168	143	129	2.68	1.37	1.254 (-100°C)
Ultem 1000-1000	10	Tactix 123	175	157	136	3.07	1.37	0.549 (25°C)
Ultem 1000-1000	20	Tactix 123	189	174	155	3.04	1.69	0.494 (25°C)
Ultem 1010-1000	10	Tactix 123	173	158	133	3.04	1.37	0.612 (-100°C)
Ultem 1010-1000	20	Tactix 123	175	160	141	3	1.69	0.696 (25°C)
Ultem 1040-1000	10	Tactix 123	173	158	133	2.94	1.33	0.877 (-100°C)
Ultem 1040-1000	20	Tactix 123	177	158	142	2.9	1.63	0.691 (25°C)
Orgasol 2001	20	Tactix 123	163	138	79	2.64	2.49	0.793 (-100°C)
Orgasol 3501	5	Tactix 123						0.585 (25°C)
IMITEC X-902	5	Tactix 123	164	146	124	3.05	1.64	0.734 (-100°C)
IMITEC X-902	10	Tactix 123	161	144	124	3.19	1.63	0.713 (25°C)
IMITEC X-902	20	Tactix 123	161	146	128	3.45	1.81	0.668 (-100°C)

1. All formulations contained OPPI at a concentration of 3 phr.

2. All specimens were cured using a total dosage of 150 kGy.

3. Initial service temperature is defined as the temperature at which the modulus is at 50% of its value at 25°C.

Table 1. Toughening of Radiation Cured Epoxy Resins with Engineering Thermoplastics and Hydroxy-Terminated Thermoplastic Oligomers^{1,2} Continued

Toughening Agent	Toughening Agent Concentration (%)	Epoxy Resin	Glass Transition Temperature (°C)		Initial Service Temperature ³ (°C)	Flexural Modulus E' (estimated) 25°C (GPa)	Weight Gain (48h H ₂ O Boil) (%)	Fracture Toughness, K _{Ic} (MPa m ^{1/2})
			Tan Delta	G"				
Hydroxy-Terminated Polysulfone Oligomer; Mn, 1500 g/mole	5	Tactix 123	173	160	137	2.94	1.06	0.508 (25°C)
Hydroxy-Terminated Polysulfone Oligomer; Mn, 1500 g/mole	20	Tactix 123	155	143	132	2.94	1.21	0.536 (25°C) 0.746 (-100°C)
Hydroxy-Terminated Polysulfone Oligomer; Mn, 1500 g/mole	30	Tactix 123	160	145	120	3.25	2.56	0.557 (25°C) 0.652 (-100°C)
Hydroxy-Terminated Polysulfone Oligomer; Mn, 2650 g/mole	20	Tactix 123	149	134	122	3.18	1.57	0.700 (25°C)
Hydroxy-Terminated Polysulfone Oligomer; Mn, 5360 g/mole	20	Tactix 123	150	134	123	3.19	2.38	0.731 (25°C)
Hydroxy-Terminated Polysulfone Oligomer; Mn, 6000 g/mole	5	Tactix 123	171	156	130	2.89	1.15	0.475 (25°C)
Hydroxy-Terminated Polysulfone Oligomer; Mn, 6000 g/mole	20	Tactix 123	159	150	135	2.81	1.26	0.593 (25°C) 0.871 (-100°C)
Hydroxy-Terminated Polysulfone Oligomer; Mn, 6000 g/mole	30	Tactix 123	161	149	134	3.02	1.64	0.705 (25°C) 1.114 (-100°C)

1. All formulations contained OPPI at a concentration of 3 phr.

2. All specimens were cured using a total dosage of 150 kGy.

3. Initial service temperature is defined as the temperature at which the modulus is at 50% of its value at 25°C.

Table 1. Toughening of Radiation Cured Epoxy Resins with Engineering Thermoplastics and Hydroxy-Terminated Thermoplastic Oligomers^{1,2} Continued

Toughening Agent	Toughening Agent Concentration (%)	Epoxy Resin	Glass Transition Temperature (°C)		Initial Service Temperature ³ (°C)	Flexural Modulus E' (estimated) 25°C (GPa)	Weight Gain (48h H ₂ O Boil) (%)	Fracture Toughness, K _{Ic} (MPa m ^{1/2})
			Tan Delta	G"				
Hydroxy-Terminated Polysulfone Oligomer: Mn, 8890 g/mole	20	Tactix 123	154	136	122	3.32	1.77	0.738 (25°C)
Udel P-1700 NT	15	ERL 2258	176		112			
Udel P-1700 NT	20	ERL 2258	164		87			0.755 (25°C)
Udel P-1700 NT	10	Tactix 742/ ERL 2258 (45:45)	106		65			0.643 (25°C)
Udel P-1700 NT	11	Tactix 556/ ERL 2258 (44.5:44.5)	157		75			0.805 (25°C)

1. All formulations contained OPPI at a concentration of 3 phr.
2. All specimens were cured using a total dosage of 150 kGy.
3. Initial service temperature is defined as the temperature at which the modulus is at 50% of its value at 25°C.

Table 2. Toughening of Radiation Cured Epoxy Resins with Reactive Flexibilizers^{1,2}

Toughening Agent	Toughening Agent Concentration (%)	Epoxy Resin	Glass Transition Temperature (°C)		Initial Service Temperature ³ (°C)	Flexural Modulus E' (estimated) 25°C (GPa)	Weight Gain (48h H ₂ O Boil) (%)	Fracture Toughness, K _{IC} (MPa m ^{1/2})
			Tan Delta	G"				
Control	None	Tactix 123	163	145	120	3.04	1.41	0.411 (25°C)
Dow DER 732	10	Tactix 123						0.423 (25°C)
Dow DER 736	10	Tactix 123						0.569 (25°C)
Shell Heloxy 32	10	Tactix 123						0.487 (25°C)
Shell Heloxy 68	10	Tactix 123	158		135			0.534 (25°C)
Shell Heloxy 71	10	Tactix 123						0.552 (-100°C)
Shell Heloxy 505	10	Tactix 123						0.529 (25°C)
								0.480 (25°C)
								0.708 (-100°)
Elf Atochem ATO POLY bd 600	10	Tactix 123	166	151	123	2.68	1.28	0.594 (25°C)
Elf Atochem ATO POLY bd 605	10	Tactix 123	163	148	124	2.85	1.62	0.463 (-100°C)
Elf Atochem ATO Vikoflex 7010	10	Tactix 123	139	121	101	2.82		0.420 (25°C)
Elf Atochem ATD Vikoflex 7170	5	Tactix 123						0.592 (25°C)
Elf Atochem ATD Vikoflex 7170	10	Tactix 123	151	133	117	2.79	2.02	0.598 (25°C)
Elf Atochem ATD Vikoflex 7170	20	Tactix 123	134		113			0.752 (-100°)
Elf Atochem ATD Vikoflex 7170	30	Tactix 123	118		94			0.559 (25°)
								0.596 (25°C)

1. All formulations contained OPPI at a concentration of 3 phr.
2. All specimens were cured using a total dosage of 150 kGy.
3. Initial service temperature is defined as the temperature at which the modulus is at 50% of its value at 25°C.

Table 2. Toughening of Radiation Cured Epoxy Resins with Reactive Flexibilizers^{1,2,c}
Continued

Toughening Agent	Toughening Agent Concentration (%)	Epoxy Resin	Glass Transition Temperature (°C)		Initial Service Temperature ³ (°C)	Flexural Modulus E' (estimated) 25°C (GPa)	Weight Gain (48h H ₂ O Boil) (%)	Fracture Toughness, K _{IC} (MPa m ^{1/2})
			Tan Delta	G"				
Elf Atochem ATD Vikoflex 7190	10	Tactix 123	172		137			0.479 (25°C)
Elf Atochem ATO Vikolox 14	10	Tactix 123	130	112	97	2.63	1.12	0.491 (25°C)
Union Carbide Tone 301	10	Tactix 123						0.810 (25°C)
Union Carbide Tone 310	10	Tactix 123						0.621 (25°C)
Elf Atochem ATO Vikoflex 7170	15	Tactix 556	175		150			0.555 (25°C)
Shell Heloxy 32	30	Tactix 742						Plaques Exothermec

1. All formulations contained OPPI at a concentration of 3 phr.

2. All specimens were cured using a total dosage of 150 kGy.

3. Initial service temperature is defined as the temperature at which the modulus is at 50% of its value at 25°C.

Table 3. Toughening of Radiation Cured Epoxy Resins with Rubbers and Elastomers^{1,2}

Toughening Agent	Toughening Agent Concentration (%)	Epoxy Resin	Glass Transition Temperature (°C)		Initial Service Temperature ³ (°C)	Flexural Modulus E' (estimated) 25°C (GPa)	Weight Gain (48h H ₂ O Boil) (%)	Fracture Toughness, K _{IC} (MPa m ^{1/2})
			Tan Delta	G"				
Control	None	Tactix 123	163	145	120	3.04	1.41	0.411 (25°C)
Ciba PY 322	5	Tactix 123	164	148	121	2.9	1.06	0.513 (25°C)
Ciba PY 322	10	Tactix 123	153	138	118	2.89	1.05	0.488 (25°C)
Ciba PY 322	20	Tactix 123	132	119	107	2.65	1.06	0.630 (25°C)
Dow XU 71790.04L	20	Tactix 123	166	151	121	2.75	2.00	0.565 (25°C)
Dow XU 71790.04L	30	Tactix 123	164	152	124	2.39	2.12	0.410 (25°C)
Dow XU 71790.04L	30	Tactix 123/ Tactix 556 (28:42)	176	161	137	2.48	2.22	0.411 (25°C) 0.520 (-100°C)
Rohm & Haas Paraloid EXL-2330	5	Tactix 123	147	129	111	2.84	2.62	0.492 (25°C)
Rohm & Haas Paraloid EXL-2330	10	Tactix 123	132	132	109	2.69	2.59	0.585 (25°C)
Rohm & Haas Paraloid EXL-2330	15	Tactix 123	129	111	92	2.31	2.47	0.600 (25°C)
Rohm & Haas Paraloid EXL-2330	20	Tactix 123	122	104	81	1.97	2.19	0.572 (25°C)
Shell Epon 58134	10	Tactix 123	183		158			0.618 (25°C)
Shell Epon 58134	30	Tactix 123	88					0.560 (25°C)

