Differential scanning calorimetry of the effects of temperature and humidity on phenol-formaldehyde resin cure

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(Received 10 October 1993; revised 22 April 1994)

Phenol-formaldehyde (PF) resin is a widely used adhesive in the manufacture of wood composites. However, curing behaviour of the resin under various environmental conditions is not well known. A differential scanning calorimeter was employed to characterize the degree of resin cure in this study. Resin-impregnated glass cloth samples with varied moisture contents (0, 31, 71%) were exposed to an environment of controlled temperature (105, 115, 125, 140°C) and relative humidity (41, 75, 90%) for a series of time periods (0–20 min). The samples were next conditioned to different levels of relative humidity (0, 64, 89%) before being sealed in d.s.c. capsules. The degree of cure of these partially cured samples was then determined by d.s.c. by measuring the residual heat of cure. The results show that the degree of resin cure increased with increasing precure temperature and time. The rate of cure increased for dry samples as precure humidity increased. However, the rate of cure decreased with an increase in the initial moisture content of samples when precured at 90% relative humidity. The effect of moisture put into a sample immediately before analysis by d.s.c. on the subsequent calculation of resin precure became less significant with increasing precure temperature and degree of resin cure.

(Keywords: phenol-formaldehyde resin; d.s.c.; degree of resin cure)

INTRODUCTION

The degree of the resin cure is one of the most important variables affecting the performance of wood composites. However the effects of environmental variables, such as temperature, relative humidity (r.h.) and moisture content, on the progressive curing behaviour of the resins is not well known. This information is especially important in evaluating phenol-formaldehyde (PF) resins, one of the most commonly and widely used adhesives in the manufacture of wood composites, because PF resins develop strength relatively slowly and have ample time to respond to changes in the environment. This study used a differential scanning calorimeter to determine the extent of PF resin cure after progressively extended exposures to precure treatments at different temperatures. Relative humidity and sample moisture content were varied before, during and after the precure treatments.

U.v. spectroscopy measurements on aqueous extracts from cured PF resins[1,2] show that the presence of water in resin during cure plays an important role. At 100°C, the curing rate of aqueous resins decreases with increasing moisture dilution. The extra water acts as an energy barrier to resin crosslinking[1,2]. Thus, the curing time is prolonged. Curing rates increase as temperatures are raised to 160°C. However, the influence of moisture diminishes with increasing temperature. Other studies[3,4] show that moisture in a solid two-step phenolic moulding compound can enhance the curing rate and the degree of cure. Enhanced reactivity is primarily attributed to moisture accelerating the decomposition of hexamethylenetetramine and also might be partially due to moisture improving the flowability of the compounds by plasticization.

D.s.c. is a valuable technique of thermal analysis for use in following the curing behaviour of PF resins. Use of hermetically sealed d.s.c. capsules permits direct analysis of the exothermic curing reaction, while minimizing interference from endotherms caused by the vaporization of water[5,6]. In calorimetry of PF resins, often one exothermic peak attributed to the addition of free formaldehyde to phenolic rings occurs at relatively low temperatures (98–129°C). Another exothermic peak attributed to the condensation reactions of methylol groups occurs at higher temperatures (139–151°C) and leads to an insoluble and infusible network[7,8]. If both peaks appear during a heating scan, they will usually overlap. In this work, all thermograms showed only one peak of the second type (condensation peak, ~140°C).

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0032-3861/94/26/5685–08

Table 1 Basic resin composition

Ingredient	Part 1 Weight (g)	Part 1 Mol per mol phenol	Part 2 Weight (g)	Part 2 Mol per mol phenol
Phenol (90% concentration)	750.00	1.00	570.00	1.00
Formaldehyde (46.5% concentration)	1020.60	2.20		
Formaldehyde (41.5% concentration)			879.30	2.23
Water (additional)	81.25		393.76	
First sodium hydroxide (50% concentration)	98.48	0.17	151.98	0.35
Second sodium hydroxide (50% concentration)	66.59	0.12	11.16	0.03
Ammonium hydroxide (28–30% concentration)	44.06		34.23	

Table 2 Initial resin properties

Resin type	Gelation time at 125($\pm$5)°C (min s)	Viscosity (cP)	pH	Solids content (%)
Part 1	14′54″	51	10.1	50.1
Part 2	10′05″	583	10.6	39.8
Mixed PF	13′40″	79	10.2	45.8

The area under the exothermic curve enclosed by a baseline is related to the amount of heat of reaction as the resin sample cures. The degree of resin cure for a partially cured resin sample can be determined by measuring the difference between the total heat of reaction for an uncured sample and the residual heat of reaction for the partially cured sample. Resin cure is expressed as a percentage of the total heat of reaction of the uncured sample[9–12].

