A VISCOELASTIC DESCRIPTION OF THE GLASS TRANSITION-CONVERSION RELATIONSHIP FOR REACTIVE POLYMERS

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The glass transition temperature, $T_g$, is a sensitive and practical parameter for following cure of reactive thermosetting systems. A new equation was developed for predicting the $T_g$-conversion relationship based on the Dillman-Seferis viscoelastic compliance model. It assumes that the changes in $T_g$ are primarily due to changes in relaxation time as chain extension and crosslinking reduce the mobility of a polymer network. Such information is essential in combining kinetic and viscoelastic measurements, which monitor transformations of thermosets during cure. The equation derived from the viscoelastic model was shown to be applicable for a variety of experimental data. The success of the methodology was further demonstrated by comparing well-established relations, such as the Fox equation and the Di-Benedetto equation, to predictions made possible by adjusting two viscoelastic model parameters. Finally, the fitting power of the proposed equation was shown by fitting published epoxy data from the literature as well as experimental data on a relatively new resin system such as dicyanates used as a model in this study.

The glass transition temperature, $T_g$, is a sensitive and practical parameter for following the cure of reactive thermosetting systems. First, $T_g$ sets an upper bound for use temperature of a polymer. Second, a wide range of values of $T_g$ is encountered during cure and many important events can be characterized in terms of $T_g$ [1, 2]. The molecular state of the unreacted material is also characterized by $T_g$ as $T_{g0}$, as well that of the fully reacted material by $T_{g\infty}$ as $T_g$. A quantitative relationship between $T_g$ and extent of

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conversion can provide a critical link in the description of the cure process [3].

It is well established that chain extension and crosslinking increase the $T_g$ of a polymer. However, for most systems, the $T_g$ is also strongly dependent on the chemical composition and phase morphologies complicating the expected behavior. Currently, there are several equations describing $T_g$ in terms of crosslink density or extent of conversion. The Fox and Loshack equation predicts linearity of $T_g$ as a function of crosslink density [4]. The DiMarzio equation predicts linearity of $1/T_g$ with crosslink density [5]. Also, the widely utilized DiBenedetto equation which accounts for the effects of both copolymer and crosslink density provides a generalized expression for $T_g$ [6]. These equations, derived primarily on a thermodynamic basis, are applicable for homogeneous systems and often fail to fit experimental data at high conversion. One example is the sharp increase in $T_g$ at higher degrees of conversion for very high crosslink density systems [7].

In this work, a methodology, based on viscoelastic modelling of the cure process, has been developed that is capable of quantitatively describing both isothermal and non-isothermal dynamic mechanical behavior of a reactive epoxy system in the vicinity of its primary viscoelastic transition [8, 9]. The present work shows that it is possible to develop a quantitative $T_g$ - Conversion relationship based on viscoelastic modelling of reactive systems. Thus, it is possible to relate changes in glass transition to changes in relaxation time of the system as chain extension and crosslinking reduce the mobility of the polymer network. The success of the new viscoelastic approach was demonstrated by comparison with experimental results generated specifically for this study as well as with previously published experimental data. Furthermore, by direct comparison of these expressions to well accepted equations used for $T_g$-conversion, the generality of the viscoelastic approach was established.

Background

It is well known that conversion or crosslinking increases the glass transition temperature of a polymer. Thus, an increase in $T_g$ may be viewed as two nearly independent effects: (1) the degree of crosslinking and (2) the copolymer effect. A number of studies has been published relating the degree of crosslinking to the shift in $T_g$ of a polymer [4-6]. However, there is lack of agreement between investigators. For example, the Fox-Loshack expression provided the linear relationship [4], viz.

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