

Effect of Catalyst on the Thermal Degradation of a Polycyanurate Thermosetting System

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ABSTRACT: The thermal degradation of a polycyanurate thermosetting material was examined by monitoring glass temperature and weight loss at various temperatures ranging from 180 to 220°C. The effect of the cocatalysts, nonylphenol and copper naphthenate, which are generally used to facilitate curing, were also studied. A decrease in T_g 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. No change in T_g occurred at long times in systems containing only nonylphenol. Weight loss studies were used to calculate an apparent activation energy of degradation. It was found to be approximately 50 kcal/mol. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 127–131, 1997

INTRODUCTION

Polycyanurate thermosetting materials are formed by trimerization of the cyanate ester monomer. Typically, the rate of the reaction is accelerated by using a blend of nonylphenol and a transition-metal complex. Both the 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 focused on the effect of catalyst concentration on the rate of thermal degradation for a particular cyanate ester thermosetting system. The effects of both catalyst components, nonylphenol and copper naphthenate, were examined. The material investigated was bisphenyl M polycyanurate, a polymer derived from the monomer 4,4[1,3-phenylene bis(1-methylethylidene)]bis-cyanatobenzene through a heterocyclic trimerization reaction (Fig. 1). Bisphenyl M polycyanurate

has a high glass temperature, ranging between 180 and 200°C for the “fully cured” material depending on the catalyst used.

Significant works have been done on the curing kinetics of cyanate ester/polycyanurate systems.^{2–6} A long-term study of bisphenyl M polycyanurate has shown 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.² However, the long-term thermal stability of the cured polymer has not been rigorously investigated, specifically with regard to the effects of catalyst concentration.

EXPERIMENTAL

Materials

Bisphenyl M dicyanate and a 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

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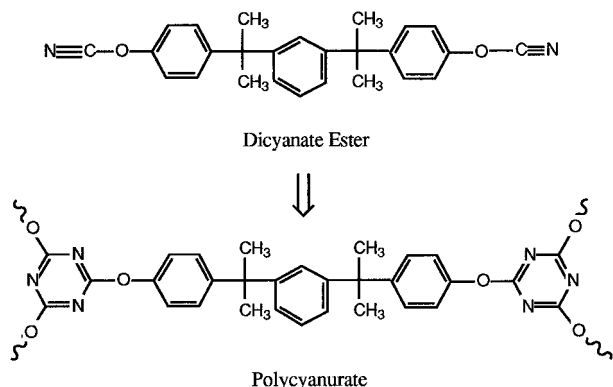


Figure 1 Structures of monomer and polymer: dicyanate ester reacts to form polycyanurate.

consisting of 1.84% nonylphenol and 0.16% copper naphthenate by weight. No solvents were used for this mixture since both the monomer and catalyst are liquids. The mixture was then degassed in a vacuum oven at 100°C for 10 min to remove any absorbed gasses and water. The glass temperature of the amorphous monomer mixture was -24°C as measured by DSC at 10°C/min. Mixtures were stored at -25°C to minimize reaction during storage. A more concentrated catalyst containing 16 wt % copper naphthenate was formulated by removing nonylphenol from the original mixture in a vacuum oven at 65°C for 2 days. This system was prepared in the previously described manner with one notable exception: The mixture was dissolved in methylene chloride prior to stirring to ensure complete mixing since the concentrated catalyst had a noticeably higher viscosity. The solvent was removed under vacuum at room temperature prior to the degassing step. The final mixture consisted of 1.84% nonylphenol and 0.32% copper naphthenate by weight.

TGA Studies

Weight loss was measured with a TA Instruments High Res TGA 2850. Studies were performed at temperatures of 180, 200, and 220°C on a thin film (~ 0.2 mm) of cured polymer. Tests were run isothermally for times up to 1 week. Multiple runs were performed to ensure reproducibility.

The film was cast using the 98 wt % monomer/2 wt % catalyst system by dissolving the mixture in methylene chloride and pouring the solution over filtered mercury. After the solvent evaporated at room temperature, the film was cured

under nitrogen at 180°C for 3 h. A thin film was used to minimize diffusion limitations.