EXPERIMENTAL

Resin synthesis

The PF resin used in this study is a laboratory-synthesized PF resin[13], which comprises a non-resinous methylolated phenol condensate (part 1) and a highly condensed PF resin (part 2). The two parts of the resin were prepared separately and then mixed together in a 1:1 (v/v) ratio. The mixed PF resin is henceforth referred to as PF resin. The syntheses of the two parts of the resin were carried out as shown below.

Part 1. The reactor vessel was charged with formaldehyde (45.6% aqueous solution), phenol (90% aqueous solution) and water. After heating the components to 40°C in the reactor, the first sodium hydroxide portion (50% solution) was slowly added over 10 min. When the temperature rose to 100°C, the resin was cooked for 2–3 min, and then cooled to 65°C, where it was cooked for 65 min. The temperature was held at 65°C until the Gardner–Holdt viscosity ranking (measured at 25°C) was AB. The resin was then cooled to 30–40°C, and the second sodium hydroxide portion (50% solution) and ammonium hydroxide (28–30% solution) were added.

Part 2. The reactor was charged with phenol (90%), water and 41.5% formaldehyde solution. When the temperature reached 40°C, the first sodium hydroxide portion (50%) was slowly added over a 10–15 min period and the temperature was allowed to rise to 95°C as soon as possible. The resin was cooked at 95°C to a Gardner–Holdt viscosity ranking (25°C) of AB, and then cooled to 80°C. The temperature was held at 80°C until the viscosity ranking (25°C) was KL. Ten minutes later, the resin was cooled to 65°C and held for 65 min. Next, the temperature was cooled to 30–40°C, and the second sodium hydroxide portion (50%) and ammonium hydroxide (28–30%) were added.

To prevent any possible chemical changes of the resin with storage time, the PF resin was frozen in small (50 ml) plastic bottles immediately after preparation. The resin compositions and their initial properties are summarized in *Tables 1* and *2*. Gelation time was measured by heating a 2 ml resin sample at 125°C ($\pm$5°C) and is quoted in minutes between the start of the test and the point at which bubbles ceased moving upwards. Viscosity was measured at 25°C by using a Haake falling ball viscometer. Resin solids content was determined by heating 3 g of resin at 103°C for 16 h. The number- and weight-average molecular weights of the PF resin have been determined in a previous publication[14].

Sample preparation

A pure borosilicate glass microfibre filter (Whatman GF/C) was selected as a substrate to facilitate sample handling. This substrate has been proved to be inert, thus not interfering with resin curing[15]. In addition, it exhibits good wet strength properties to support the aqueous resin during sample preparation and precure treatment. It also possesses a fine porous structure, allowing the resin to be uniformly absorbed during impregnation.

A 15 cm disc of the glass filter was immersed in a container of the PF resin. After soaking up the resin for 30 min, the disc was removed and excess resin was uniformly squeezed out by using a soft rubber roller under hand pressure. The sample was then hung up to dry for 30 min at ambient conditions, and put into a desiccator over phosphorous pentoxide (P_2O_5) overnight. The sample was then weighed to determine the resin loading. Resin loading is defined by dividing the resin weight (P_2O_5 dried) by the total sample weight (P_2O_5 dried) to give a value in milligrams of resin per milligram of filter plus resin. The resin loading was controlled at 0.838–0.848 mg mg^{-1} between the discs of filters. All samples were cut into strips (12 mm wide) prior to precure treatment.

