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THERMOGRAVIMETRIC ANALYSIS OF A POLYCYANURATE THERMOSETTING MATERIAL

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Abstract

The thermal degradation of a fully cured polycyanurate thermosetting material was examined by monitoring the mass loss at various temperatures ranging from 200 to 220°C. The effect of the copper naphthenate catalyst, generally used to facilitate curing, is also studied. A decrease in weight is observed with increasing time at elevated temperatures in the systems containing copper naphthenate, with the onset of degradation occurring sooner with higher concentrations of the copper compound. The apparent activation energy for degradation is 220±30 kJ mol^{-1}.

Keywords: catalyst, degradation, polycyanurate, thermal stability

Introduction

Polycyanurate thermosetting materials are formed by the trimerization of cyanate ester monomer. Typically the rate of the reaction is accelerated by using a blend of nonylphenol and a transition metal complex as a catalyst. Both the transition metal and the nonylphenol have been shown to have a catalytic effect [1]. Existing work indicates that copper compounds, including copper naphthenate, allow for the achievement of the highest conversions without promoting hydrolysis of the cyanurate ester linkage [1]. This study focuses on the effect of catalyst concentration on the rate of thermal degradation for a fully cured cyanate ester thermosetting system at temperatures near T_g.

The material investigated was bisphenyl *M* polycyanurate, a polymer derived from the monomer 4,4[1,3 phenylene bis(1-methylethylidene)]bis-cyanato-benzene through a heterocyclic trimerization reaction (Fig. 1). Bisphenyl *M* polycyanurate has a high glass temperature, ranging between 180–200°C for the fully cured material depending on the catalyst used. Bisphenyl *M* polycyanurate also has extremely low moisture absorption, 0.7% at 100°C [2] compared to 1.4–2.5% for other polycyanurates and 4–6% for competitive bismaleimides and epoxy resins [1], resulting in less outgassing and structural deformation upon deployment.

It is emphasized that the phrase "fully cured" is used to indicate that the maximum T_g of the system was reached. Fully cured does not mean that all cyanate

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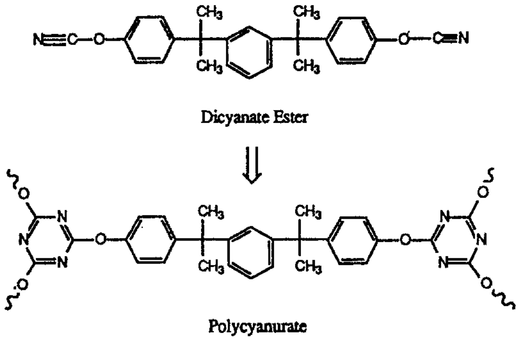

Fig. 1 Structure of monomer and polymer: dicyanate ester reacts to form polycyanurate

groups reacted since complete conversion is not possible in highly crosslinked systems [3].

Significant works have been done on the curing kinetics of cyanate ester/polycyanurate systems [4–8]. A long term study of bisphenyl *M* polycyanurate showed no appreciable effects of degradation in the uncatalyzed system at 200°C for over 200 h whereas effects of degradation were seen in a catalyzed system after several hours at 200°C [4]. However, the long term thermal stability of the cured polymer has not been rigorously investigated, specifically with regards to the effects of catalyst concentration.

Experimental

Materials

Bisphenyl *M* dicyanate and the traditional catalyst (92% nonylphenol, 8% copper naphthenate) were obtained from Rhone-Poulenc High Performance Resins (now Ciba-Geigy). The monomer and catalyst were fully mixed with a magnetic stirrer at 60°C in a weight ratio of 98 to 2 to obtain material consisting of 1.84% nonylphenol and 0.16% copper naphthenate by weight. No solvents were used since both the monomer and catalyst are liquids. The mixture was then degased in a vacuum oven at 100°C for 10 min to remove any absorbed gases and water. Mixtures are stored at –25°C to minimize reaction during storage. A more concentrated catalyst containing 16 wt% copper naphthenate was formulated by pulling off nonylphenol from the original mixture in a vacuum oven at 65°C for two days. This system was prepared in the previously described manner with one notable exception: the monomer/catalyst system was mixed in methylene chloride to ensure a well-mixed system. The solvent was pulled off in a vacuum oven and the final composition consisted of 1.84% nonylphenol and 0.32% copper naphthenate by weight.

TG studies

Mass loss was measured with a TA Instruments High Res TGA 2950. Isothermal degradation studies were performed at temperatures of 200, 210 and 220°C for times up to a week using nitrogen as the purge gas. Multiple runs were performed at 200 and 220°C to ensure reproducibility. The TG studies were performed on a thin film (~0.02 mm) in order to minimize diffusion limitations. The typical initial sample weight was about 10 mg. Films were cast by dissolving each monomer/catalyst mixture in methylene chloride and pouring the solution over filtered mercury. After the solvent evaporated at room temperature, the film was fully cured under nitrogen at 180°C for about 2 h.