DSC Studies

Glass temperatures were determined using a Perkin-Elmer DSC 7. A TA Instruments DSC 2910 was used for a few of the samples; no difference in the results from the two instruments was noted. All samples used in the DSC studies were hermetically sealed in a dry, nitrogen-purged glove box. The typical sample size was 6 mg. Glass temperatures were measured during heating scans at 10°C/min.

The evolution of the glass temperature of initially uncured samples was examined as a function of time for isothermal reaction temperatures of 200 and 220°C and for times up to 1 month. Two experimental methods were used depending on the cure time: For times under 6 h, isothermal reaction was done in the DSC. The samples were then quenched and scanned during heating in the DSC at 10°C/min under a nitrogen purge. For longer times, isothermal cure was performed in a separate oven. The samples were then quenched and scanned in the DSC. The two methods give the same results when the long time method (>6 h) was occasionally used for shorter times (<6 h) and vice versa. In some cases, endothermic relaxation peaks in the glass temperature region due to physical aging were detected; these samples were then quenched after heating to just above the relaxation peak to remove the effects of physical aging and then rescanned at 10°C/min. To avoid the endothermic relaxation peak, samples that were not scanned immediately after quench were generally reheated on a hot plate at approximately 180°C for 15–30 s to remove any effects of physical aging and then quenched.

RESULTS AND DISCUSSION

Figure 2 shows the results of TGA experiments on thin films of cured polymer with 2 wt % standard catalyst. The rate of weight loss increases as the temperature increases. A reduced curve of the weight loss can be obtained by time–temperature superposition of the weight loss vs. log time data. This reduced curve is shown in Figure 3 with one of the runs at 200°C chosen as the reference temperature. The apparent activation energy of deg-

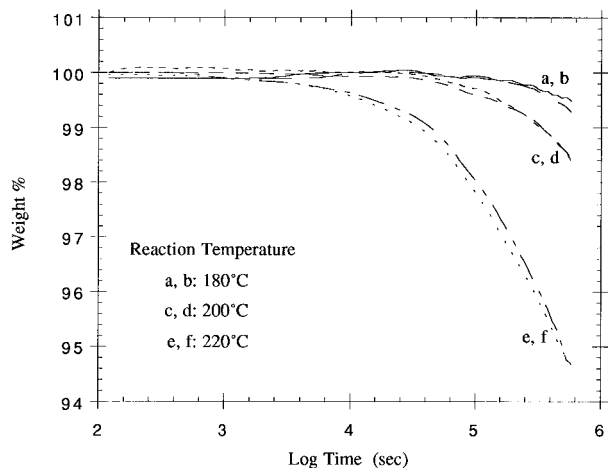


Figure 2 Weight loss vs. log time for thins films of catalyzed polymer reacted isothermally at temperatures of (a,b) 180°C, (c,d) 200°C, and (e,f) 220°C in the TGA after full cure at 180°C.

radiation can be obtained by an Arrhenius plot of the temperature shift factors vs. inverse temperature. Previous works have illustrated the method through which the shift factors yield an activation energy.^{2,7,8} The apparent activation energy of the degradation reaction(s) was found to be 50 ± 14 kcal/mol. The relatively large error arises from the inaccuracy involved in shifting the 180°C data due to the limited data obtained at that temperature after the onset of degradation. Interpretation of the reduction procedure assumes a one-to-one relationship between weight loss and degree of degradation, that the degradation reaction(s) is kinetically controlled, and that the rate of weight loss is not diffusion-limited. Preliminary work on the relationship between weight loss and drop in T_g suggests a one-to-one relationship independent of reaction temperature for the fully cured polymer at extended times, which would indicate that the first assumption is valid in the regime where degradation significantly affects properties. However, it is noted that in the early stages of degradation a finite amount of degradation is expected to occur before weight loss begins.

The apparent activation energy of the cure reactions had been found to be 22 kcal/mol for the uncatalyzed monomer and 13 kcal/mol for the catalyzed system.² Previous work has shown that the glass temperature of the fully cured polymer, $T_{g\infty}$, for the uncatalyzed system is not a function of curing temperature at 180 and 200°C.² This work indicates that full cure is achievable in the

uncatalyzed system over the range of reaction temperatures studied. The difference between the apparent activation energies for degradation and cure means that the ratio of the rate constants for degradation and cure doubles approximately every 10°C. As the reaction temperature is increased, the competition between cure and degradation reactions favors degradation. Thus, at very high cure temperatures, full cure cannot be reached because of this competition.