Before precure treatment, initial moisture contents of samples, i.e. weight of water per total P_2O_5 dried sample

Table 3 Sample preparation conditions

Precure pre-conditioning		Precure conditions				Pre-analysis conditioning	
Medium	R.h. (%)	R.h. (%)	Moisture content (%)	Temp. (°C)	Time (min)	Medium	R.h. (%)
P_2O_5	0	0	0	105	0, 1, 2, 5, 12, 20	P_2O_5	0
P_2O_5	0	0	0	105	0, 1, 2, 5, 12, 20	-	64
P_2O_5	0	0	0	105	0, 1, 2, 5, 12, 20	$ZnSO_4$	89
P_2O_5	0	0	0	115	1, 2, 5, 12, 20	P_2O_5	0
P_2O_5	0	0	0	115	1, 2, 5, 12, 20	-	64
P_2O_5	0	0	0	115	1, 2, 5, 12, 20	$ZnSO_4$	89
P_2O_5	0	0	0	125	0.5, 1, 2, 4, 6	P_2O_5	0
P_2O_5	0	0	0	125	0.5, 1, 2, 4, 6	-	64
P_2O_5	0	0	0	125	0.5, 1, 2, 4, 6	$ZnSO_4$	89
P_2O_5	0	0	0	140	0.5, 1, 2, 4, 6	P_2O_5	0
P_2O_5	0	0	0	140	0.5, 1, 2, 4, 6	-	64
P_2O_5	0	0	0	140	0.5, 1, 2, 4, 6	$ZnSO_4$	89
P_2O_5	0	41	0	105	1, 2, 5, 9, 14	$ZnSO_4$	89
P_2O_5	0	75	0	105	1, 2, 4, 8, 12	$ZnSO_4$	89
P_2O_5	0	90	0	105	0.5, 1, 3, 6, 10	$ZnSO_4$	89
KNO_3	92.5	90	31	105	1, 2, 5, 9, 14	$ZnSO_4$	89
-	-	90	71	105	1, 2, 5, 9, 14	$ZnSO_4$	89

weight, could be varied by conditioning the samples over a desiccant or over a salt-saturated aqueous solution at room temperature. This step is referred to as precure preconditioning.

Precure treatment

The combinations of precure preconditioning, precure moisture content, precure temperature and precure time which were examined in this study are given in *Table 3*. The P_2O_5 dried samples, with ~1% initial moisture content (oven dry), were precured in a dry oven or a steam chamber. The steam chamber is a specially designed environmental treatment chamber which can create a wide variety of constant r.h. environments at various temperatures[10]. The desired conditions above 100°C can be obtained by superheating saturated steam and controlling the final temperature and pressure in the treatment chamber. The P_2O_5 dried samples were precured for various time intervals at 105, 115, 125 or 140°C in the dry oven, or at 105°C in the steam treatment chamber at 41, 75 or 90% r.h.

All moist samples were precured in the steam treatment chamber at 105°C and 90% r.h. The samples with 71% moisture content (on average) were obtained by using them directly after they had soaked up resin for 30 min in the resin jar. The samples with 31% moisture content (on average) were obtained by conditioning the P_2O_5 dried samples overnight at room temperature in a desiccator containing potassium nitrate (KNO_3) saturated solution, which provides 92.5% r.h.[16].

After precure treatment, all the samples were cut to 35 mm lengths, sealed in bottles and put into a freezer to avoid any chemical changes of resin samples prior to d.s.c. testing. Prior to the pre-analysis conditioning, the P_2O_5 dried samples were cut into small circles with diameters of ~5 mm and weights of ~7 mg. The weight of each sample multiplied by its resin loading gave the neat dry resin weight for the sample, which was taken into account in calculation of the residual heat of cure.

Pre-analysis conditioning

To investigate how d.s.c. sample moisture affects the measurement of the d.s.c. residual heat of cure, precured samples were conditioned overnight at different levels of r.h. prior to their being quickly transferred to capsules and sealed before the d.s.c. scan (*Table 3*). This humidification procedure is referred to as pre-analysis conditioning. In this study, three levels of r.h. were chosen, namely, 0, 64 and 89%, provided by conditioning the samples either in a desiccator over P_2O_5 (0% r.h.), in a constant humidity room (64% r.h.) or in a desiccator over a saturated solution of zinc sulfate ($ZnSO_4$, 89% r.h.). The samples had been dried over P_2O_5 before being precured in an oven at temperatures of either 105, 115, 125 or 140°C for various times. Unless pre-analysis conditioning itself was being studied, the r.h. for conditioning d.s.c. samples prior to analysis was 89%.