1. All formulations contained OPPI at a concentration of 3 phr.

2. All specimens were cured using a total dosage of 150 kGy.

3. Initial service temperature is defined as the temperature at which the modulus is at 50% of its value at 25°C.

Table 3. Toughening of Radiation Cured Epoxy Resins with Rubbers and Elastomers^{1,2} Continued

Toughening Agent	Toughening Agent Concentration (%)	Epoxy Resin	Glass Transition Temperature (°C)		Initial Service Temperature ³ (°C)	Flexural Modulus E' (estimated) 25°C (GPa)	Weight Gain (48h H ₂ O Boil) (%)	Fracture Toughness, K _{1c} (MPa m ^{1/2})
			Tan Delta	G''				
Shell Epon 58134	100	None	142		108			0.635 (25°C)
Shell Kraton FG 1901X (Solvent Mixed)	10	Tactix 123	171		131			0.919 (25°C) 1.224 (-100°C)
Shell Kraton FG 1901X (Solvent Mixed)	20	Tactix 123	86/176		111			0.841 (25°C) 1.124 (-100°C)

1. All formulations contained OPPI at a concentration of 3 phr.

2. All specimens were cured using a total dosage of 150 kGy.

3. Initial service temperature is defined as the temperature at which the modulus is at 50% of its value at 25°C.

Table 4. Toughening of Radiation Cured Epoxy Resins with Mixtures of Tougheners

Toughening Agent	Toughening Agent Concentration (%)	Epoxy Resin	Glass Transition Temperature (°C)		Initial Service Temperature ³ (°C)	Flexural Modulus E' (estimated) 25°C (GPa)	Weight Gain (48h H ₂ O Boil) (%)	Fracture Toughness, K _{1c} (MPa m ^{1/2})
			Tan Delta	G"				
Control	None	Tactix 123	163	145	120	3.04	1.41	0.411 (25°C)
Udel P-1700 NT	10	Tactix 123	158		138			0.766 (25°C)
Shell Heloxy 68	10							1.025 (-100°C)
Udel P-1700 NT	10	Tactix 123	90					0.708 (25°C)
Shell Heloxy 71	10							0.932 (-100°C)
Udel P-1700 NT	10	Tactix 123	153		124			0.707 (25°C)
Shell Heloxy 505	10							
Udel P-1700 NT	10	Tactix 123						0.885 (25°C)
Dow DER 732	10							
Udel P-1700 NT	10	Tactix 123	153		128			0.716 (25°C)
Elf Atochem ATO	10							1.058 (-100°C)
Vikoflex 7170								
Udel P-1700 NT	18	Tactix 123	140		98			0.858 (25°C)
Elf Atochem ATO	10							
Vikoflex 7170								
Udel P-1700 NT	20	Tactix 123	151		104			0.965 (25°C)
Elf Atochem ATO	20							
Vikoflex 7170								
Udel P-1700 NT	10	Tactix 123	80					0.772 (25°C)
Elf Atochem ATO	10							
Vikoflex 7190								

1. All formulations contained OPPI at a concentration of 3 phr.
2. All specimens were cured using a total dosage of 150 kGy.
3. Initial service temperature is defined as the temperature at which the modulus is at 50% of its value at 25°C.

Table 4. Toughening of Radiation Cured Epoxy Resins with Mixtures of Tougheners
Continued

Toughening Agent	Toughening Agent Concentration (%)	Epoxy Resin	Glass Transition Temperature (°C)		Initial Service Temperature ³ (°C)	Flexural Modulus E' (estimated) 25°C (GPa)	Weight Gain (48h H ₂ O Boil) (%)	Fracture Toughness, K _{IC} (MPa m ^{1/2})
			Tan Delta	G"				
Udel P-1700 NT Hydroxy-Terminated Polysulfone Oligomer; Mn, 6000 g/mole	10 10	Tactix 123	171		153			0.799 (25°C) 1.003 (-100°C)
Udel P-1700 NT Hydroxy-Terminated Polysulfone Oligomer; Mn, 6000 g/mole Elf Atochem ATO Vikoflex 7170	10 10 10	Tactix 123	151		120			0.538 (25°C)
Udel P-1700 NT Rhone-Poulenc Heloxy 69	15 42.5	Tactix 556	185		172			0.734 (25°C) 0.935 (-100°C)

1. All formulations contained OPPI at a concentration of 3 phr.
2. All specimens were cured using a total dosage of 150 kGy.
3. Initial service temperature is defined as the temperature at which the modulus is at 50% of its value at 25°C.

Table 5. Electron Beam Cured Composite Laminate Properties

¹ Undirectional carbon fiber prepreg (Hercules carbon fiber IM7/GP-12K) laminates laid up at a nominal thickness of 0.080-inches and hot debulked at 70°C for 1 hour. Laminates electron beam cured at a dose of 150 kGy.											
² Initial Service Temperature is defined as the temperature at which the DMA modulus is at 50% of its value at 25°C.											
³ Flexural strength and modulus determined using ASTM D 790; 3 point bend, span/depth = 32, Normalized to 60% fiber volume. Interlaminar shear strength (ILSS) determined using ASTM D 2344; Short beam shear method, span/depth = 4.											
⁴ CYCLING Procedure: Specimens placed in -78.5°C (or -194°C) for 30 minutes (min.); returned to room temperature (RT) for 30 min.; placed in oven at 121°C for 30 min.; returned to RT for 30 min.; procedure performed 3 times. Tested at RT.											
Prepreg Resin System ¹	Tg, °C (Tan delta)	² Initial Service Temperature (°C)	Resin Viscosity @70°C, cps (Debulk Temp.)	% Fiber Volume, ASTM D 3171	% Void Vol., ASTM D 3171 (resin density =1.2)	³ Room Temp. O° Flexural Strength, ksi	³ Room Temp. O° Flexural Modulus, msi	^{3,4} RT O° Flex. Str., ksi; [AFTER CYCLING]	^{3,4} RT O° Flex. Mod., msi; [AFTER CYCLING]	³ Room Temp. O° ILSS, ksi	^{3,4} Room Temp. O° ILSS, ksi; [AFTER CYCLING]
Tactix 123 (73.9%)/DER 661 (13%)/Udel P-1700 NT (13%)/OPPI (3phr)	103, 175	163	44,750	58.16	2.62	180	19.2	195 (176)	21.9 (20.8)	11	11.9 (11.4)
Tactix 123 (65.2%)/DER 661 (13%)/Udel P-1700 NT (13%)/ATO Vikoflex 7170 (8.7%)/OPPI (3phr)	89, 160	153	37,200	59.6	2.77	189	21.6	183 (177)	20.5 (20.5)	11.1	10.6 (11.8)
Tactix 123 (9%)/Tactix 556 (81%)/Kraton FG 1901X (10%)/OPPI (3phr)	210	204	27,100	51.02	6.06	153	21.4	169 (145)	22.4 (20.1)	7.3	7.9 (9.1)
Epon 828 (44.73%), Kraton FG 1901X (7.9%)/DER 661 (47.36%)/OPPI (3phr)	147	145	28,600	59.96	2.06	147	20.2	151 (146)	20.2 (19.7)	7.2	6.6 (7)
Tactix 742 (70.06%)/DER 332 (16.9%)/DER 661 (13%)/OPPI (3.09 phr)	157, 420	212	7,450	57.74	1.2	190	20.3	192 (190)	21.5 (21.3)	10.1	10.7 (11.2)
Tactix 123 (68.64%)/DER 661 (8.48%)/Hydroxy terminated Polysulfone Mn, 6000 g/mole (22.88%)/OPPI (2.75phr)	94, 172	107	11,500	62.22	2.6	157	18.6	151 (156)	18.1 (18.5)	9	10.8 (11.1)