The evolution of glass temperature over time at 200°C for the uncatalyzed monomer² and the 98% monomer/2% standard catalyst system is shown in Figure 4. The glass temperature initially increases due to cure in both reaction systems. The maximum glass temperature achieved, $T_{g\infty}$, is lower for the catalyzed system due to plasticization by the nonylphenol cocatalyst. The glass temperature of the uncatalyzed system remains constant at 196°C over the course of 1 month, implying thermal stability. Conversely, the catalyzed system shows a slight decrease in glass temperature starting at 10,000 s (3 h), with a more pronounced drop after 100,000 s.

Since the drop in glass temperature seems to occur only in systems with nonylphenol and copper naphthenate present, it is hypothesized that one or both of these compounds thermally destabilize the polymer. To examine the long-term stability effect of nonylphenol on the network, 2 wt % of nonylphenol, in the absence of copper naphthenate, was blended into the monomer in the same manner as was the standard catalyst mixture. The effect of nonylphenol concentration on

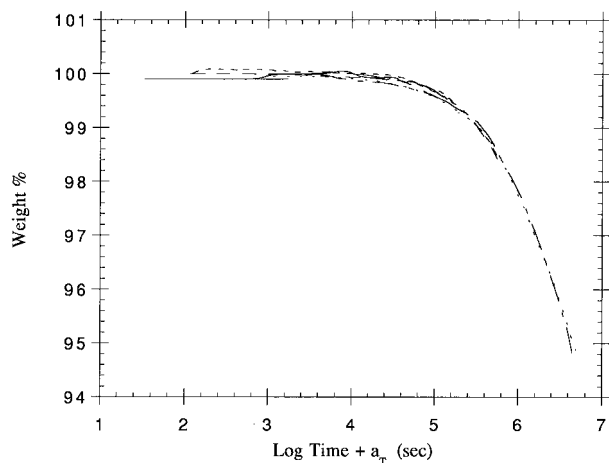


Figure 3 Reduced curve of weight loss vs. log time; 200°C is used as the reference temperature.

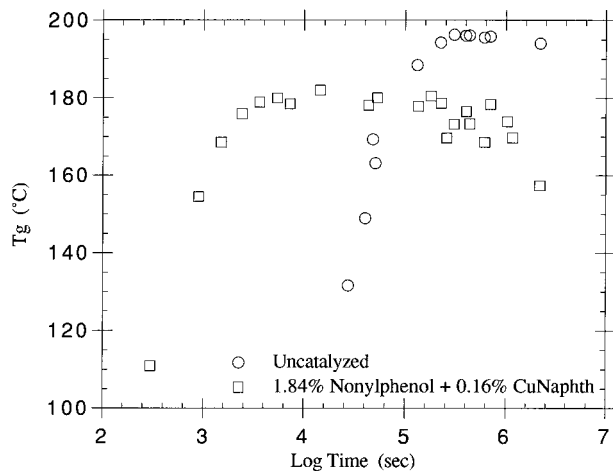


Figure 4 T_g vs. log time for the uncatalyzed and catalyzed polymer systems reacted isothermally at 200°C. The catalyzed system contains 1.84% nonylphenol and 0.16% copper naphthenate.

glass temperature can be seen in Figure 5. The nonylphenol increases the rate of the cure reaction to some extent and also lowers T_g due to plasticization, as previously discussed. However, the T_g drops seen in Figure 6 were not reproduced with just the nonylphenol present even at times exceeding 1 month. This implies that the nonylphenol does not adversely effect the long-term thermal stability of the polycyanurate.

The effect of the copper compound on the thermal stability of the polymer was analyzed by comparing the behavior of two systems with varying

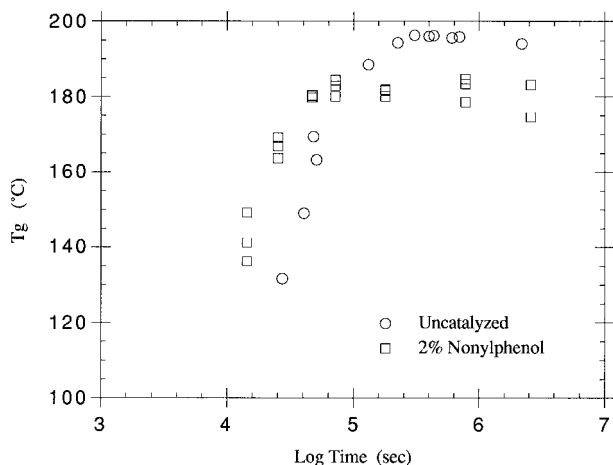


Figure 5 T_g vs. log time for the uncatalyzed polymer system and a system containing 2 wt % nonylphenol reacted isothermally at 200°C.