Measurement of degree of resin cure

All d.s.c. measurements were conducted on a Mettler DSC 20 with a Mettler TA4000 thermal analysis system[17], using a large sealed capsule (ME-29889/V)[18]. The capsule with a volume of 270 μl can withstand vapour pressure up to 10 MPa. The temperature range scanned was from 30 to 300°C at a heating rate of 5°C min^{-1}. The residual heat of cure was measured from the area under the exothermic curve enclosed by the sigmoid baseline which is set by the computer to correct for the change in heat capacity for the sample with the transition[19]. The reference value for the total heat of cure, Q_T, was determined from a sample which had no precure (*Figure 1*). The initial degree of cure of this sample therefore is defined to be 0% cure or conversion. The

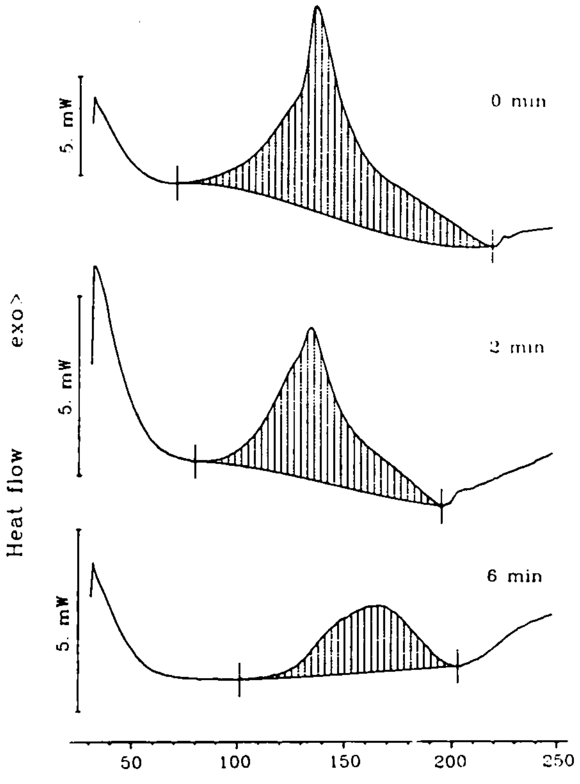

Figure 1 D.s.c. scan of PF resin samples (5°C min^{-1}) after precure for various time periods at 125°C and conditioning at 89% r.h.

residual heat of cure of a partially precured sample, Q_R, was then converted into a per cent cure or degree of cure, α, by the following equation:

$$\alpha=\frac{Q_T-Q_R}{Q_T}$$

RESULTS AND DISCUSSION

Effect of relative humidity in the steam treatment chamber

The relationship between the degree of cure and the precure time for initially dry samples, as a function of r.h. in the steam treatment chamber at 105°C, is shown in *Figure 2*. The resin cured faster at 90% r.h. than it did at 41 or 75% r.h. The resin apparently also cured faster at 75% r.h. than it did at 41% r.h. after 2 min precure treatment. The rates of cure slowed greatly beyond 40% cure range, and the maximum cures recorded were in the 60% cure range. The resin curing faster at a higher r.h. is caused by the effect of moisture. The positive effect of higher r.h. in resin cure resulted from (1) better heat transfer because of moisture condensing on the samples when they are put into the steam treatment chamber or (2) improved resin flowability because of moisture diffusing into the samples during precuring. Moreover, the condensed water may help to keep CH_2O in solution as methylene glycol instead of escaping as monomer. Samples precured at 90% r.h. for 3 min or 75% r.h. for 4 min became plastic and flexible. However, plasticization of this sort was not evident by a visual check for the samples precured at 41% r.h. even after treatment for 14 min.

Effect of moisture within samples

Wet samples could not be precured in the dry oven because of sample cracking and blistering by rapid release of moisture when the precure temperature is >100°C. However, the steam treatment chamber can provide a highly humid environment that can prevent catastrophic moisture release[13]. Therefore the chamber can be used to precure wet samples, even those with a very high initial moisture content. The change of the degree of cure with time, as affected by the initial moisture content of samples, is shown in *Figure 3*. The samples were precured in the steam treatment chamber at 90% r.h. and 105°C. The initial moisture contents of the samples were 0, 31 or 71%. Under high humidity curing conditions, high sample moisture content retarded the rate of resin cure. Samples with a moisture content of 71% had a much lower rate of cure than those with moisture content of 0 and 31%. Excess moisture in the resin does not escape during cure under these conditions and likely dilutes the