Table 5. Electron Beam Cured Composite Laminate Properties Continued

¹ Unidirectional carbon fiber prepreg (Hercules carbon fiber IM7/GP-12K) laminates laid up at a nominal thickness of 0.080-inches and hot debulked at 70°C for 1 hour. Laminates electron beam cured at a dose of 150 kGy.											
² Initial Service Temperature is defined as the temperature at which the DMA modulus is at 50% of its value at 25°C.											
³ Flexural strength and modulus determined using ASTM D 790; 3 point bend, span/depth = 32, Normalized to 60% fiber volume. Interlaminar shear strength (ILSS) determined using ASTM D 2344; Short beam shear method, span/depth = 4.											
⁴ CYCLING Procedure: Specimens placed in -78.5°C (or -194°C) for 30 minutes (min.); returned to room temperature (RT) for 30 min.; placed in oven at 121°C for 30 min.; returned to RT for 30 min.; procedure performed 3 times. Tested at RT.											
Prepreg Resin System ¹	Tg, °C (Tan delta)	² Initial Service Temperature (°C)	Resin Viscosity @70oC, cps (Debulk Temp.)	% Fiber Volume, ASTM D 3171	% Void Vol., ASTM D 3171 (resin density =1.2)	³ Room Temp. O° Flexural Strength, ksi	³ Room Temp. O° Flexural Modulus, msi	^{3,4} RT O° Flex. Str., ksi; [AFTER CYCLING]	^{3,4} RT O° Flex. Mod., msi; [AFTER CYCLING]	³ Room Temp. O° ILSS, ksi	^{3,4} Room Temp. O° ILSS, ksi; [AFTER CYCLING]
Tactix 123 (8.1%)/Tactix 556 (72.8%)/DER 661 (9.9%)/Shell EKP 206 (9.3%)/OPPI (2.97 phr)	202	197	10,800	59.57	5.6	169	19.9	175 (164)	20.9 (21.1)	6.7	8 (9.2)
Tactix 123 (14.7%)/Tactix 556 (58.7%)/DER 661 (16.8%)/Shell EKP 207 (10%)/OPPI (3phr)	137, 195	185	11,400	53.28	2.9	171	22	181 (180)	22.6 (22.7)	7.3	8.4 (8.5)
Tactix 742 (100%)/OPPI (3 phr)	435	344	10,200	60.52	4.38	188	21.1	211 (195)	21.6 (20.4)	6.9	7.7 (8)
Tactix 742 (85%)/Shell EKP 206 (15%)/OPPI (3phr)	128, 435	365	22,300	57.47	4.23	159	20.1	184 (172)	20.5 (20.7)	5.8	7.1 (7.5)
Tactix 742 (85%)/Shell EKP 207 (15%)/OPPI (3phr)	144, 435	365	23,100	57.59	6.75	155	21	175 (163)	19.9 (20.7)	5.5	6.5 (7)

Table 6. Electron Beam Cured Composite Laminate Thermal Properties

Prepreg Resin System*	Tg, °C (Tan Delta by Dynamic Mechanical Analysis)	Resin Viscosity @70°C (cps)
Tactix 123 (74%)/DER 661 (13%)/Udel P-1700 NT (13%)/Sartomer CD-1012 (3 phr)	182	44,750
Tactix 123 (55%)/Tactix 556 (35%)/Udel P-1700 NT (10%)/Sartomer CD-1012 (3 phr)	202	21,700
Tactix 123 (55%)/Tactix 742 (35%)/Udel P-1700 NT (10%)/Sartomer CD-1012 (3 phr)	212	25,700
Tactix 123 (50%)/DEN 438 (40%)/Udel P-1700 NT (10%)/Sartomer CD-1012 (3 phr)	212	27,400

*Unidirectional carbon fiber prepreg (Hercules carbon fiber, IM7/GP-12K) laminates electron beam cured with a dose of 150 kGy.

Table 7. Results on EBeam Cured Resins and Resin Blends

Resin, %	Resin, %	Photoinitiator	PI (Phr)	Dose (kGy)	Dry Tg or Wet Tg (48 hr. H ₂ O boil)	Tg, (°C) Tan Delta	Tg, (°C) Peak G" or E"	Tg Onset, (°C)	Initial Service Temp. (°C @ 0.5 G' or E')	E' - DMA Mod., Ksi (GPa)	% Wt. gain (after 48hr H ₂ O boil)
T123		IRG261	4	100	dry	54	30		40		
T123		IRG261	3	100	dry	56	30		40		
T123		IRG261	5	100	dry	72	30		40		
T123		UVI6974	0.5	100	dry	82	59		59		
ERL 4299		OPPI	3	100	dry	92	75	67	71	321 (2.21)	3.85
GY 502		OPPI	2	100	dry	98	77	74	70	428 (2.95)	1.31
E862		UVI6974	0.5	100	dry	102	79		75		
T123		UVI6974	1	100	dry	102	77		77		
E862		OPPI	0.5	100	dry	104	76		74		
GY 509		OPPI	2	100	dry	105	90	85	79	371 (2.56)	1.37
T556, 80	DY027, 20	OPPI	3	100	wet	107	85			352 (2.43)	1.24
T556, 80	DY027, 20	OPPI	3	100	dry	116	98	93	85	379 (2.61)	1.24
CY 9729		OPPI	3	100	dry	121	67	74	68	259 (1.78)	
T123		UVI6974	2	100	dry	121	92		89		
E862		UVI6974	1	100	dry	124	92		89		
T123		OPPI	0.5	100	dry	124	92		92		
D431		OPPI	1	100	dry	128	81	76	86	505 (3.48)	
T123		UVI6974	5	100	dry	129	79		82		
E862, 80	PY322, 20	OPPI	3	150	dry	129	112		102		
E862		UVI6974	5	100	dry	131	107		100		
T123		CD-1012	1	150	dry	131	94		131		
T123		UVI6974	4	100	dry	134	92		87		
T123		UVI6974	3	100	dry	134	92		94		
E862		UVI6974	2	100	dry	134	107		95		
D431, 100		OPPI	1	100	wet	142	133		119	423 (2.91)	2.05
E862		UVI6974	4	100	dry	144	124		117		
D431, 100		OPPI	2	100	wet	147	135		123	415 (2.86)	2.13
2258		OPPI	1	100	wet	147	123		103	400 (2.76)	5.98
D431		OPPI	2	100	dry	147	107	93	99	469 (3.23)	
T556, 90	DY027, 10	OPPI	3	100	dry	148	126	125	109	424 (2.92)	1.47
ERL 4205		OPPI	2	100	dry	148	85	198	133	563 (3.88)	
E862		UVI6974	3	100	dry	149	102		104		

Table 7. Results on EBeam Cured Resins and Resin Blends
Continued

Resin, %	Resin, %	Photoinitiator	PI (Phr)	Dose (kGy)	Dry Tg or Wet Tg (48 hr. H ₂ O boil)	Tg, (°C) Tan Delta	Tg, (°C) Peak G" or E"	Tg Onset, (°C)	Initial Service Temp. (°C @ 0.5 G' or E')	E' - DMA Mod., Ksi (GPa)	% Wt. gain (after 48hr H ₂ O boil)
T556, 80	DY023, 20	OPPI	3	100	dry	150	135	132	118	476 (3.28)	1.24
LY9703		OPPI	2	100	wet	151	133			265 (1.83)	1.39
T123		OPPI	2	100	wet	156	138			388 (2.67)	2.09
D354		OPPI	2	100	dry	157	148	144	126	421 (2.90)	1.27
PY306		OPPI	4	100	dry	160	144		130	440 (3.03)	1.21
D431, 100		OPPI	4	100	wet	160	138			417 (2.87)	2.28
CY179		OPPI	1	100	dry	160	129	73	110	501 (3.45)	
E862, 100		OPPI	2	100	dry	161	149	144	128	505 (3.48)	1.51
E862, 47.5	T742, 47.5 + Eth. Glycol, 5	OPPI	3	150	dry	161	136		116		
E862		OPPI	4	100	dry	161	134		133		
T556		DPISbF6	3	150	wet	162	143			427 (2.94)	2.43
E862		OPPI	5	100	dry	162	129		121		
HPT1079		OPPI		50	dry	162	141		139		
PY306, 100		OPPI	2	100	dry	163	154		130	446 (3.07)	1.27
2258		OPPI	1	100	dry	163	85	113	97	575 (3.96)	5.98
E862		OPPI	3	100	dry	164	141		134		
D431, 100		OPPI	3	100	wet	166	145			416 (2.87)	1.94
E862		RP-DW	1	150	dry	167	154		144		
E862		OPPI	1	100	dry	167	156		146		
E862		OPPI	1	100	dry	167	167		146		
E862		OPPI	2	100	dry	167	154		147		
LY9703		OPPI	2	100	dry	168	156	151	129	422 (2.91)	1.39
PY306, 100		OPPI	2	100	dry	168	150	141	134	409 (2.82)	1.75
D431, 100		OPPI	5	100	wet	170	142		135	230 (1.58)	2.08
GY281		OPPI	2	100	dry	171	159		130	436 (3.00)	1.53
E862, 47.5	T742, 47.5 + Tone 301, 5	OPPI	3	150	dry	172	149		143		
E862, 45	T123, 45 + Vect. 4020	OPPI	3	150	dry	172	146		146		

