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Cure Behavior of Some Resin–Glass Cloth Systems

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Synopsis

Changes in the dynamic modulus E'_{dyn} of some phenolic glass cloth systems were studied as a function of cure temperatures and formaldehyde factors. The modulus changes were followed by continuously monitoring in situ the fundamental frequency of vibration of resin-impregnated glass cloth systems bonded to metallic cantilever reeds. The apparent activation energy of crosslinking was a direct function of the formaldehyde content in the resin synthesis, ranging from 9 kcal/mole for a 1.2 formaldehyde factor phenolic, to 20 kcal/mole for a 1.8 factor. Two cure parameters at 50% and 100% apparent mechanical conversion were established.

INTRODUCTION

Numerous experimental techniques and data on the study of cure rates and thermomechanical behavior of resin systems have been reported in the literature.[1-7] Most of the techniques are limited in their application owing to the difficulty in handling a curing resin system as it changes its state from liquid to gel to solid. The technique of employing a nonreactive substrate[5,7-9] to support the various resin systems while monitoring the changes in selected physical or mechanical properties offers one attractive solution to the problem. This paper reports the cure rate data obtained by continuous monitoring in situ the changes in the dynamic modulus of phenolic-impregnated glass cloth laminates as a function of temperature and formaldehyde content. The apparent cure activation energy of the "prepregs" was directly proportional to the amount of formaldehyde used in the phenolic resin synthesis, ranging from 9 kcal/mole to 20 kcal/mole for the 1.2 and 1.8 factor phenolics, respectively.

EXPERIMENTAL

Synthesis

The phenolic resins were synthesized in our laboratories using standard resin chemistry methods. All resins were prepared in a 1-liter resin reaction kettle equipped with a reflux condenser, mechanical stirrer, dropping funnel, thermometer, and facilities for partial pressures. The resins were cooked at reflux for a period equivalent to one half their gellation time and concentrated at reduced pressure and temperature to a solids content of about 65% following the initial condensation reaction.

A specific example of the resin synthesis is given: One mole of phenol was placed into the resin flask and 1.2 moles of 37% formaldehyde containing 12% methanol was added. Heat was applied, and one third of the catalyst charge was added (the catalyst consists of a 50% aqueous solution of NaOH based upon 2.0 g NaOH per 100 g phenol). An exotherm was observed at 60°C driving the temperature to about 80°C. Additional catalyst was added to reach and maintain the temperature at reflux (100°C). The resin solution was held at reflux for 90 min, concentrated to 65% solids at reduced pressure and temperature, and stored at 4°C.

Resin Impregnation of Glass Cloth

Sections of 1581 glass cloth, approximately 12 square inches each, were impregnated with the resins by means of a rubber spatula by which the resin was worked into the fabric. Removal of excessive resin and B staging of the system was accomplished by exposing the cloth to room temperature environment for 24 hr. The resin-impregnated cloth was stored at 4°C.

Mechanical Technique

The dynamic modulus changes of the curing resin impregnated in glass cloth were followed continuously in situ by use of a modified vibrating reed technique previously described in this journal.[4] Briefly, the vibrating reed apparatus consists essentially of an inert metallic reed to which was bonded, by room-temperature curing epoxy, the phenolic-impregnated cloth. The vertically mounted composite reed was driven into its fundamental frequency of vibration by use of a mechanically linked loudspeaker head driven by a low-frequency oscillator. A metal pin, mounted on the free end of the reed, generated a variable amplitude sinusoidal signal as it moved in a linear variable differential transformer (LVDT). The maximum height of the signal as a function of frequency was taken as the polymer–substrate resonance frequency, from which data the cure of the resin-impregnated cloth was followed by plotting the change of the squared fundamental frequency of vibration (ν^2) of the composite as a function of time.