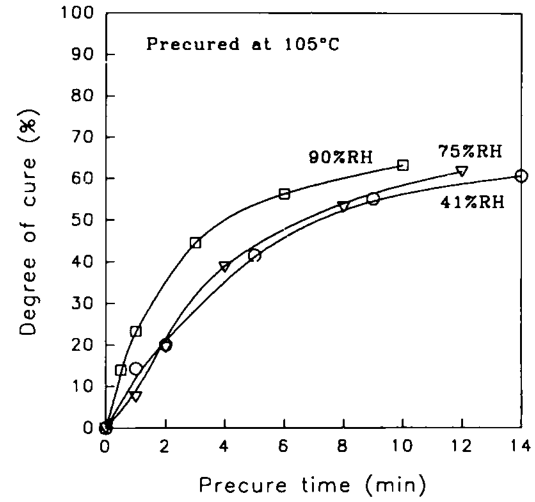

Figure 2 Degree of cure (measured by d.s.c.) for initially dry samples precured at 105°C in a steam treatment chamber at 41, 75 or 90% r.h. All samples were conditioned to 89% r.h. prior to d.s.c.

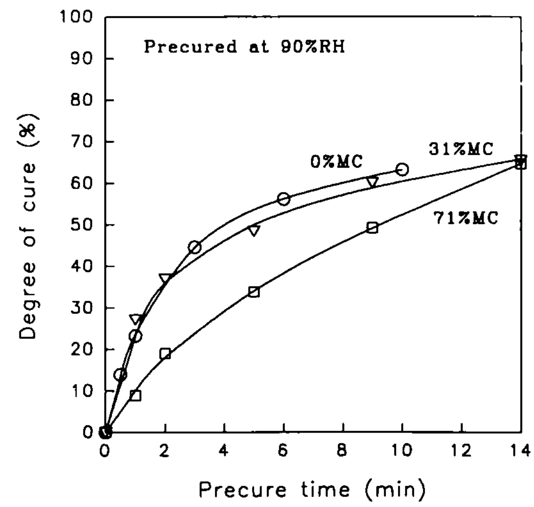

Figure 3 Degree of cure (measured by d.s.c.) for samples having either 0, 31 or 71% moisture content (MC) precured in the steam treatment chamber at 105°C and 90% r.h. All samples were conditioned to 89% r.h. prior to d.s.c.

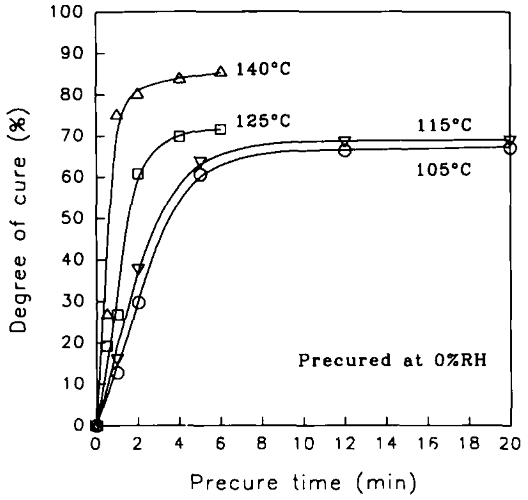

Figure 4 Degree of cure (measured by d.s.c.) for dry samples precured in a dry oven at 105, 115, 125 and 140°C. Samples were conditioned to 89% r.h. prior to d.s.c.

reactive components of the resin. Hence, dilution appears to be a stronger effect than the plasticizing effect of moisture that can increase reactivity. Chow *et al.*[1,2] believed that excessive amounts of water in the samples act as an energy barrier to resin cure and consequently reduce the initial cure rate of resin.

In *Figure 3* it is also interesting to note that although the higher sample moisture retarded the initial rate of cure, the degree of cure at the largest precure times used was almost equal in all samples. This apparent equality of cure at long times suggests that water enhances the resin polymer mobility, via plasticization, thus allowing greater eventual cure. In addition, no sign of vitrification occurred at any of the moisture conditions, which would have been indicated by a degree of cure plateau beyond which further chemical reaction was inhibited. It thus appears that further increasing the precure time would increase the degree of cure under each moisture condition, especially for the samples with 71% moisture content, because the degree of cure for these moisture samples still kept increasing at approximately the same curing rate from 5 min to at least 14 min, the longest selected precure time.

