Final Report

NAG-1-1939

THE DESIGN AND SYNTHESIS OF EPOXY MATRIX COMPOSITES CURABLE BY ELECTRON BEAM INDUCED CATIONIC POLYMERIZATION

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SUMMARY

Several new series of novel, high reactivity epoxy resins are described which are designed specifically for the fabrication of high performance carbon fiber reinforced composites for commercial aircraft structural applications using cationic UV and e-beam curing. The objective of this investigation is to provide resin matrices which rapidly and efficiently cure under low e-beam doses which are suitable to high speed automated composite fabrication techniques such as automated tape and tow placement. It was further the objective of this work to provide resins with superior thermal, oxidative and atomic oxygen resistance.

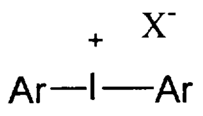
BACKGROUND

At the present time, two of the major impediments to the use of high performance composites are their high cost and difficult and time consuming processing techniques.. Both of these impediments are interrelated. Currently, composites are fabricated using techniques that are neither rapid, nor suitable for automation. These include complex hand lay-up and preforming processes, as well as long devolatilization and thermal curing cycles involving high temperatures. In this laboratory, we are attempting to solve these problems by introducing new chemistry and processing techniques to the field of high performance composites that will markedly change the way in which composites will be fabricated in the future. We anticipate that these improvements will have a major impact on both the cost and range of uses for high performance composites. Specifically, we are attempting to develop new materials that upon e-beam cure will meet the mechanical requirements as detailed in Boeing specification document BMS 8256 directed towards structural uses in commercial aircraft.

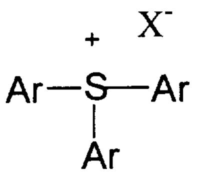
The use of electron beam (e-beam) radiation to carry out rapid, pollution free, low energy crosslinking polymerizations (curing) make it a highly attractive technique replacing complex, time-consuming thermal cures for many applications including composite fabrication.[1] "E-beam curing" as it is called has been applied chiefly to multifunctional monomers polymerizable by free radical mechanisms, i.e. monomers such as unsaturated polyesters, and multifunctional epoxy acrylates and methacrylates. Although these monomers have been employed for the fabrication of composites,[2,3,4,5,6,7] the thermal and mechanical properties of such composites are notably deficient. Epoxy resins are the most commonly used monomers as composite matrices due to their excellent mechanical properties and thermal and chemical resistance. However, attempts to carry out the e-beam induced polymerization of epoxy monomers have met with little success.

In three recent publications from this laboratory[8,9,10] we have described the results of investigations partially conducted under NASA sponsorship (SBIR program) that have led to the development of electron-beam initiated cationic polymerization as a fast, efficient method for the fabrication of epoxy resin matrix carbon fiber reinforced composites. Although direct e-beam irradiation is highly inefficient for the polymerization of epoxy resins, it has been discovered in this laboratory that when irradiation is carried out in the presence of certain onium salts, facile cationic polymerization takes place. It was demonstrated that using this technology, the polymerization of certain epoxy resins could be carried out using e-beam doses less than those employed for the polymerization of acrylates. Thick (1/4-1/2 inch) carbon fiber reinforced composites were fabricated using a 1 second e-beam exposure that had good mechanical and thermal properties. The low doses and the high rate of cure of these epoxy resins are potentially compatible with high-speed automated composite fabrication techniques.

The most effective onium salts for cationic e-beam curing are those that we have previously developed[11] and described for photoinduced cationic polymerizations namely: diaryliodonium (**I**) and triarylsulfonium salts (**II**). The general structures of these two classes of onium salts are depicted below.