Table 7. Results on EBeam Cured Resins and Resin Blends
Continued

Resin, %	Resin, %	Photoinitiator	PI (Phr)	Dose (kGy)	Dry Tg or Wet Tg (48 hr. H ₂ O boil)	Tg, (°C) Tan Delta	Tg, (°C) Peak G" or E"	Tg Onset, (°C)	Initial Service Temp. (°C @ 0.5 G' or E')	E' - DMA Mod., Ksi (GPa)	% Wt. gain (after 48hr H ₂ O boil)
T123, 80	OH-term. Udel (2650), 20	OPPI	3	150	dry	172	162		154		
PY306, 75	T556, 25	OPPI	2	100	dry	173	158	152	136	484 (3.34)	1.66
GY308		OPPI	2	100	dry	174	158	153	133	421 (2.90)	1.48
T123		OPPI	5	100	dry	174	151		146		
T556		OPPI	3	150	wet	175	156			286 (1.98)	2.1
T123, 80	OH-term. Udel (8890), 20	OPPI	3	150	dry	177	169		155		
E862, 75	T556, 25	OPPI	2	100	dry	178	163	158	137	503 (3.47)	1.88
CY179, 75	T556, 25	OPPI	2	100	dry	178	153	147	138	518 (3.87)	4.76
T123		RP-DW	1	150	dry	179	152		139		
T123		OPPI	4	100	dry	179	167		156		
T556, 90	DY023, 10	OPPI	3	100	dry	180	165	163	138	552 (3.80)	1.59
2258		OPPI	5	100	dry	180	163	163	142	505 (3.48)	5.05
E862, 75	T742, 25	OPPI	1	150	dry	181		162	156		
E862, 75	T742, 25	OPPI	3	100	dry	181	162		156		
T123		OPPI	3	100	dry	182	164		156		
T123		OPPI	3	150	dry	182	164		156		
D383, 100		OPPI	2	100	dry	183	170	164	143	498 (3.43)	2.1
CY179, 75	T742, 25	OPPI	2	100	dry	183	150	145	129	566 (3.90)	5.59
E862, 75	T742, 25	OPPI	1	100	dry	185		164	162		
D383		OPPI	3	100	dry	186	172	166	142	441 (3.04)	2.04
T123		OPPI	2	100	dry	186	174	166	138	440 (3.03)	2.09
PY306, 75	T742, 25	OPPI	2	100	dry	187	165	160	138	506 (3.49)	1.74
T138		OPPI	2	100	dry	187	175	167	142	432 (2.98)	1.91
D431		OPPI	4	100	dry	187	156	155	129	473 (3.26)	
T123		RP-DW	2	150	dry	187	157		142		
PY306, 50	T556, 50	OPPI	2	100	dry	188	173	165	146	476 (3.28)	2.02
2258		OPPI	4	0	dry	188	170	171	144	498 (3.43)	5.23

Table 7. Results on EBeam Cured Resins and Resin Blends
Continued

Resin, %	Resin, %	Photoinitiator	PI (Phr)	Dose (kGy)	Dry Tg or Wet Tg (48 hr. H ₂ O boil)	Tg, (°C) Tan Delta	Tg, (°C) Peak G" or E"	Tg Onset, (°C)	Initial Service Temp. (°C @ 0.5 G' or E')	E' - DMA Mod., Ksi (GPa)	% Wt. gain (after 48hr H ₂ O boil)
E862, 75	T742, 25	OPPI	2	100	dry	189	174	149	140	476 (3.29)	1.92
E862, 75	T742, 25	OPPI	1	50	dry	189	156		154		
D383, 75	T556, 25	OPPI	2	100	dry	191	176	174	143	501 (3.46)	2.26
E862, 45	T742, 45 + SR 297, 10	OPPI	3	150	dry	191	144		156		
T556		RP-SH	3	150	wet	192	162			390 (2.69)	1.03
2258		OPPI	3	100	dry	192	174	175	147	502 (3.46)	5.3
T123, 80	Imitec, 20	OPPI	3	150	dry	192	182		164		
E862, 50	T556, 50	OPPI	2	100	dry	193	178	177	148	479 (3.30)	2.06
D431		OPPI	3	100	dry	193	171	169	142	481 (3.31)	
E862, 75	T742, 25	OPPI	1	100	dry	194	157		157		
E862, 75	T742, 25	OPPI	1	100	dry	194	157		157		
E862, 75	T742, 25	OPPI	1	150	dry	194	162		158		
T123		OPPI	2	100	dry	194	181		164		
D383, 50	T556, 50	OPPI	2	100	dry	197	182	180	150	503 (3.47)	2.17
D431		OPPI	5	100	dry	197	176	169	143	458 (3.16)	
E862, 45	T742, 45 + Ebecryl 639, 10	OPPI	3	150	dry	201	189		187		
D383, 75	T742, 25	OPPI	2	100	dry	203	188	182	158	504 (3.47)	2.48
E862, 25	T742, 75	OPPI	1	150	dry	204	106		154		
T123, 50	T556, 50	OPPI	3	150	dry	204	192		170		
2258		OPPI	2	100	dry	205	155	184	142	494 (3.40)	5.49
PY306, 50	T742, 50	OPPI	2	100	dry	206	164	167	148	502 (3.46)	2.59
CY179, 50	T556, 50	OPPI	2	100	dry	206	184	179	162	516 (3.56)	3.86
E862, 50	T742, 50	OPPI	3	150	dry	206	186		175		
E862, 25	T556, 75	OPPI	2	100	dry	207	191	192	124	552 (3.80)	2.25
T123		OPPI	1	100	dry	207	131		142		
D383, 25	T556, 75	OPPI	2	100	dry	208	196	197	146	523 (3.61)	2.24
E862, 50	T742, 50	OPPI	2	100	dry	211	194	187	159	292 (2.01)	2.75
E862, 25	D438, 75	OPPI	1	150	dry	216	189		191		

Table 7. Results on EBeam Cured Resins and Resin Blends
Continued

Resin, %	Resin, %	Photoinitiator	PI (Phr)	Dose (kGy)	Dry Tg or Wet Tg (48 hr. H ₂ O boil)	Tg, (°C) Tan Delta	Tg, (°C) Peak G" or E"	Tg Onset, (°C)	Initial Service Temp. (°C @ 0.5 G' or E')	E' - DMA Mod., Ksi (GPa)	% Wt. gain (after 48hr H ₂ O boil)
D383, 50	T742, 50	OPPI	2	100	dry	222	102	200	171	567 (3.91)	3.61
CY179, 50	T742, 50	OPPI	2	100	dry	224	183	167	172	561 (3.87)	5.89
T556		OPPI	2	100	dry	225	128	212	110	533 (3.68)	2.26
T556		OPPI	3	150	dry	229	211		169		
CY179, 25	T742, 75	OPPI	2	100	dry	240	114		204	492 (3.39)	5.69
D383, 25	T742, 75	OPPI	2	100	dry	242	107	217	203	542 (3.74)	3.97
T742		OPPI	3	150	dry	362			299		
T556		RP-DW	3	150	dry	189, 244	184, 224		179		
T123, 80	E2330, 20	OPPI	3	150	dry	72, 177	62		70		
THF, 10	T556, 90	OPPI	3	150	dry	82, 162	82, 154		139		
E862, 25	T742, 75	OPPI	2	100	dry				198	517 (3.56)	3.66
PY306, 25	T742, 75	OPPI	2	100	dry				191	571 (3.94)	3.95
T742		OPPI	2	100	dry				226	581 (4.00)	4.66
E862		IRG261	5	100	dry				44		
E862		IRG261	3	100	dry				49		
E862		IRG261	4	100	dry				56		
E862, 75	T742, 25	OPPI	1	50	dry				101		

Table 8. Gamma Screening Studies Using the OPPI Photoinitiator and Various Resin Systems

Resin System	% of Each Component	Phr OPPI	Gamma ΔT ($^{\circ}C$) (relative to reference)	Dose @ Peak Exotherm (kGy)	Physical Effect @ RT
<i>Bisphenol A based Epoxies</i>					
Tactix 123	100	0.5	(30.6 ¹)		
Tactix 123	100	1	27.8 (40.2 ¹)	5.8	H
Tactix 123	100	2	59.4 (43.9 ¹)	6.1	H
Tactix 123	100	3	(60.1 ¹)		
Tactix 123	100	4	62.8 (58.7 ¹)	7.4	H
Tactix 123	100	5	(21.1 ¹)		
Tactix 138	100	1	34.3	5.4	H
Epon 828	100	1	34	6.4	H
<i>Bisphenol F (Epoxy Novolac) based Epoxies</i>					
Epon 862	100	0.25	17.8	9	H
Epon 862	100	0.5	32.8 (41.2 ¹)	6.6	H
Epon 862	100	1	42.4 (57.4 ¹)	6.4	H
Epon 862	100	2	62.8 (68.5 ¹)	6	H
Epon 862	100	3	(78.4 ¹)		
Epon 862	100	4	73.5 (77.8 ¹)	8.2	H
Epon 862	100	5	(70.7 ¹)		
DEN 431	100	1	52.6	5.2	H
Epon 862/DEN 438	25/75	1	18.9	3.6	H
DEN 438	100	1	3	6.1	H
<i>Multifunctional Epoxies & Blends w/Other Materials</i>					
Epon 862/Epon 1031	50/50	1	4.7	14.5	H
Epon 862/Epon 1031	50/50	2	3.6	10.9	H
Epon 862/Epon 1031	50/50	4	4.4	14.3	H

Table 8. Gamma Screening Studies Using the OPPI Photoinitiator and Various Resin Systems
Continued

Resin System	% of Each Component	Phr OPPI	Gamma ΔT ($^{\circ}C$) (relative to reference)	Dose @ Peak Exotherm (kGy)	Physical Effect @ RT
<i>Multifunctional Epoxies & Blends w/ Other Materials</i>					
Epon 862/HPT 1079	50/50	1	1.7	5.7	S
Epon 862/Tactix 556	72/25	1	33.6	5.7	H
Epon 862/Tactix 556	50/50	1	26.7	5.8	H
Epon 862/Tactix 556	25/75	1	9.4	6	H
Tactix 556	100	1	1	8.7	H
Epon 862/Tactix 742	75/25	1	37.7	12.1	H
Epon 862/Tactix 742	50/50	1	18.2	17.2	H
Epon 862/Tactix 742	50/50	3	20.1	16.6	H
Epon 862/Tactix 742	25/75	1	9.6	19	H
Tactix 742	100	1	1.9	7.4	H
Epon 862/Tactix 742/Vectomer 4020	45/45/10	3	7	9.5	H
Epon 862/Tactix 742/Ebecryl 639	45/45/10	3	3.4	18.4	S
Tactix 742/ERL 4205/Vectomer 4020	45/45/10	3	5.2	13.2	H?
Tactix 742/ERL 4205	50/50	3	3.6	13.2	S?
<i>Cycloaliphatic based Epoxies</i>					
ERL 4205	100	1	1.8	10.1	VI
ERL 4205	100	2	3.4	7.8	VI
ERL 4205	100	4	5.6	7.7	VI
ERL 2258	100	1	18.3	5.4	H
ERL 4617	100	1	0.6	0.2	VI