Effect of precure temperature

The effect of precure temperature on the degree of resin cure for dry resin is shown in *Figure 4*. The data were obtained from d.s.c. measurements of the P_2O_5 dried samples which were precured in the dry oven at temperatures of 105, 115, 125 or 140°C, respectively. The rate and final degree of cure increased with increasing precure time at each precure temperature. The resin cured at a much higher rate and achieved a higher final degree of cure at higher temperatures. The rate of cure seemed to be greatly depressed or inhibited after 5 min precure treatment at 105 and 115°C, after 2 min at 125°C, and after 1 min at 140°C. Inhibition of cure is probably due to the onset of vitrification, a consequence of physical immobilization of reactive chains when a liquid thermoset is transformed to a glassy state[20–23].

The glass transition temperature (T_g) of the fully cured PF resin as a function of the pre-analysis r.h. was also measured in this study. The uncured resin samples were conditioned to 0, 64 and 89% r.h. prior to d.s.c. and were then scanned from 30 to 300°C at a heating rate of 5°C min^{-1}. The T_g defined in this study was the point where the transition of the resin sample was 50% complete, which was the point between the intersection of the regression line from the start of the transition with the inflection tangent and the intersection of the inflection tangent with the regression line after the transition. The T_g values were 153, 156 and 156°C for the samples conditioned to 0, 64 and 89% r.h., respectively. Since all these T_g values were greater than the precure temperatures (105–140°C), it is expected that the resin could be cured more completely later and achieve a higher final degree of cure in the dry oven by further increasing the precure temperature up to its T_g, via devitrification.

Effect of pre-analysis conditioning

In this study, the total amount of heat of cure reaction is the sum of the heat evolved during precure treatment and the residual heat of cure determined by d.s.c. analysis. Since moisture affects the cure rate of resin exposed to the precure treatment, it is also important to determine the effect of moisture on the measure of residual cure from which the degree of cure is calculated. In other words, this is an extension of the study on investigating how moisture affects the degree of resin cure. An important point here is that the samples have already been partially precured.

The effect of pre-analysis moisture conditioning on the residual heats of cure is shown in *Figure 5*. The results show that resin cure determined by d.s.c. is dependent on pre-analysis moisture conditioning. The residual heat was highest for the samples conditioned to 89% r.h. and decreased with reduction in the pre-analysis r.h. The larger quantities of heat generated during resin cure for samples equilibrated at higher humidities confirms results given above that moisture in solid resin indeed promotes resin reactivity and increases resin cure. However, a fixed level of precure dictates a fixed level of actual residual cure. Thus these results imply that having insufficient moisture in the sample during measure of residual cure could lead to inaccurate (low) values of residual cure. Inaccurately measured levels of residual cure would give inaccurate (high) calculated levels of precure.

The results of *Figure 5* were converted into degree of cure in *Figure 6*. For all the values at each particular r.h., the value of Q_T in the equation was the heat value obtained for an uncured sample analysed after conditioning at that particular r.h. The results in *Figure 6* for precured resins conditioned at 64% r.h. do not fall between those for 0 and 89% r.h. If we consider *Figure 5* again, the residual heats of cure for uncured samples were 619, 367 and 309 J g^{-1} at 89, 64 and 0% pre-analysis r.h. values, respectively. So the value obtained with 64% r.h. was much closer to that for 0% r.h. than for 89% r.h. However, after just a few minutes precure the residual cure values with 64% r.h. pre-analysis conditioning were much closer to those for 89% r.h. than for 0% r.h. At this point we do not know if the data accurately portray a change of response of samples pre-conditioned at 64% r.h. depending on precure times, or whether some experimental problems have given inaccurate data at the very shortest precure times for the 64% r.h. data. Interestingly, the curves for data at