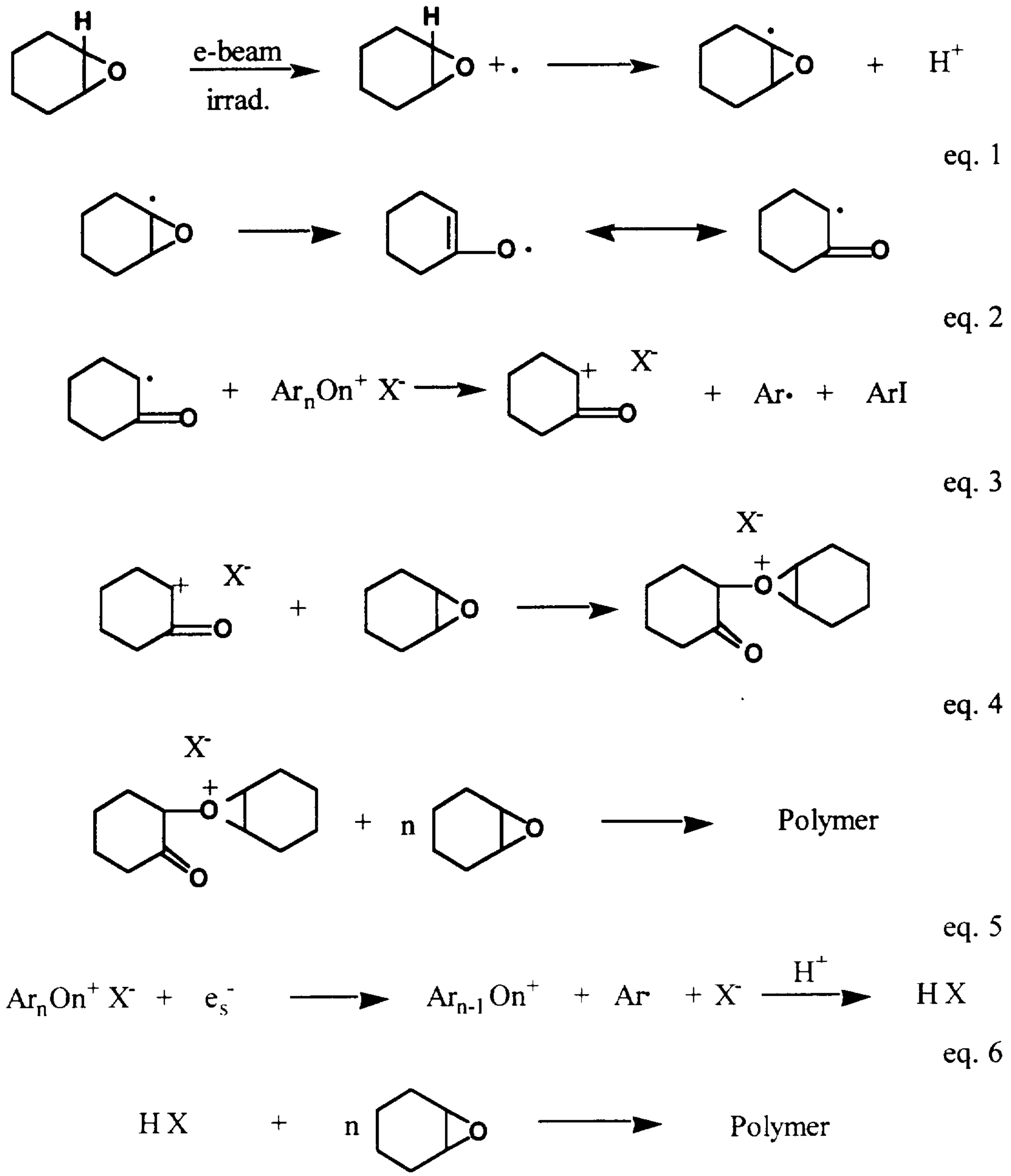
I



II

The mechanism that we propose for the e-beam induced cationic polymerization of epoxide monomers is shown in Scheme 1.[10]