Table 8. Gamma Screening Studies Using the OPPI Photoinitiator and Various Resin Systems
Continued

Resin System	% of Each Component	Phr OPPI	Gamma ΔT ($^{\circ}C$) (relative to reference)	Dose @ Peak Exotherm (kGy)	Physical Effect @ RT
Cycloaliphatic based Epoxies					
CY-179	100	1	7.4	8.6	H
Other Materials					
DVE-3	100	0	2.3	4.5	NC
DVE-3	100	1	109.3	0.2	H*
Vectomer 4010	100	0	4.7	1.7	NC
Vectomer 4010	100	1	91.7	1.1	H
Vectomer 4020	100	0	7.4	1.7	VI
Vectomer 4020	100	1	75.1	0.4	H
DER 736	100	1	105.6	6.7	H*
Notes:					
1 - Performed at a different time.					
H - Hard, MH - Medium Hard, S - Soft, VI - Viscosity increase, NC - No Change, S-H - Soft after irradiation, then Hard next day, NC-S - No Change after irradiation, then Soft next day.					
? Exothermed in oven.					
* Cured very vigorously.					

Table 9. Gamma Screening Studies Using Various Photoinitiators and Resin Systems

Resin System	%	PI	PIPhr	Gamma ΔT ($^{\circ}C$) (relative to reference)	Dose @ Peak Exotherm (kGy)	Effect @ RT
<i>Bisphenol A based Epoxies</i>						
Tactix 123	100	OPPI	0.5	(30.6 ¹)		
Tactix 123	100	OPPI	1	27.8 (40.2 ¹)	5.8	H
Tactix 123	100	OPPI	2	59.4 (43.9 ¹)	6.1	H
Tactix 123	100	OPPI	3	(60.1 ¹)		
Tactix 123	100	OPPI	4	62.8 (58.7 ¹)	7.4	H
Tactix 123	100	OPPI	5	(21.1 ¹)		
Tactix 123	100	DPIAsF ₆	1	12.4	3.5	H
Tactix 123	100	DPIPF ₆	1	8.2	5.6	MH
Tactix 123	100	6974	2 (1% Active)	4.2	9.9	S-H
Tactix 123	100	6990	2 (1% Active)	4	8.7	NC-S
Tactix 123	100	KI-85	2 (1% Active)	3.3	8.7	NC-S
Tactix 123	100	IRG 261	1	3	9.2	VI
Tactix 123	100	IRG 261	4	(3 ¹)		
Tactix 123	100	DPITF	1	1.8	6.1	NC
Tactix 138	100	OPPI	1	34.3	5.4	H
Epon 828	100	OPPI	1	34	6.4	H
<i>Bisphenol F (Epoxy Novolac) based Epoxies</i>						
Epon 862	100	OPPI	0.25	17.8	9	H
Epon 862	100	OPPI	0.5	32.8 (41.2 ¹)	6.6	H
Epon 862	100	OPPI	1	42.4 (57.4 ¹)	6.4	H
Epon 862	100	OPPI	2	62.8 (68.5 ¹)	6	H
Epon 862	100	OPPI	3	(78.4 ¹)		
Epon 862	100	OPPI	4	73.5 (77.8 ¹)	8.2	H
Epon 862	100	OPPI	5	(70.7 ¹)		
Epon 862	100	BBI-103	1	(14.2 ¹)	(7.2 ¹)	(H ¹)
Epon 862	100	BBI-103A	1	(10.5 ¹)	(10 ¹)	(H ¹)
Epon 862	100	6974	0.5 (25% Active)	(7.4 ¹)		
Epon 862	100	6974	1 (0.5% Active)	(7.9 ¹)		

Table 9. Gamma Screening Studies Using Various Photoinitiators and Resin Systems
Continued

Resin System	%	PI	PI Phr	Gamma ΔT (°C) (relative to reference)	Dose @ Peak Exotherm (kGy)	Effect @ RT
<i>Bisphenol F (Epoxy Novolac) based Epoxies</i>						
Epon 862	100	6974	2 (1% Active)	6.6 (7.1 ¹)	3.4	S-H
Epon 862	100	6974	3 (1.5% Active)	(6.6 ¹)		
Epon 862	100	6974	4 (2% Active)	(6.9 ¹)		
Epon 862	100	6974	5 (2.5% Active)	(2.5 ¹)		
Epon 862	100	KI-85	2 (1% Active)	4.3	4.2	NC-S
Epon 862	100	IRG-261	4	(3 ¹)		
Epon 862	100	BBI-102	1	(3.9 ¹)	(4.3 ¹)	(H ¹)
Epon 862	100	6990	2 (1% Active)	3.4	4.2	NC-S
Epon 862	100	BBI-101	1	(0.6 ¹)	(0 ¹)	(S ¹)
Epon 862	100	BBI-105	1	(0.5 ¹)	(0 ¹)	(S ¹)
Epon 863	100	BDS-105	1	(0.4 ¹)	(0 ¹)	(S ¹)
Epon 862	100	TAZ-101	1	(0.4 ¹)	(0 ¹)	(S ¹)
Epon 862	100	DPDS	1	(0.2 ¹)	(0 ¹)	(S ¹)
DEN 431	100	OPPI	1.2	52.6	5.2	H
DEN 438	100	OPPI	1	3	6.1	H
DEN 438	100	6974	2 (1% Active)	0.6	0.2	H
DEN 438	100	6990	2 (1% Active)	0.6	0.2	MH
DEN 438	100	FX-512	1.7 (1% Active)	4.1	7.9	S
DEN 438	100	KI-85	2 (1% Active)	0.6	0.2	S
<i>Multifunctional Epoxies</i>						
Tactix 556	100	OPPI	1	1	8.7	H
Tactix 742	100	OPPI	1	1.9	7.4	H
HPT 1079	100	6974	2 (1% Active)	1	4.4	H

Table 9. Gamma Screening Studies Using Various Photoinitiators and Resin Systems
Continued

Resin System	%	PI	PI Phr	Gamma ΔT (°C) (relative to reference)	Dose @ Peak Exotherm (kGy)	Effect @ RT
<i>Epoxy Blends</i>						
Epon 862/Tactix 742	50/50	BBI-103	1	(8.8 ¹)	(17 ¹)	(H ¹)
Epon 862/Tactix 742	50/50	BBI-103A	1	(3.2 ¹)	(12 ¹)	(H ¹)
Epon 862/Tactix 742	50/50	BBI-102	1	(1.5 ¹)	(15 ¹)	(H ¹)
Epon 862/Tactix 742	50/50	BBI-105	1	(1.3 ¹)	(0 ¹)	(S ¹)
Epon 862/Tactix 742	50/50	BBI-101	1	(0.9 ¹)	(0 ¹)	(S ¹)
Epon 862/Tactix 742	50/50	TAZ-101	1	(0.6 ¹)	(0 ¹)	(S ¹)
Epon 862/Tactix 742	50/50	BDS-105	1	(0.4 ¹)	(0 ¹)	(S ¹)
Epon 862/Tactix 742	50/50	DPDS	1	(0.1 ¹)	(0 ¹)	(S ¹)
<i>Cycloaliphatic based Epoxies</i>						
ERL 4205	100	OPPI	1	1.8	10.1	VI
ERL 4205	100	OPPI	2	3.4	7.8	VI
ERL 4205	100	OPPI	4	5.6	7.7	VI
ERL 4205	100	DPIAsF ₆	1	2.4	6	VI
ERL 4205	100	DPIPF ₆	1	2	7.9	VI
ERL 4205	100	6974	2 (1% Active)	1.9	6.3	VI
ERL 4205	100	DPITF	1	1.5	9.9	VI
ERL 2258	100	OPPI	1	18.3	5.4	H
ERL 2258	100	6974	2 (1% Active)	5.1	4.6	S
ERL 4617	100	OPPI	1	0.6	0.2	VI
CY-179	100	OPPI	1	7.4	8.6	H
CY-179	100	DPIAsF ₆	1	2.3	7.2	S
CY-179	100	DPIPF ₆	1	1.6	7.2	VI
CY-179	100	DPITF	1	0.9	0.8	NC
¹ Performed at a different time.						

Table 10. Description of Materials.

