(Fourier transform infrared) analysis is often used to monitor the conversion of the oxazine rings to polymers to provide an estimate of the rate of polymerization at different temperatures. NMR (nuclear magnetic resonance) spectroscopy can also be used to monitor conversion of benzoxazine monomers to polymer.

Epoxy adhesives have been widely used in structural adhesive applications and satisfy many demanding industrial applications. However epoxies have many noted deficiencies that limit their use including limited high temperature stability, high moisture uptake, shrinkage, and a large exotherm on polymerization.

Polybenzoxazines have been proposed to overcome many of the limitations on epoxies. They have lower exotherms on curing, less shrinkage, have higher thermal stability, low byproducts and may be readily prepared from benzoxazines, which in turn, are readily prepared from an amine, formaldehyde and a phenol in high yields. However, current methods of preparing polybenzoxazines require relatively high temperatures, and typically produce brittle, highly crosslinked polymers.

Efforts to reduce the polymerization temperature have included the addition of various phenols or Lewis acid accelerators, or copolymerization of the benzoxazine with epoxides or other monomers such as phenol-formaldehyde. However the resultant polybenzoxazine-epoxy hybrids retain many of the limitations of the epoxies, and compromise many desirable features thereof, such as epoxy toughness.

Summary

The present disclosure is directed to novel benzoxazine/epoxy/amine adducts. Further, the present disclosure is directed to a method of preparing the adducts, which comprises reacting a mixture of benzoxazine compound and an epoxy compound with a primary or secondary amine compound, the reaction resulting in ring-opening of the oxazine ring resulting in a mixture of aminomethyl aminophenolic compounds, which may further react with the epoxy compounds. Independently, the amine compound ring opens the epoxy ring. The present benzoxazine/epoxy/amine adducts may be cured to produce cured compositions useful in coating, sealants, adhesive and many other applications. The present disclosure further provides a curable composition comprising a benzoxazine compound, a primary or secondary amine compound and an epoxy compound, which when cured is useful in adhesive, coating and bonding applications. Unexpectedly, the amine compounds independently contribute to the ring opening of the benzoxazine and epoxy compounds.

In one aspect, there is provided a curable composition comprising a benzoxazine, an epoxy compound and an amine compound of the formula:

$R^{10}(NHR^9)_m$,

wherein

R^{10} is a polymeric polyoxyalkylene;

each R^9 is independently H or a hydrocarbyl group, including aryl and alkyl, and

m is 1 to 6.

In the process of preparing the benzoxazine/epoxy/amine adducts, each of the starting materials may be mono- or higher functionality. The benzoxazine may be a mono- or higher