Scheme 1



eq. 7

In the above scheme, the epoxy resin is represented by cyclohexene oxide. The reason for the use of this model compound will be given later in this report. The primary interaction of e-beam radiation takes place with the epoxy resin to generate free radical species (eqs. 1 and 3). Then, these free radicals can interact with the onium salt to cause its reduction (eq. 3). In subsequent reactions, the cationic species produced initiate polymerization (eqs. 4 and 5). During e-beam irradiation, solvated electrons are also produced which can reduce onium salts (eq. 6) resulting in polymerization (eq. 7). Consideration of the above mechanistic scheme led to three important conclusions. First, since the reduction of the onium salt is the crucial step in the mechanism, the reduction potential of the onium salt is a key factor in the generation of the catalytically active species. We have found that diaryliodonium salts with low reduction potentials are the best accelerators in e-beam induced cationic polymerizations. Second, the reactivity of the propagating cationic species depends markedly on the character of the counterion. Accordingly, diaryliodonium salts bearing the least nucleophilic anion, SbF_6^-, are the most active. Thirdly, the epoxy resin participates in the overall process both by interacting with the e-beam irradiation, and most importantly, undergoing polymerization. Therefore, the structure and reactivity of the epoxy monomer is crucial to the success of e-beam induced cationic polymerizations conducted for practical applications.

In particular, very rapid e-beam curing is required for automated composite fabrication methods such as tape and tow placement[12] in which a continuous resin impregnated carbon fiber tow or ribbon of several tows (a tape) is dispensed through a heated head and is wound onto a mandrel or fixture. Coincident with the winding operation, the cure would be initiated by impinging an e-beam onto the mandrel or fixture at the point of contact with the tow. This would require a rather low energy source of e-beam irradiation since one thin layer would be cured at a time. If the polymerization was rapid and efficient, the cure of high performance composites with complex three-dimensional structures could be accomplished as fast as the winding process itself. Further, if the monomer is sufficiently reactive, long thermal postcure cycles could also be avoided. A number of small, compact e-beam sources are currently being developed by several companies including Energy Sciences, Wilmington, MA, American International Technologies, Inc. Torrance, CA. and Oberflächenmodifizierung e.V. Leipzig, Germany. Such low power devices are self-shielded and do not require additional shielding to comply with OSHA health and safety requirements.

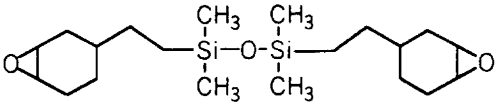
It was also the goal of this research to further the development of both the epoxy resins and the cationic e-beam curing process itself to provide materials compatible with rapid, automated composite fabrication techniques, in particular, for the tow placement-filament winding methods. As part of the goal, novel e-beam curable resins were targeted to meet the mechanical requirements as detailed in Boeing specification document BMS 8256 directed towards structural uses in commercial aircraft.

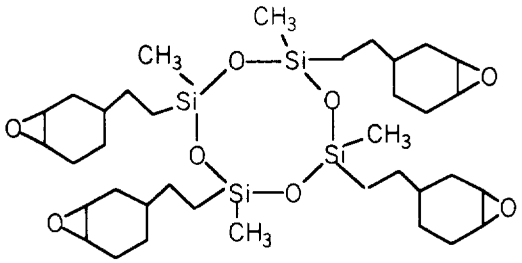
Results and Discussion

Work done under NAG-1-1939 is briefly summarized in this final report.

Epoxy Monomer and Oligomer Design

During initial evaluations, it was observed that while cationic e-beam polymerizations (curing) could be carried out using virtually any epoxy resin, provided that an onium salt accelerator is also used, there was a marked difference in the reactivities of those resins. Glycidyl ethers and glycidyl esters polymerize extremely sluggishly while cycloaliphatic epoxy resins are considerably more reactive. Most of these resins require a thermal postcure to complete the polymerization. All commercially available resins required unacceptably high e-beam doses for cure and all possess too low a reactivity for use in automated composite fabrication processes. Further, it should be pointed out that commercially available epoxy monomers were designed for use together with various hardeners such as amines or anhydrides. They were not designed or intended for use in cationic ring-opening polymerizations. It was necessary, therefore, to tailor more reactive epoxy monomers specifically for use in e-beam curing applications. One class of epoxy monomers which display rates of e-beam cure which are greater than acrylate resins are epoxy silicones.[10] The structures of two of these monomers that have been prepared and investigated previously in this laboratory are shown below.[13]