Resins	Description	Viscosity at 25°C, cps	W. P. E (EEW)
<i>Bisphenol A based Epoxies</i>			
Dow Tactix 123	High purity, low viscosity diglycidyl ether of Bisphenol A based liquid epoxy resin.	4,400-5,600	172-176
Dow Tactix 138	High purity, low viscosity diglycidyl ether of Bisphenol A based liquid epoxy resin.	9,200-9,800	178-182
Dow D.E.R 383	Low visc. BPA resin.	9,000-10,500	176-183
Shell Epon 828	Diglycidyl ether of Bisphenol A based liquid epoxy resin. Same as Araldite GY 2600 or GY 6010 or Dow DER 331.	11,000-15,000	185-192
<i>Diluted/Modified Liquid Epoxies</i>			
Araldite GY 502	BPA epoxy resin diluted w/ dibutyl phthalate (a non-reactive diluent that increases resiliency of cured product).	2,100-3,100	230-250
Araldite GY 509	BPA liquid epoxy resin diluted w/ an alkyl glycidyl ether (D 027 a mono func. reac. diluent containing C ₈ & C ₁₀ alkyl groups).	500-700	189-200
<i>Flexible Epoxy Resins</i>			
Araldite PY 322	Modified BPA diglycidyl ether flexible epoxy resin. Chemical identity trade secret. The flexibility and toughness in this matl. results in improved impact resis.	2000-5000	317-357
<i>Bisphenol F (Epoxy Novolac) based Epoxies</i>			
Araldite PY 306	Bisphenol F epoxide reactive diluent. Very low viscosity.	1,200-1,800	159-170
Araldite LY 9703	Epoxy phenol novolac resin, EPN [Methane, bis[(2,3-epoxypropoxy)phenyl]]. Lower visc. Bis F resin.	3,000-4,000	160-180
Dow D.E.N. 354	Bisphenol F epoxy resin that is a low molec. wt. member of the Dow Epoxy Novolac family. Features low functionality (only 2.1) and low viscosity. Is very resistant to strong solvents (acetone, CH ₃ OH) or conc. sulfuric acid compared to conv. epoxies.	3900	172
Shell Epon 862	Diglycidyl ether of Bisphenol F based liquid epoxy resin. Is similar to Dow DER 354.	3,000-4,500	166-177
Araldite GY 281	Epoxy phenol novolac resin, EPN. Better chem. resis. esp. to organic solvents than Araldite GY 6010. Low visc., good flexibility.	5,000-7,000	158-175

Table 10. Description of Materials.
Continued

Resins	Description	Viscosity at 25°C, cps	W. P. E (EEW)
<i>Bisphenol F (Epoxy Novolac) based Epoxies</i>			
Araldite GY 308 (GY 302-2)	BPA diglycidyl ether [Phenol, 4,4'-(1-methylethylidene)bis-, polymer w/(chloromethyl)oxirane], w/ epoxy phenol novolac resin. Non-crystallizing, good chem/solvent resis., low visc., excellent mechanicals.	6,500-8,000	173-182
Dow D.E.N. 431	Epoxy phenolic novolac resin with a functionality of 2.2. Same as Araldite EPN 1139	1,100-1,700 @125°F	172-179
Dow D.E.N. 438	High viscosity epoxy phenolic novolac resin with a functionality of 3.6. Same as EPN 1138.	20,000-70,000 @ 125 °F	176-181
<i>Multifunctional Epoxies</i>			
Dow Tactix 556	Semi-solid epoxy novolac w/ a functionality of 2.2 & a lower moisture abs. than many mult-func. epoxies used in advcd. comps. The dicyclopentadiene backbone has extremely low avg. molecular polarity (lower than DEN 431 or 438).	1,000-1,500 @ 85°C or 185°F	220-240
Dow Tactix 742	Semi-solid tri-functional epoxy composed of triglycidyl ether of tris (4-hydroxyphenyl)methane-based epoxy. Tactix 742 has the highest dry Tg of any Tactix resin.	2,860 @ 79°C or 175°F	150-170
Shell Epon 1031	High performance solid epoxy resins w/ functionalities of 3.5 and w/ no amine present. Same as Araldite MT 0163.	Z ₂ - Z ₇	200-240
Shell Epon HPT 1079	A difunctional epoxy based on bisphenol-9-fluorenone w/ a m.p.=74-85°C.	50-70 @ 350°F	240-270
<i>Cycloaliphatic based Epoxies</i>			
Ciba Araldite CY 179	100% 3',4'-Epoxy Cyclohexylmethyl 3,4-Epoxy cyclohexanecarboxylate. Is a low visc., high Tg, brittle alicyclic di-epoxy carboxylate, mp= -37°C(-35°F), mw=252.30. Same as Union Carbide ERL 4221 or UVR 6110.	350-450	131-143
Union Carbide ERL 4205	Contains isomeric mixtures of Bis (2,3-epoxycyclopentyl) ether.	<100 @ 45°C	
Union Carbide ERL 2258	Is a 50/50 blend of Bis(2,3-epoxycyclopentyl) ether (ERL 4205) + Diglycidylether of bisphenol A.		
Union Carbide ERL 4299	100% Bis (3,4-Epoxy Cyclo Hexyl Methyl) Adipate. mp=-25°C(-13°F), mw=366.45	550-750	190-210
Union Carbide ERL 4617	Isomeric mixtures of Bis (2,3-epoxycyclopentyl) ether (ERL 4205) + HOCH ₂ CH ₂ OH. Has extremely high resin modulus = 783 Ksi if cured w/ m-PDA.	80-150	

Table 10. Description of Materials.
Continued

Resins	Description	Viscosity at 25°C, cps	W. P. E (EEW)
<i>Cycloaliphatic based Epoxies</i>			
Ciba CY 9729	3,4-Epoxy cyclohexylmethyl-3,4-epoxycyclohexane carboxylate. Toughened CY 179 material, two phase system, good thermal shock resis., HDT of 132°C. Contains reacted glycol.	400-500	178-192
<i>Reactive Diluents</i>			
Ciba DY 027	Monofunctional epoxy. Alkyl glycidyl ether - alkyl groups are primarily C ₈ and C ₁₀ . Very effective visc. reducer.	5 to 15	215-235
Ciba DY 023	O-Cresyl glycidyl ether - mono functional epoxy - less volatile and better water resis. than RD-1.	5 to 15	175-192
Allied Signal VEctomer 4010	Reactive diluent based on Bis (4-vinylxybutyl) isophthalate w/ a MW = 348.	85	
Allied Signal VEctomer 4020	Reactive diluent based on Bis (4-vinylxymethylcyclohexylmethyl) glutarate w/ a MW = 436.	430	
<i>Other Materials</i>			
THF	Tetrahydrofuran		
Union Carbide Tone 301	Caprolactone polyol crosslinker - hydroxyl equiv. wt. = 98-103.	2250	
OH-term. Udel	Hydroxyl terminated Udel thermoplastic (3 diff. molec. wts. = 2650, 5360, or 8890).		
Imitec	Polyimide sulfone thermoplastic (Imitec)		
Rohm & Haas E2330	Core-shell rubber, EXL-2330.		
Dow D.E.R. 736	Shorter chain polyglycol di-epoxide than D.E.R. 732	30-60	175-205
UCB Ebecryl 639	Epoxy Novolac Acrylate.		
Sartomer SR 297	1,3-Butylene Glycol Dimethacrylate.		
Union Carbide Tone 301	Union Carbide Caprolactone Polyol Crosslinkers. Hydroxyl Equiv. wt. = 98-103.		
Ethylene Glycol			
<i>Cationic Photoinitiators</i>			
Union Carbide Cyracure UVI-6974 or Sartomer CD-1010	Liquid that is 50% Mixed triarylsulfonium hexafluoroantimonate salts & 50% Propylene Carbonate. bp=>200°C(>428°F), sp. gr.=1.4, visc.=21 cps. Is twice as efficient as 6990, therefore only requires half as much.	λ max. (ε)	

Table 10. Description of Materials.
Continued

Cationic Photoinitiators	Description	λ max. (g)
Union Carbide Cyracure UVI -6990 or Sartomer CD-1011	Liquid that is 50% Triaryl Sulfonium hexafluorophosphate salts & 50% Propylene Carbonate solvent. bp=>220°C(>428°F), sp. gr.=1.35, visc.=29 cps.	
Degussa Degacure KI 85	Liquid that is 50% Triaryl sulfonium hexafluorophosphate & 50% propylene carbonate solvent. mp=-54°C, bp= 243°C, sp. gr.= 1.33 g/ml, visc. = 71.6 mPa.s	
3M FX-512	Liquid that is 1-5% Triphenyl sulfonium hexafluorophosphate w/ 48-66% Aromatic sulfonium coproducts & 40% 2(3H) Dihydrofuranone solvent. BP = 204°C, sp. gr. = 1.3.	
Ciba Irgacure 261	(n ⁵ -2,4-Cyclopentadien-1-yl)n ⁶ -isopropylbenzene)-Iron(II) hexafluorophosphate. mp = 85-88°C.	
TCI DPIAsF6	Diphenyliodonium hexafluoroarsenate. MW = 470.03.	
TCI DPIPf6	Diphenyliodonium hexafluorophosphate. MW= 426.08, mp = 146-148°C.	210nm, 17,400 226nm, 16,900
TCI DPITF	Diphenyliodonium triflate. MW = 430.19, mp = 178-179°C.	230nm, 14,900
GE OPPI	(4-Octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI or Octacat), mp = 55 60°C. Soluble in DVE-3, ERL4221 or CY 179, etc.	255nm
Sartomer CD-1012	(2-hydroxytetradecyloxyphenyl) phenyliodonium hexafluoroantimonate	
RP-DW	Diphenyliodonium tetrakis (pentafluorophenylborate)	
RP-SH	Diphenyliodonium tetrakis (pentafluorophenylborate) - made internally	
Midori BBI-101	98% Bis(4-tert-butylphenyl)iodonium fluoroborate. Is a crystalline powder w/ mp = 146-148°C.	238nm, 20,800
Midori BBI-102	98% Bis(4-tert-butylphenyl)iodonium hexafluorophosphate. Is a crystalline powder w/ a mp = 171-174°C.	238nm, 20,000
Midori BBI-103	97% Bis(4-tert-butylphenyl)iodonium hexafluoroantimonate. Is a crystalline powder w/ a mp = 183-185°C.	238nm, 21,200
Midori BBI-105	97% Bis(4-tert-butylphenyl)iodonium triflate. Is a crystalline powder w/ a mp = 162-166°C.	
Midori BDS-105	97% (4-tert-Butylphenyl)diphenylsulfonium triflate. Is an oil.	
Midori TAZ-101	97% 2,4,6-Tris(trichloromethyl)-1,3,5-triazine. Is a crystalline powder w/ a mp = 95-96°C.	220nm, 6585 285nm, 1656
MMES BBI-103A	Diphenyliodonium hexafluoroantimonate, mp = 108-110°C.	210nm, 17,200 225nm, 16,480
MMES DPDS	Diphenyldisulfone. A crystalline powder w/ a mp = 192°C.	