Results and discussion

Figures 2 and 3 show the results of TG experiments on thin films of fully cured polymer with 0.16% copper naphthenate and 0.32% copper naphthenate, respectively. The rate of mass loss increases as the temperature increases. A reduced curve of the mass loss can be obtained for both systems by time-temperature superposition of the mass loss *vs.* log time data. The two reduced curves are compared in Fig. 4 with 220°C chosen as the reference temperature. Clearly, increasing the amount of copper in the system decreases the thermal stability. The time to the onset of degradation is taken as the intersection of lines drawn parallel to the curves at short and long times. Doubling the amount of copper decreases the time to the onset to degradation at 220°C from 40000 s (ca. 11 h) to 10000 s (<3 h).

The apparent activation energy of degradation can be obtained by an Arrhenius plot of the temperature shift factors, which were used to obtain the reduced curves, *vs.* inverse temperature. Previous works have illustrated the method through which the shift factors yield an activation energy [4, 9, 10]. The apparent activation energy of the degradation reaction is found to be 220±30 kJ mol^{-1} assuming that the degradation mechanism for both systems is the same. Analyzing each system separately yields activation energies of 205±30 and 250±50 kJ mol^{-1} for the polymer systems with 0.16 wt% and 0.32 wt% copper naphthenate, respectively. Interpretation of the reduction procedure assumes a one-to-one relationship between mass

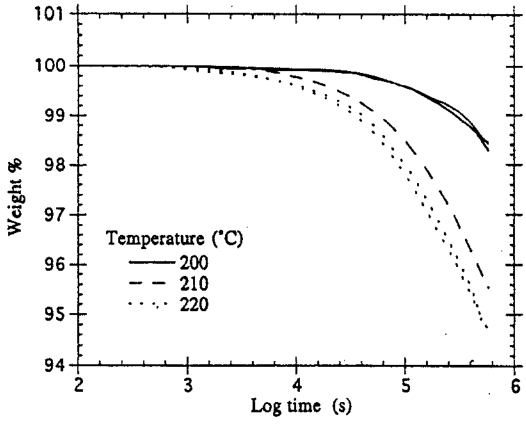

Fig. 2 Mass loss *vs.* log time for thin films of polymer with 0.16% copper naphthenate reacted isothermally at temperatures of 200, 210 and 220°C

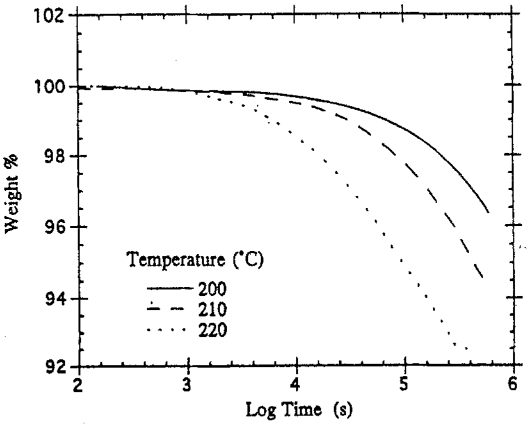

Fig. 3 Mass loss *vs.* log time for thin films of polymer with 0.32% copper naphthenate reacted isothermally at temperatures of 200, 210 and 220°C

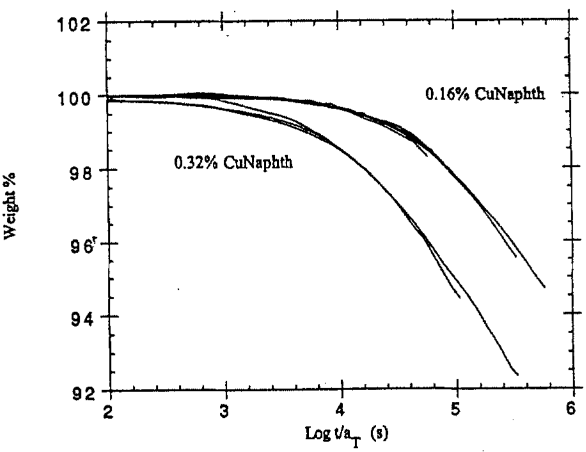

Fig. 4 Reduced curve of mass loss *vs.* log time for both monomer/catalyst systems, 220°C is used as the reference temperature

loss and degradation, that the reaction is kinetically controlled and that the overall degradation reaction can be described by one apparent activation energy. The activation energy for degradation is greater than that for cure, the latter of which was found to be 54 kJ mol^{-1} [4].

Since the apparent activation energy for degradation is significantly higher than that for cure, full cure can be obtained provided the curing temperature remains low enough. At high curing temperatures, competition between cure and degradation reactions occurs, leading to a decrease in final value of properties dependent on conversion such as T_g.

Conclusions

TG studies have provided insight into the thermal degradation of polycyanurates during long term isothermal reactions at temperatures of 200–220°C. Increasing the level of the copper naphthenate catalyst has an adverse effect on the long term thermal stability. From the temperature dependence of mass loss, the apparent activation energy for the degradation reaction is found to be approximately 220 kJ mol^{-1}.

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