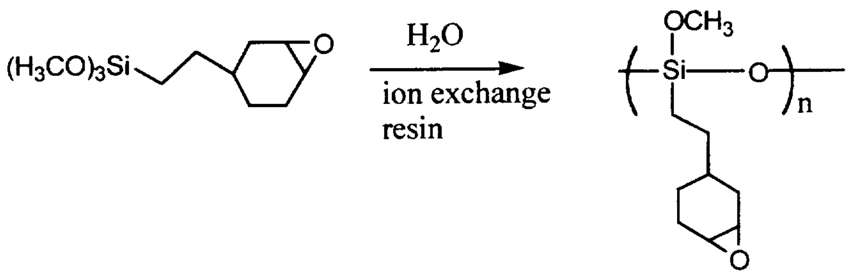


(PC 1000) **III** **IV**

Monomers **III** and **IV** contain siloxane linkages to which are attached highly reactive epoxycyclohexyl groups. The polymers derived from these monomers by UV induced cationic polymerization have glass transition temperatures (T_gs) as high as 180-200 °C and thermal degradation temperatures exceeding 300-350 °C in air. The high reactivity of these monomers can be attributed to two factors. First, both monomers bear epoxycyclohexane groups which are strained and consequently, highly reactive. Second, the monomers do not contain other Lewis basic functional groups that can compete with and interfere in the cationic ring-opening polymerization of the epoxy moieties. Although monomers **III** and **IV** have many of the properties including the high reactivity required for e-beam curing applications, they do have the drawback that they are comparatively low viscosity liquids. For this reason, they are unsuited for the tow and tape placement fabrication techniques described above that require high viscosity, semisolid resins.

Based on the above structure-reactivity relationships, in this program we have prepared and evaluated several new classes of highly reactive epoxy resins for cationic e-beam curing. Besides high reactivity, the other requirements which these resins must include are: excellent mechanical properties (as per BMS 8256), good thermal resistance, good solvent and chemical resistance and the ability to be fabricated into impregnated fiber tows and woven cloth with the desired tack and drape properties. Further, the novel resins we have designed and synthesized were prepared using synthetic methods that were amenable for commercial scale-up.

Recently, we have described the preparation of a new class of high molecular weight silicone epoxy resins. These materials are prepared using the route depicted in equations 8 and 9. Starting with the commercially available (4-trimethoxysilylethyl)-1,2-epoxycyclohexane **V**, hydrolysis followed by condensation in the presence of a basic ion exchange resin results in silicone epoxy resin with the generalized structure **VI**.



V **VI** eq. 8

Surprisingly, this reaction results in the production of oligomers with degrees of polymerization up to approximately 12. Despite the fact that **V** is trifunctional, the reaction proceeds without the formation of gel and to approximately 85% consumption of the methoxy groups. Thus, there are some cyclic structures present in the resins as well as linear units. Figure 1 shows the increase in the molecular weight with time as hydrolysis and condensation proceed in refluxing isopropanol.

The oligomeric resins **VI** are colorless, clear liquids or semisolids depending on their molecular weights. Molecular weight control can be exerted by both the amount of water added and the reaction time. Quantitative removal of the ion exchange resin catalyst can be achieved by simple filtration. This is important, since basic materials strongly inhibit the cationic polymerization of these as well as other cationic e-beam curable resins.

Successful scale-up of these resins has been achieved on the multi-killogram scale at the Polyset Company in Mechanicville, New York. As a result, the new silicone epoxy resins are now commercially available in developmental quantities from the Polyset Company as PC-2000 resins. Scale-up and further development is continuing to provide a broader range of these materials, to optimize process conditions and to lower their cost.

Previously, we have shown that the reactivity of monomers in cationic e-beam induced polymerizations can be predicted based on their behavior under cationic UV curing conditions. Resins **VI** display outstanding reactivity when UV cured in the presence of triarylsulfonium or diaryliodonium salt photoinitiators. The photopolymerization of one of these resins is depicted in Figure 2. Exceedingly rapid polymerization proceeds to high conversion after a short induction period. These oligomers exhibit reactivities that are comparable to acrylates in free radical polymerizations. Furthermore, the cationic UV cure of the new resins is not inhibited by oxygen. Preliminary results in the e-beam cure of these resins are also very encouraging. Further, these resins can be thermally cured using typical diaryliodonium salt photoinitiators as shown in Figure 3. It may be noted that the polymerization displays a threshold and that, once initiated, it is exceedingly rapid.