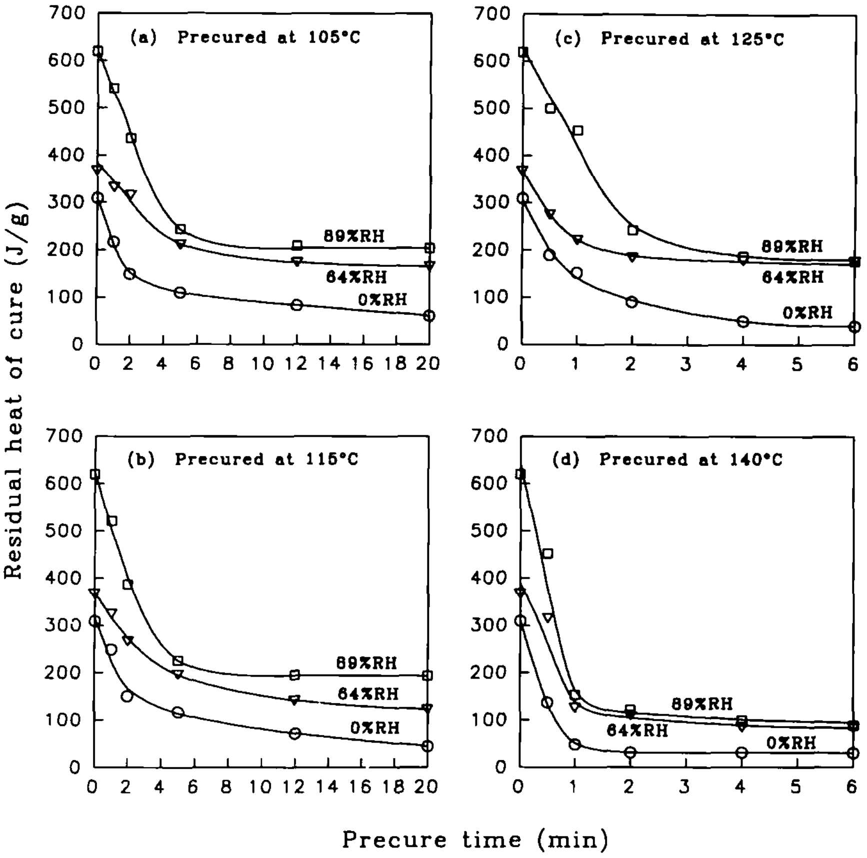

Figure 5 Residual heat of cure measured by d.s.c. for dry samples precured in a dry oven at (a) 105°C, (b) 115°C, (c) 125°C and (d) 140°C. Samples were conditioned to 0, 64 or 89% r.h. prior to d.s.c. (Note that plots c and d have shorter precure time-scales than plots a and b)

0 and 89% r.h. in *Figure 5* appear to be parallel, while those for 64% r.h. obviously are not consistently parallel to the others.

It is also observed, in *Figure 5*, that the residual heats of cure after 1 min at 140°C appeared to level off and the final values, obtained with the various pre-analysis moisture conditions, came closer to each other than for the final values at any of the other precure temperatures. This indicates that with an increase in precure temperature, the effect of pre-analysis moisture on the resin cure becomes less significant.

Effect of precure temperature on the rate of cure in the early stages

If the rate of cure during the first several minutes of precure treatment is considered as a linear function of precure time at each precure temperature and pre-analysis condition (*Figure 6*), we can plot the slopes of each curve in their linear regions against precure temperature to express the rate of cure (% min^{-1}) in the early stages. Since the pre-analysis r.h. values could change the calculation of the actual initial precure rate fixed by precure, only the data from 89% r.h. were used for this evaluation, which we assume is sufficient to give a good measure of residual cure. The relationship between the rate of cure and precure temperature at 89% r.h. is plotted in *Figure 7*. The results show that the precure temperature below 115°C does not have a significant effect on the rate of cure. Above that temperature, the rate of cure linearly increased with increasing precure temperature.

CONCLUSIONS

The extent of resin cure experienced by samples exposed to successively extended precure time periods of controlled temperature, moisture and r.h. has been measured by d.s.c. The results can be summarized as follows.

The precure temperature had a significant effect on the degree of cure. The rate of resin cure increases with increasing precure temperature. This is especially true in the early stages of cure, where the rate of cure is linearly related to the precure temperature (above 115°C). The maximum degree of cure also increases with an increase of precure temperature.

Moisture within a sample can either promote or retard the resin cure. On one hand, moisture acts as a plasticizer to promote resin reactivity via molecular mobility, allowing the resin to cure more completely and achieve a higher final degree of cure by increasing curing time. On the other hand, moisture may dilute the reactive components of resin, thus retarding the resin cure rate and prolonging cure time.

Environmental r.h. (in the steam treatment chamber) had a positive effect on the resin cure for the dry samples. The resin cured faster and achieved a higher final degree of cure with increasing r.h. This indicates that the absorbed moisture in the samples during precure treatment enhanced the reactivity of resin, probably via water plasticization.