RESULTS AND DISCUSSION

Figure 1 depicts the results obtained as the normalized per cent relative cure of a 1.5 factor phenolic–glass system was plotted as a function of time at four selected temperatures. Extrapolation of a line tangent to the curve at which the change in relative cure as a function of time is a maximum yields three cure time parameters. These cure parameters, designated $\tau_{100\%}$, $\tau_{50\%}$, and $\tau_{0\%}$ in Figure 1, arise from the formation of initial crosslinks at $\tau_{0\%}$ and a highly crosslinked system at $\tau_{100\%}$ representing a C-staged phenolic. At time $\tau_{100\%}$, the glass transition temperature of the phenolic, T_g, is greater than the cure temperature, T_c, so that the rate

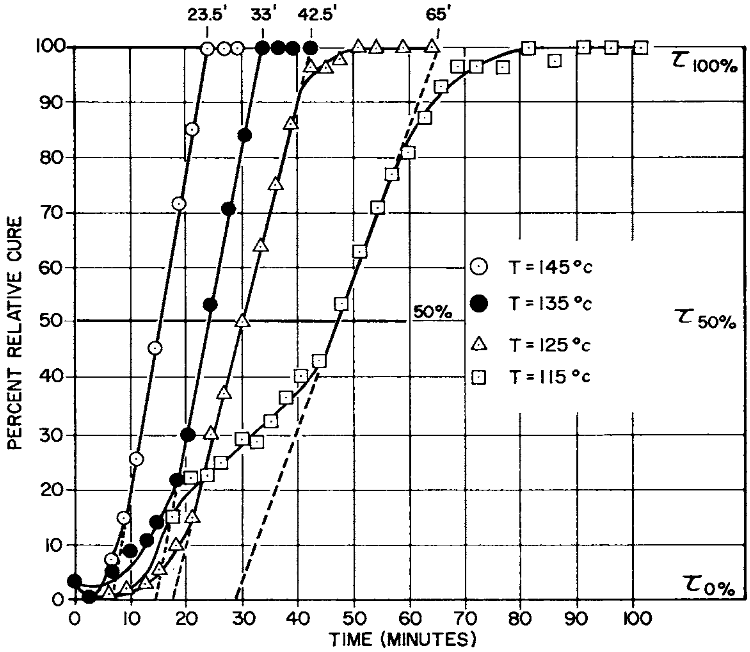

Fig. 1. Per cent relative cure of a 1.5 factor phenolic–glass system as a function of time and temperature.

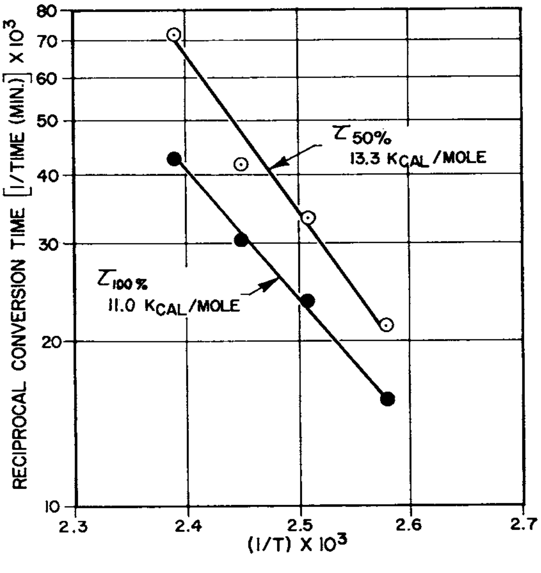

Fig. 2. Reciprocal conversion time vs. reciprocal absolute temperature for a 1.5 factor phenolic–glass system.

TABLE I

Cure Rates of Some Phenolic–Glass Systems

Sample	Cure temp.		Cure time, min		[1/Time] × 10^3, min^{-1}		(1/°K) × 10^3	$d\tau_{50\%}/dT$, min/°C	Activation energy, kcal/mole	
	°C	°K	$\tau_{50\%}$	$\tau_{100\%}$	$1/\tau_{50\%}$	$1/\tau_{100\%}$			$\tau_{50\%}$	$\tau_{100\%}$
1.2 *f* Phenolic	145	418	17	26	58.8	38.4	2.39			
	135	408	24	35	41.6	28.6	2.45		9.3	9.3
	115	388	41	62	24.4	16.1	2.58	0.8		
1.5 *f* Phenolic	145	418	14	23.5	71.4	42.5	2.39			
	135	408	24	33	41.6	30.3	2.45			11.0
	125	398	30	42.5	33.3	23.5	2.51	1.12	13.3	
	115	388	47.5	65.0	21.0	15.4	2.58			
1.8 *f* Phenolic	145	418	← too rapid →							
	135	408	13	23	77	43.5	2.45			
	125	398	23	33.5	43.5	29.9	2.51	1.7	19.9	17.3
	115	388	47	71	21.3	14.1	2.58			