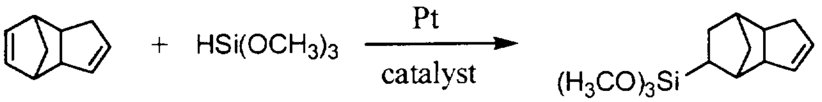
The mechanical properties of UV and e-beam cured **VI** (PC-2000) resins are impressive and this can be regarded as a breakthrough in epoxy resin performance in all areas. Shown in Figure 4 is the thermomechanical analysis curves for the modulus and tan δ versus temperature for these materials. A similar study is shown in Figure 5 for low molecular weight **VI** resin. It may be noted in both cases that the modulus does not change significantly over the entire measured temperature range. In contrast, conventional epoxy resins display a catastrophic loss of modulus in the temperature range of 200 - 250 °C. The tan δ peak in this figure is very small and does not represent a "true" T_g transition. No glass transition temperature could be detected by DSC measurement techniques up to 300 °C. Curing by either e-beam or UV techniques results in colorless, transparent, brittle, crosslinked resins. The cured resins are insoluble in all solvents. The use of these resins in future structural composite applications will require the development of toughening agents to reduce brittleness. Figure 6 shows a plot of the thermal expansion coefficient as a function of temperature for these resins. The linearity of this curve thoughout the entire temperature range is very unusual and is more indicative of a metal than an organic polymer. A summary of the mechanical behavior for three different molecular weight versions of resin **VI** is shown in Table 1.

In an uncured state, **VI** resins are soluble in a wide variety of common solvents including acetone, MEK and isopropanol. They are also compatible with a variety of commercially available epoxy resins as well and can be blended. This makes possible the facile impregnation of the resins into a wide variety of fibrous and particulate reinforcing agents. Due to the presence of the residual methoxysilane groups in the resin, the adhesion of the resins to most substrates is excellent. The resins, in analogy with similar monomers **III** and **IV**, are expected to possess excellent oxygen plasma resistance for use in low earth orbit.

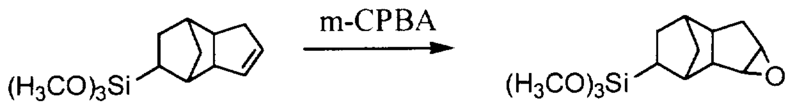
Additional work is underway to further modify the above resins in a number of ways. First, the incorporation of other substituted trialkoxysilanes into the resins as a means to modify their structure and reduce brittleness is being attempted. We are also using dialkyl and diaryldialkoxysilanes to increase the linearity of the resins to improve flexibility. Lastly, resins with blocky structures of reactive and non-reactive repeating units are being prepared with the aim of developing materials with different mechanical properties.

The principal investigator (J.V. Crivello) has fostered direct contacts between Polyset Company and Richard Moulton of Applied Polaramics for future development of the new resins in aerospace applications. Moulton has been supplied with resins and is currently engaged in formulation development. Commercial development of the resins is continuing with many additional applications as well.

Efforts in this laboratory have also proceeded toward the extension of the chemistry shown above to the design of other monomers and oligomers. For example, the regioselective hydrosilation of dicyclopentadiene with trimethoxysilane yields compound **VII**.



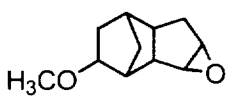
VII eq. 9



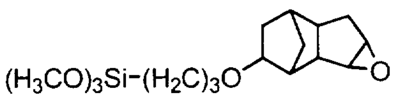
VIII eq. 10

Subsequent epoxidation gives **VIII**. The base catalyzed hydrolysis and condensation of **VIII** can be carried out under the same reaction conditions as depicted in equation 8 to give an oligomeric resin that is a semi-solid. Cationic photopolymerization of both **VIII** and the resulting resin were carried out. The cationic photopolymerizations of these materials were rapid and efficient.