The actual degree of resin cure measured by d.s.c. greatly depended on the pre-analysis conditioning. Higher pre-analysis r.h. tended to yield a larger residual

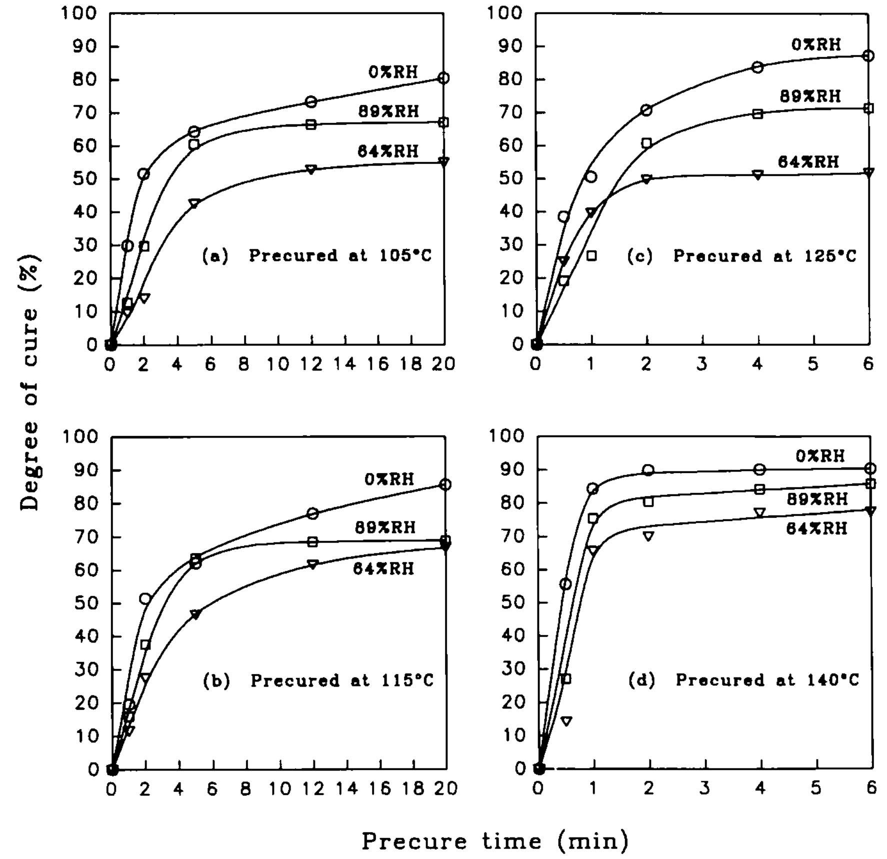

Figure 6 Degree of cure calculated after residual cure was measured by d.s.c. for dry samples precured in a dry oven at (a) 105°C, (b) 115°C, (c) 125°C and (d) 140°C. Samples were conditioned to 0, 64 or 89% r.h. prior to d.s.c. (Note that plots c and d have shorter precure time-scales than plots a and b)

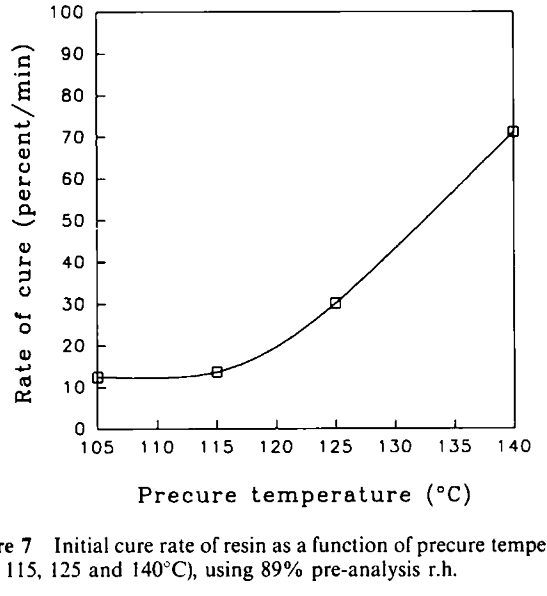

Figure 7 Initial cure rate of resin as a function of precure temperature (105, 115, 125 and 140°C), using 89% pre-analysis r.h.

heat of cure; consequently, a lower degree of precure would be calculated. The effect of pre-analysis r.h. on the resin cure became less significant with greater resin cure and with increasing precure temperature.

ACKNOWLEDGEMENTS

This material is based on work supported by the Ministry of International Affairs, Quebec Government, the Natural Sciences and Engineering Research Council of Canada, and Laval University (Quebec City). The work was also supported by the US Department of Agriculture under research joint venture agreement FP-92-1835.

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