What is claimed is:

1 1. A toughened epoxy resin system mixture composition comprising an epoxy
2 resin, a cationic initiator, and a toughening agent; said cationic initiator having a specific
3 anion selected from the group consisting of a diaryliodonium salt, a triarylsulfonium salt
4 and combinations thereof.

1 2. A toughened epoxy resin system mixture composition in accordance with
2 claim 1 wherein said toughening agent is selected from the group consisting of a
3 thermoplastic, hydroxy-containing thermoplastic oligomer, epoxy-containing
4 thermoplastic oligomer, reactive flexibilizer, rubber, elastomer, and mixtures thereof.

1 3. A toughened epoxy resin system mixture composition in accordance with
2 claim 1 wherein said anion is selected from the group consisting of hexafluoroarsenate
3 (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorophosphate (PF_6^-), boron tetrafluoride
4 (BF_4^-), trifluoromethane sulfonate (CF_3SO_3^-), tetrakis (pentafluorophenylborate),
5 ($\text{B}[\text{C}_6\text{F}_5]_4^-$), tetrakis [3,5-bis(trifluoromethyl) phenyl]borate ($\text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4^-$).

1 4. A toughened epoxy resin system mixture composition in accordance with
2 claim 1 wherein said cationic initiator comprises a diaryliodonium salt.

1 5. A toughened epoxy resin system mixture composition in accordance with
2 claim 1 wherein said cationic initiator comprises a triarylsulfonium salt.

1 6. A toughened epoxy resin system mixture composition in accordance with
2 claim 1 wherein said toughened epoxy resin system mixture composition includes
3 fibers selected from the group consisting of carbon, graphite, glass, aramid ,
4 polyethylene and mixtures thereof.

1 7. A toughened epoxy resin system mixture composition in accordance with
2 claim 1 wherein said toughened epoxy resin system mixture composition includes
3 fillers selected from the group consisting of clay, minerals, glass particles, silica
4 particles, alumina particles, aluminum powder and mixtures thereof.

1 8. A toughened epoxy resin system mixture composition in accordance with
2 claim 1 wherein said cationic initiator is about 0.25 to about 10 pph of said toughened
3 epoxy resin system mixture composition.

1 9. A method for making a toughened epoxy resin system comprising the
2 following steps:

3 Step 1. providing a toughened epoxy resin system mixture composition
4 comprising an epoxy resin, a cationic initiator, and a toughening agent; said cationic
5 initiator is selected from the group consisting of a diaryliodonium salt of a specific anion,
6 a triarylsulfonium salt of a specific anion and combination thereof; and

7 Step 2. exposing said toughened epoxy resin system to high energy ionizing
8 radiation for a period of time sufficient to cure said toughened epoxy resin system
9 forming a cured toughened epoxy resin system.

1 10. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 9 wherein said toughening agent is selected from the group
3 consisting of a thermoplastic, hydroxy-containing thermoplastic oligomer, epoxy-
4 containing thermoplastic oligomer, reactive flexibilizer, rubber, elastomer, and mixtures
5 thereof.

1 11. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 9 wherein said anion is selected from the group consisting of
3 hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorophosphate (PF_6^-
4), boron tetrafluoride (BF_4^-), trifluoromethane sulfonate (CF_3SO_3^-), tetrakis
5 (pentafluorophenylborate), ($\text{B}[\text{C}_6\text{F}_5]_4^-$), tetrakis [3,5-bis(trifluoromethyl) phenyl]borate
6 ($\text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4^-$).

1 12. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 9 wherein said cationic initiator comprises a diaryliodonium
3 salt.

1 13. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 9 wherein said cationic initiator comprises a triarylsulfonium
3 salt.

1 14. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 9 wherein said high energy ionizing radiation has a dose rate
3 greater than about 0.75 kilogray/sec.

1 15. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 9 wherein said high energy ionizing radiation has a dose rate
3 equal to or greater than about 100 kilogray/sec.

1 16. A method for making a toughened epoxy resin system comprising the
2 following steps:

3 Step 1. providing a toughened epoxy resin system mixture composition
4 comprising an epoxy resin, a cationic initiator, and a toughening agent; said cationic
5 initiator is selected from the group consisting of a diaryliodonium salt of a specific anion,
6 a triarylsulfonium salt of a specific anion and combination thereof; and

7 Step 2. exposing said toughened epoxy resin system to high energy radiation
8 from the sun for a period of time sufficient to cure said toughened epoxy resin system
9 forming a cured toughened epoxy resin system.

1 17. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 16 wherein said toughening agent is selected from the group
3 consisting of a thermoplastic, hydroxy-containing thermoplastic oligomer, epoxy-
4 containing thermoplastic oligomer, reactive flexibilizer, rubber, elastomer, and mixtures
5 thereof.

1 18. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 16 wherein said anion is selected from the group consisting of
3 hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorophosphate
4 (PF_6^-), boron tetrafluoride (BF_4^-), trifluoromethane sulfonate (CF_3SO_3^-), tetrakis
5 (pentafluorophenylborate), ($\text{B}[\text{C}_6\text{F}_5]_4^-$), tetrakis [3,5-bis(trifluoromethyl) phenyl]borate
6 ($\text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4^-$).

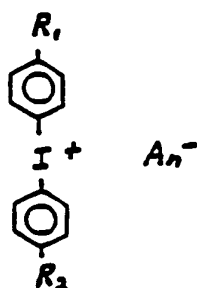
1 19. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 16 wherein said cationic initiator comprises a diaryliodonium
3 salt.

1 20. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 16 wherein said cationic initiator comprises a triarylsulfonium
3 salt.

1 21. A method for making a toughened epoxy resin system mixture composition
2 in accordance with claim 16 wherein said high energy radiation is ultraviolet radiation.

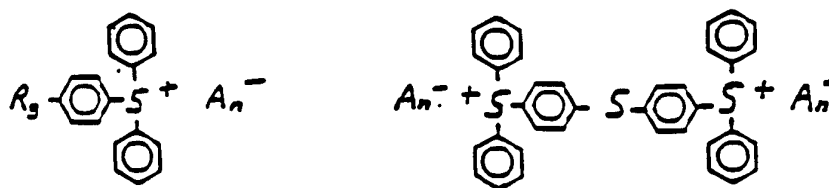
1 22. A method for curing an epoxy resin system comprising the following steps:
2 Step 1. providing a blend of an epoxy resin system, said epoxy resin system
3 comprising an epoxy resin and a cationic photoinitiator, said epoxy resin being selected
4 from the group consisting of:
5 glycidyl ethers of bisphenol A, epoxy phenolic novolacs, epoxy cresol novolacs,

6 bisphenol F epoxies, tetraglycidyl ether of tetrakis (4-hydroxyphenyl) ethane,
 7 diglycidyl ether of 9, 9- bis (4-hydroxyphenyl) fluorene, glycidyl ether of the
 8 condensation product of dicyclopentadiene and phenol, triglycidyl ether of tris
 9 (hydroxyphenyl) methane, 3',4'-epoxycyclohexylmethyl 3,4-
 10 epoxycyclohexanecarboxylate, diglycidylester of hexahydrophthalic anhydride, bis
 11 (3,4-epoxycyclohexylmethyl) adipate, isomeric mixture of bis (2,3-
 12 epoxycyclopentyl) ether, isomeric mixture of bis (2,3-epoxycyclopentyl) ether
 13 reacted with ethylene glycol, isomeric mixture of bis (2,3-epoxycyclopentyl) ether
 14 blended with a bisphenol A based glycidyl ether, and mixtures thereof,
 15 said cationic photoinitiator being selected from the group consisting of: diaryliodonium
 16 salts, triarylsulfonium salts, and mixtures thereof, said diaryliodonium salts have the
 17 following formula:



26 where R_1 and R_2 are selected from the group consisting of: H, methyl, ethyl, n-
 27 propyl, isopropyl, n-butyl, tert-butyl, Cl, Br, $\text{OC}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CH}(\text{CH}_3)\text{C}_n\text{H}_{2n+1}$,
 28 $\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CH}(\text{OH})\text{C}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CO}_2\text{C}_n\text{H}_{2n+1}$,
 29 $\text{OCH}(\text{CH}_3)\text{CO}_2\text{C}_n\text{H}_{2n+1}$, $\text{OCH}(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_n\text{H}_{2n+1}$, and mixtures thereof, where n is
 30 an integer between 0 and 18 and An^- is an anion selected from the group consisting
 31 of: hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-),
 32 hexafluorophosphate (PF_6^-), boron tetrafluoride (BF_4^-), trifluoromethane sulfonate

(CF₃SO₃⁻), and tetrakis (pentafluorophenylborate) (B[C₆F₅]₄⁻), and mixtures thereof and said triarylsulfonium salts have the following formulas:



where R₃ is selected from the group consisting of: H, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, phenylsulfide (PhS), and phenoxy (PhO),

A_n⁻ is an anion selected from the group consisting of:

hexafluoroarsenate (AsF₆⁻), hexafluoroantimonate (SbF₆⁻), hexafluorophosphate (PF₆⁻), boron tetrafluoride (BF₄⁻), trifluoromethane sulfonate (CF₃SO₃⁻), and tetrakis (pentafluorophenylborate) (B[C₆F₅]₄⁻), and mixtures thereof; and

Step 2. irradiating said blend with ionizing radiation to form a cross-linked epoxy resin polymer.

