FLUORINATED EPOXY RESINS WITH HIGH GLASS TRANSITION TEMPERATURES

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ABSTRACT

Easily-processed liquid resins of low dielectric constants and high glass transition temperatures are useful for the manufacture of certain composite electronic boards. That combination of properties is difficult to acquire when dielectric constants are below 2.5, glass transition temperature are above 200°C and processability is of conventional practicality. A recently issued patent (U.S. 4,981,941 of Jan. 1, 1991) teaches practical materials and are the culmination of 23 years of research effort and 15 patents owned by the Navy in the field of fluorinated resins of several classes. In addition to high fluorine content, practical utility has been emphasized.

INTRODUCTION

The lowest dielectric constants obtainable with solid polymeric materials are just below 2.0, and these are fluoropolymers which have inconvenient processing characteristics for the production of composite structures. A combination of properties which include dielectric constants around 2.5 ± 0.2, convenient processability due to neat liquid solidification, and glass transition temperatures above 200°C can now be obtained with fluorinated epoxy resins and mixed fluoroanhydride curing agents. Commercial facilities for the production of these resins in quantity exist and await sufficient demand to provide the potential markets. The most obvious and immediate market is the electronic printed circuit or composite component board manufacture in which the low dielectric constants would enhance performance and the high glass transition temperatures would aid construction.

MATERIALS

Fluoroepoxy Resins

The synthesis of heavily fluorinated epoxy resins with convenient processing characteristics was undertaken at the Naval Research Laboratory in 1968 and effective materials were in hand in the early 1970's (1,2). Several basic materials patents were generated regarding the fluoroepoxies (3,4) as well as fluoropolymurethanes (5) and fluoroacrylics (6). In this presentation the discussion will be confined to the fluoroepoxies and means of producing high glass transition temperature versions which is accomplished by the proper selection of curing agents and processes.

Curing Agents

Since the dielectric constant of a polymer is roughly inversely proportional to the fluorocarbon content, it is desirable to have fluorine in the curing agent as well as the resin. However, the glass transition temperature also has an inverse relationship to the fluorine content and since the dielectric constant and glass transition temperature both fall with increasing fluorine, it is necessary to offset the declining glass transition temperature with an additional structural factor. An effective factor for this is the crosslink density which is controlled largely by the functionality of the curing agent. The glass transition temperature increases with increasing crosslink density while the dielectric constant is not affected.

These considerations suggest anhydride curing agents as the materials of choice and we have patented several fluorinated versions (7). There is at least one fluorinated diianhydride that is commercially available, and the dianhydrides are particularly effective for raising glass transition temperatures. However,
they always have very high melting points, are usually of limited solubility in the resins, and cause premature gelation of the resin system if forced into compatibility by heating. On the other hand, the monoanhydrides, including fluoro varieties, are often low melting, convenient materials. The dianhydrides will often dissolve to a limited extent in the molten monoanhydrides, and this fact offers a practical means by which a relatively high glass transition resin can be obtained. Thus, the dianhydride is dissolved into the monoanhydride and upon sudden cooling, a glass is obtained which may be dissolved at will in the resin of choice. When the lowest possible dielectric constants are required, all of the components may have fluorocarbon in the molecular structures.

Catalysts

Anhydride-cured epoxy resins, whether fluorinated or not, require minimum cure temperatures of about 80°C and it is common that final temperatures of about 150°C are employed. The gel times of such systems are strongly influenced by the type and quantity of catalyst used and the quarternary ammonium salts are often the catalysts of choice. Very small quantities (about 0.1% of resin mass) are commonly used and small changes in quantity can have large reaction rate effects. For a practical manufacturing technique the exact compositions of the resin must be derived empirically although this is not a difficult, or impossible, determination when the mixed monoanhydride-dianhydride system is employed.

Solvents

It is not necessary to employ a solvent in the production of a fiber filled composite or circuit board since the neat liquids are often of sufficiently low viscosity to infiltrate effectively. Because of the fluorocarbon content they also have low surface tensions and are thus excellent wetting fluids. However, if the gelation times are too short for a given manufacturing technique, or the viscosities are too high, it is possible to employ a solvent. Ketones such as methyl ethyl ketone or acetone are often the solvents of choice. It is also possible to employ the "prepreg" technique since the impregnated systems are relatively stable at room temperature or below and this technique makes the elimination of the volatile solvent relatively easy.

CHEMICAL FORMULAS

The following structural formulas identify the more important materials available, or potentially available:

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\[
\begin{align*}
\text{MONO ANHYDRIDE} & \quad \begin{array}{c}
\text{CF}_3 \\
\text{HOC} \\
\text{CF}_3
\end{array} \\
\text{DI ANHYDRIDE} & \quad \begin{array}{c}
\text{CF}_3 \\
\text{CF}_3 \\
\text{CF}_3
\end{array}
\end{align*}
\]
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The highest glass transition temperatures are obtained with the more highly functional components. For example, the highest value obtained to date is 249°C which resulted from a composition of the trifunctional epoxy rich in the dianhydride. It is probable that even higher glass transition temperatures can be obtained, approaching 300°C, but the processing difficulties involved in reaching such levels may be formidable.
"C-0" FLUOROEPOXY

"C-6" if Rf is perfluorohexyl,

FOR EXAMPLE

"TRI"FUNCTIONAL FLUOROEPOXY

REFERENCES