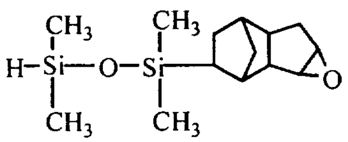
In a similar fashion, several other epoxides based on dicyclopentadiene were prepared. The structures of these materials are given below.



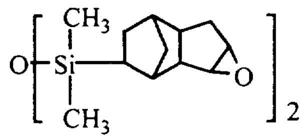
methoxyDCPDO



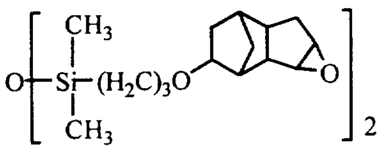
TMSDCPDO



TMDSDCPDO



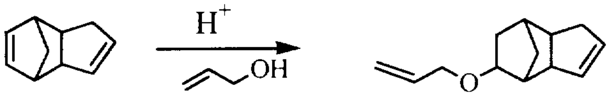
TMDSDDCPDO



TMSAllylDCPDO

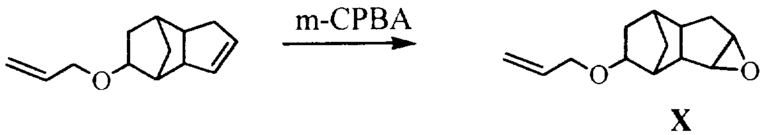
Figure 8 shows a comparative real-time infrared spectroscopic study of the photopolymerization of **VIII** along with the polymerization of two related compounds we have prepared based on dicyclopentadiene. The polymerizations of these compounds are very rapid due to the high strain of the cyclopentene oxide group that is present in all the compounds. Figure 9 depicts the polymerization of a monofunctional and two difunctional monomers based on dicyclopentadiene along with **III** (PC-1000). PC-1000 is more reactive that the dicyclopentadiene monomers probably due to the greater steric hindrance in the latter compounds.

Resins based on dicyclopentadiene are very interesting and have potentially interesting mechanical properties due to their very stiff cores. For this reason, we have continued to investigate the synthesis and properties of other such resins as well. Dicyclopentadiene is an inexpensive substrate and it is readily functionallized using simple, straightforward reaction chemistry. For example, the reaction of dicyclopentadiene with allyl alcohol takes place readily in the presence of an acid catalyst to yield compound **IX**.



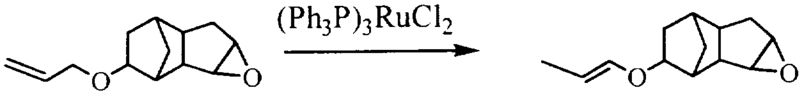
IX eq. 11

IX can be directly and regioselectively epoxidized to give **X**.



X eq. 11

Catalytic isomerization of the allylic double bond of **X** using tris(triphenylphosphineruthenium(II) dichloride gives the hybrid monomer **XI** which bears both cationically polymerizable epoxide and vinyl ether groups.



XI eq. 12

Hybrid monomer, **XI**, is a colorless, low viscosity liquid monomer. Due to the presence of both stereo and geometric isomers, **XI** does not crystallize even at low temperatures. As shown in Figure 5, the simultaneous photoinitiated cationic polymerizations of the 1-propenyl ether and epoxide groups of **XI** take place rapidly and efficiently to give a crosslinked matrix. The presence of the two reactive functional groups in this molecule gives rise to a synergistic interaction that increases the rate of the epoxide polymerization.

Conclusions

Several new classes of rapidly curing silicone-epoxy resins have been developed that display high reactivity in photoinitiated and e-beam initiated cationic polymerization. Several of these resins also possess outstanding thermal and mechanical properties. We believe that these resins represent a breakthrough in materials for aerospace applications. Preliminary experiments with carbon fiber reinforced composites confirm this conclusion. At the present time, several of these new resins are under commercial development and are available in development quantities. Work is continuing at Applied Polaramics to develop practical formulations for aerospace applications.

ACKNOWLEDGEMENT

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