23. A method in accordance with claim 22 wherein said ionizing radiation is selected from the group consisting of: electron beam radiation, x-ray radiation, gamma-ray radiation, and combinations thereof.

24. A cross-linked epoxy resin polymer made by a method in accordance with claim 22.

25. A method for curing an epoxy resin system comprising the following steps:

2 **Step 1. providing a blend of an epoxy resin system, said epoxy resin system**
 3 **comprising epoxy resins and a cationic photoinitiator, said epoxy resins being a blend of**
 4 **a semi-solid epoxy, triglycidyl ether of tris (hydroxyphenyl) methane, and a low viscosity**
 5 **epoxy, glycidyl ether of bisphenol A, said cationic photoinitiator being (4-octyloxyphenyl)**
 6 **phenyliodonium hexafluoroantimonate; and**

7 **Step 2. irradiating said blend of an epoxy resin system with ionizing radiation to**
 8 **form a crosslinked epoxy resin polymer.**

1 **26. A method for curing an epoxy resin system comprising the following steps:**

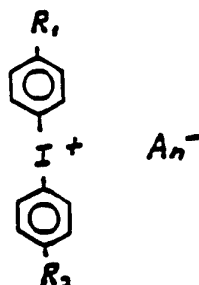
2 **Step 1. providing a blend of an epoxy resin system, said epoxy resin system**
 3 **comprising epoxy resins and a cationic photoinitiator, said epoxy resins being a blend of**
 4 **a glycidyl ether of the condensation product of dicyclopentadiene and phenol, and a low**
 5 **viscosity epoxy, glycidyl ether of bisphenol A, said cationic photoinitiator being**
 6 **(4-octyloxyphenyl) phenyliodonium hexafluoroantimonate; and**

7 **Step 2. irradiating said blend of an epoxy resin system with ionizing radiation to**
 8 **form a crosslinked epoxy resin polymer.**

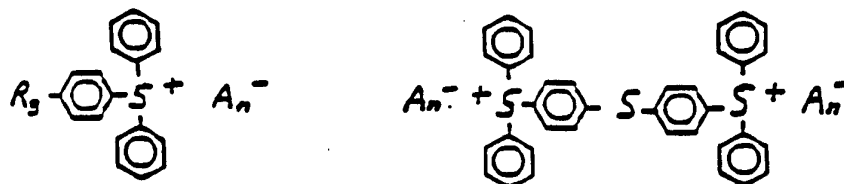
1 **27. An epoxy resin system comprising a blend of an epoxy resin and a cationic**
 2 **photoinitiator, said epoxy resin being selected from the group consisting of:**

3 **glycidyl ethers of bisphenol A, epoxy phenolic novolacs, epoxy cresol novolacs,**
 4 **bisphenol F epoxies, tetraglycidyl ether of tetrakis (4-hydroxyphenyl) ethane,**
 5 **diglycidyl ether of 9, 9- bis (4-hydroxyphenyl) fluorene, glycidyl ether of the**
 6 **condensation product of dicyclopentadiene and phenol, triglycidyl ether of tris**
 7 **(hydroxyphenyl) methane, 3',4'-epoxycyclohexylmethyl 3,4-**
 8 **epoxycyclohexanecarboxylate, diglycidylester of hexahydrophthalic anhydride, bis**
 9 **(3,4-epoxycyclohexylmethyl) adipate, isomeric mixture of bis (2,3-**
 10 **epoxycyclopentyl) ether, isomeric mixture of bis (2,3-epoxycyclopentyl) ether**

reacted with ethylene glycol, isomeric mixture of bis (2,3-epoxycyclopentyl) ether blended with a bisphenol A based glycidyl ether, and mixtures thereof, said cationic photoinitiator being selected from the group consisting of: diaryliodonium salts, triarylsulfonium salts, and mixtures thereof, said diaryliodonium salts have the following formula:



where R_1 and R_2 are selected from the group consisting of: H, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, Cl, Br, $\text{OC}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CH}(\text{CH}_3)\text{C}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CH}(\text{OH})\text{C}_n\text{H}_{2n+1}$, $\text{OCH}_2\text{CO}_2\text{C}_n\text{H}_{2n+1}$, $\text{OCH}(\text{CH}_3)\text{CO}_2\text{C}_n\text{H}_{2n+1}$, $\text{OCH}(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_n\text{H}_{2n+1}$, and mixtures thereof, where n is an integer between 0 and 18 and An^- is an anion selected from the group consisting of: hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorophosphate (PF_6^-), boron tetrafluoride (BF_4^-), trifluoromethane sulfonate (CF_3SO_3^-), and tetrakis (pentafluorophenylborate) ($\text{B}[\text{C}_6\text{F}_5]_4^-$), and mixtures thereof and said triarylsulfonium salts have the following formulas:



38 where R_3 is selected from the group consisting of: H, methyl, ethyl, n-propyl,
39 isopropyl, n-butyl, tert-butyl, phenylsulfide (PhS), and phenoxy (PhO),
40 An⁻ an anion selected from the group consisting of:
41 hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorophosphate
42 (PF_6^-), boron tetrafluoride (BF_4^-), trifluoromethane sulfonate ($CF_3SO_3^-$), and
43 tetrakis (pentafluorophenylborate) ($B[C_6F_5]_4^-$), and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12302**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : Please See Extra Sheet.

US CL : 522/31, 79, 81, 83, 129, 146, 170

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)

U.S. : 522/25, 31, 79, 81, 83, 129, 146, 170

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,318,766 (SMITH) 09 March 1982, Abstract, columns 3-12, column 13, lines 9-17, column 14, lines 35-40.	1-15
X	US, A, 4,394,403 (SMITH) 19 July 1983, Abstract, column 2, line 35, to column 4, line 9, column 4, line 45, to column 6, line 20, column 6, line 64, to column 7, line 2, column 7, lines 32-39, column 7, line 67, to column 8, line 8.	1-15
X	US, A, 4,256,828 (SMITH) 17 March 1981, Abstract, columns 3-12, column 13, lines 9-16, column 14, lines 36-47.	1-15

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
16 OCTOBER 1996

Date of mailing of the international search report

24 OCT 1996

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INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US96/12302

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,201,640 (WATT) 06 May 1980, Abstract, column 2, lines 54-68, column 5, line 18, to column 6, line 36, column 7, lines 12-17, and Example 2.	1-15
X	US, A, 4,593,051 (KOLESKE) 03 June 1986, Abstract, column 4, line 9, to column 9, line 62, column 13, line 8, to column 14, line 31, column 15, lines 49-56, column 16, lines 29-36.	1-15
X --- Y	US, A, 5,328,940 (ZIMMER) 12 July 1994, Abstract, column 2, line 34, to column 5, line 47.	1-8 --- 9-15
X --- Y	US, A, 5,302,438 (KOMAMURA ET AL) 12 April 1994, Abstract, column 6-7.	1-7 --- 8-15
X	US, A, 5,268,489 (KOLESKE ET AL) 07 December 1993, Abstract, columns 14-16,	1-7, 9-13 ----- 8, 14, 15
X	Kobunshi Ronbunshu, Vol. 44, No. 10, issued 1987, N. Okada et al, "Electron Beam Curing of Bisphenol-A Type Epoxy Resin", pages 1-14, see entire document.	1-5, 8-15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12302

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-15

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12302

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

C08F 2/54, 4/14, 4/24; C08J 3/28; C08K 3/04, 3/08, 3/36, 3/40, 5/01, 5/20; C08L 7/00, 9/00, 63/00, 63/02, 63/04, 75/04, 77/00, 81/02, 81/06, 83/04.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-15, drawn to an epoxy composition and method of curing the composition using ionizing radiation.

Group II, claim(s) 16-21, drawn to a method of curing the epoxy composition using energy from the sun.

Group III, claim(s) 22-24, drawn to a method of curing the specified epoxy resin using ionizing radiation and the resulting product.

Group IV, claim(s) 25, drawn to a method of curing the specified epoxy resin using ionizing radiation.

Group V, claim(s) 26, drawn to a method of curing the specified epoxy resin using ionizing radiation.

Group VI, claim(s) 27, drawn to an epoxy resin system.

The inventions listed as Groups I-VI do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The claims of Group I recite a composition and a method of curing the composition. The method claims of Group II lack the same technical feature because the composition must be exposed to high energy radiation from the sun while the composition of Group I may be exposed to any form of high energy ionizing radiation. The claims of Groups III-V require different technical features because each group of claims recites a specific species of epoxy composition which is encompassed by but not required by the claims of Group I. The claims of group VI do not require the technical features of a toughening agent in the composition or of the radiation curing required in Group I.