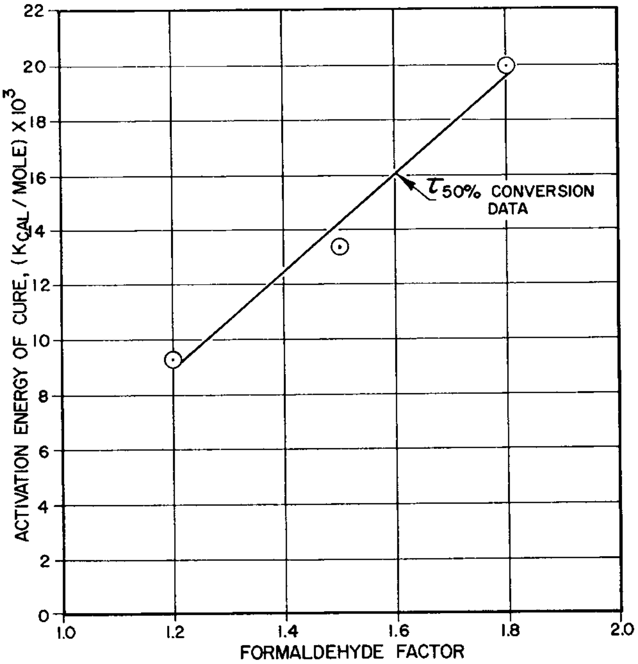

Fig. 3. Activation energy vs. formaldehyde factor.

of change of the cure curve approaches zero as the remaining reactive groups are more or less locked in.[7]

Three phenolic–glass systems were evaluated by this technique utilizing the $\tau_{50\%}$ and $\tau_{100\%}$ cure parameters in which the formaldehyde factor in the resin synthesis was varied from 1.2 to 1.8 moles per mole of phenol. Table I lists the phenolic–glass systems studied and the cure times determined at the indicated temperatures, whereas Figure 2 depicts a typical Arrhenius plot of reciprocal conversion time versus reciprocal absolute temperatures at $\tau_{50\%}$ and $\tau_{100\%}$ for the 1.5 factor system. Figure 3 depicts the apparent energy of crosslinking as a function of formaldehyde factor. At high cure temperatures and high formaldehyde factors, the times required to reach the $\tau_{50\%}$ and $\tau_{100\%}$ are much less when compared to the low-factor phenolic; however, at low cure temperatures the high-factor phenolic requires more time to reach $\tau_{100\%}$ and $\tau_{50\%}$ than does the low-factor phenolic. Thus we see that the rate of change of the $\tau_{50\%}$ cure parameters with respects to a change in temperature at various formaldehyde factors, as shown in Table I, may be represented as

$$\left(\frac{d\tau_{50\%}}{dT}\right)_{1.2f} < \left(\frac{d\tau_{50\%}}{dT}\right)_{1.5f} < \left(\frac{d\tau_{50\%}}{dT}\right)_{1.8f}.$$

These data are surprising in that one would assume that, if the reaction rate of a low-factor phenolic were more rapid at high temperatures than a high-factor phenolic, the same relative rates would hold at reduced temperatures. At T_1,

$$(\tau_{50\%})_{1.8f} > (\tau_{50\%})_{1.5f} > (\tau_{50\%})_{1.2f}$$

whereas at T_2 $(T_2 > T_1)$,

$$(\tau_{50\%})_{1.8f} < (\tau_{50\%})_{1.5f} < (\tau_{50\%})_{1.2f}.$$

This type of cure behavior may be caused by the multiplicity of possible condensation and elimination reactions associated with this resin system each with its specific reaction rate.

CONCLUSIONS

An in situ technique which allowed measurements of apparent activation energy of crosslinking of some phenolic glass systems was described. The activation energy of crosslinking was found to be directly proportional to the formaldehyde factor used in the resin synthesis. These data indicate a rather abnormal cure behavior of the phenolic–glass system as a function of formaldehyde factor.

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