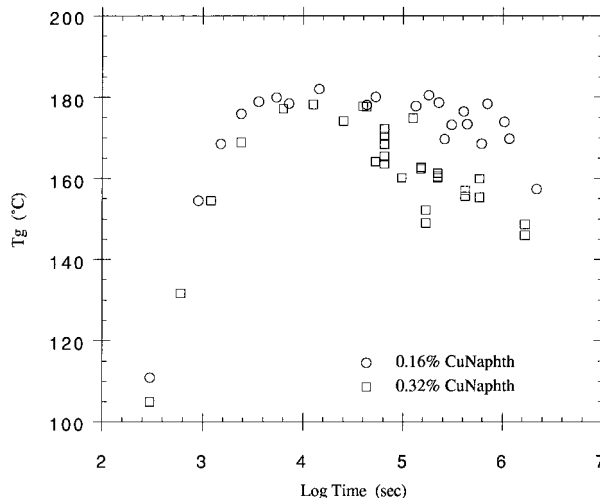


Figure 6 T_g vs. log time for polymer systems containing 0.16 and 0.32% copper naphthenate reacted isothermally at 200°C. Both systems contain 1.84% nonylphenol.

amounts of copper, 0.16 and 0.32%. The nonylphenol concentration was 1.84% in both cases. Figure 6 shows evolution of glass temperature over time for the two systems. It is interesting to note that doubling the concentration of the copper naphthenate has no appreciable effect on the curing rate. $T_{g_{sc}}$ is slightly lower in the system containing additional copper—whether this is due to plasticization or competition between cure and degradation is not clear. It is obvious, however, that the system containing additional copper shows more drastic signs of degradation: The time when T_g begins to drop is earlier and the magnitude of the drop is greater.

There is considerable scatter in the DSC data after the onset of degradation. Preliminary experiments yielded an even greater degree of scatter which was considered to result from catalyst concentration gradients within the mixture such that different DSC samples contained differing amounts of catalyst. The implementation of more thorough blending procedures (e.g., magnetic stirrer, solvents) significantly improved the scatter of the data. Despite the scatter in the data, significant differences in thermal stability are observed with changes in catalyst concentration.

CONCLUSIONS

TGA and DSC studies have provided insight into the thermal degradation of a polycyanurate during

long-term isothermal reactions at temperatures of 180–220°C. From the temperature dependence of weight loss, the apparent activation energy for the degradation reaction was found to be approximately 50 kcal/mol. The nonylphenol co-catalyst does not appear to adversely affect thermal stability, whereas increasing the level of the copper naphthenate catalyst does have a negative effect.

REFERENCES

1. D. A. Shimp, J. R. Christenson, and S. J. Ising, *Cyanate Ester Resin—Chemistry, Properties and Applications*, Preprint, Hi-Tek Polymers Inc.
2. S. L. Simon and J. K. Gillham, *J. Appl. Polym. Sci.*, **47**, 461–485 (1993).
3. M. Bauer, J. Bauer, and G. Kuhn, *Acta Polym.*, **37**, 715 (1986).
4. A. M. Gupta and C. W. Macosko, *Makomol. Chem. Macromol. Symp.*, **45**, 105–115 (1991).
5. A. Osei-Owusu, G. C. Martin, and J. T. Grotto, *Polym. Eng. Sci.*, **31**(22), 1604 (1991).
6. O. Georjon, J. Galy, and J. P. Pascault, *J. Appl. Polym. Sci.*, **49**, 1441–1452 (1993).
7. G. Wisanrakkit and J. K. Gillham, *J. Coat. Tech.*, **62**(783), 35 (1990); *J. Appl. Polym. Sci.*, **41**, 2885 (1990).
8. S. Gan, J. K. Gillham, and R. B. Prime, *J. Appl. Polym. Sci.*, **37**, 803 (1989).