

Effects of Resin and Curing Parameters on the Degree of Cure of Resole Phenolic Resins and Woodflour Composites

SOLOMON SO* and ALFRED RUDIN,† *Guelph-Waterloo Centre for Graduate Work in Chemistry, and Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

Synopsis

The degree of cure of various resole phenolic resins was assessed from their resistance to acetone extraction. Cured woodflour composites of resoles were also characterized by dynamic mechanical tests in linear viscoelastic behaviour regions. Acetone extraction is not a sensitive discriminator between highly cross-linked resins. In addition, residual basic catalyst promotes aldol condensation reactions of acetone to produce materials that are absorbed in the phenolic resin so as to provide negative weight loss data on extraction. Despite its inaccuracies, however, this solvent resistance test is still useful as a go/no-go specification technique. Dynamic mechanical tests were performed on molded resole/woodflour composites. This is a useful method for characterizing degree of cure and residual reactivity of the phenolic resin. Degree of cure increases with curing time, temperature and resin pH, with pH being the most important variable. Resins cured at pH's near neutral are linked by ether linkages rather than the more stable methylene bridges. The final degree of cure of woodflour composites depends heavily on the curing conditions (pH, time, temperature). It does not appear to be crucial how the initial resoles were made (i.e., catalyst, phenol/formaldehyde mole ratio or duration of the condensation reaction time) so long as the resoles have relatively high molecular weight. Curing should preferably be at temperatures below 180°C to minimize degradation of the polymer.

INTRODUCTION

The state of cure of phenolics has been studied by ^{13}C NMR¹⁻³ and infrared spectroscopy.^{4,5} A number of more empirical techniques are also used. Although these methods do not provide detailed insights into the structures of cured resins or the chemistry of crosslinking reactions they can nevertheless add some valuable information to our knowledge of these processes and products. Techniques like solvent resistance,⁶ Rockwell hardness at elevated temperatures,⁷ and differential scanning calorimetry (DSC)⁸⁻¹² have also been used for this purpose. DSC is particularly convenient in this regard, but its results are somewhat ambiguous. This experiment measures the consequences of at least two independent processes: the unzipping of oxymethylene oligomers and the formation of methylene bridges. Both reactions are exothermic.¹³

Acetone extraction is a simple and inexpensive characterization method, although it is fairly time consuming. A few results from this technique have

* To whom correspondence should be addressed.

† Present address: Fiberglas Canada Inc., 704 Mara Street, Point Edward, Ontario, N7T 7X4, Canada.

been obtained for neat novolac phenolics,⁶ and for woodflour-filled resoles and novolacs.⁷ In these reports the effects of curing time and curing temperature were investigated. It is assumed in these analyses that the resin and solvent are chemically inert to each other and that phenolic resins with relatively low degrees of crosslinking would be extractable by the acetone. Consequently, the amount of extractable resin should diminish with increasing cure.

The objective of the present work is to investigate the extent of cure of a variety of resoles which have been cross-linked under different conditions. The acetone extraction method was employed, since it is commonly used in industry. Dynamic mechanical tests were also conducted on some cured resoles that were used as adhesives for woodflour composites. Both techniques are shown to provide useful information about the effects of resin and curing parameters on the degree of crosslinking of resoles.

EXPERIMENTAL

Preparation of Resoles

The resole preparation procedures were reported in a previous paper.² Neat resoles were used mainly for the acetone extraction experiments. Several variations of the resole preparation method are given below for resoles used as woodflour adhesives. These latter materials included three different $\text{Ba}(\text{OH})_2$ -catalysed resoles with formaldehyde-phenol (F/P) mole ratios 1.37, 1.70, and 2.03, as well as NaOH- and Na_2CO_3 -catalysed resoles (F/P = 1.37). All were synthesized with reaction times of $5\frac{1}{2}$ h, instead of 2 h, to obtain resoles with relatively high viscosities to facilitate the molding of woodflour composites. Part of the $\text{Ba}(\text{OH})_2$ -catalysed resole solution (F/P = 1.37) with 2 h reaction time and pH of 8.3 was adjusted to pH 6.5 with oxalic acid solution and to pH 9.5 with NaOH solution. As much water as possible was then removed from the resole solution by rotary evaporation at temperatures up to 45°C.

Viscosity Measurement of Resoles Used for Woodflour Adhesive

The viscosities of different uncured neat resoles was measured in a Rheometrics Mechanical Spectrometer (model 605) equipped with a 2000 g cm torque transducer. The sample was placed between cone and plate fixtures having a diameter of 50 mm and a cone angle of 0.04 radian. All measurements were carried out at ambient temperature with steady rotation. A shear rate range from 1 s^{-1} to 10 s^{-1} was used.

Acetone Extraction

Only neat resoles were used in this experiment. The cured resin was ground with a dental amalgamator and then sieved to pass a 40 mesh screen. The powdered resin was vacuum dried initially overnight at room temperature, and then dried further at 90°C for 1 h. It was then conditioned in a dessicator under vacuum for 2 h before weighing. A dried cellulose thimble (which had been conditioned under identical conditions as the resin) was weighed and reweighed after about 0.5 to 1.5 g of resin was added. The resin and thimble were placed inside a Soxhlet extractor and refluxed with acetone for 48 h. The extracted

resin and thimble were dried and weighed as described above and the change of weight was recorded. Preliminary work indicated that 48 h extraction time was necessary to complete the extraction with powdered resin with mesh size larger than 40. Sintered glass thimbles (ASTM 40-60 C) were also tried, but these were easily blocked by swollen resin particles so that the extraction was often incomplete. As a consequence, cellulose thimbles were used even though they are more susceptible to the effects of humidity fluctuations.

Dynamic Mechanical Measurements

With the available equipment, it was not possible to prepare completely blister-free and highly uniform, cured rectangular bars from neat resole phenolics. Therefore, resole-woodflour composites (60/40 w/w) were used to prepare all test specimens for dynamic mechanical tests.

The test specimens were cured to rectangular bar shapes ($3 \times 25 \times 63 \text{ mm}^3$) in a stainless steel picture frame mold between polytetrafluorethylene parting sheets. Pressings were for 4 min at 160°C and 720 kg/cm^2 pressure, unless otherwise specified. Each cured bar-shaped composite was cut into two, with approximate dimension $3 \times 12.5 \times 63 \text{ mm}^3$, and then trimmed to uniform thickness and width with emery cloth. The exact dimension of each test specimen was measured after trimming.

All dynamic mechanical tests were performed on a Rheometrics Mechanical spectrometer (model 605). Trial experiments in the forced-torsion and 3 point-bending tests indicate that the dynamic storage moduli of these materials were independent of both frequency (0.1 to 10 Hz) and strain (0.01 to 6%, and 0.01 to 0.1% for forced-torsion and 3 point-bending tests, respectively). Therefore, the chosen test frequency was 1 Hz; while the strains for optimum sensitivity for forced-torsion and 3 point-bending tests were 0.2% and 0.06%, respectively. For temperature sweeps in a cure mode, the test specimen was heated under nitrogen atmosphere at a rate of 5°C per minute.

RESULTS AND DISCUSSIONS

Viscosity Measurements

All the neat resoles were Newtonian fluids. The viscosities shown in Table I were measured at shear rate of 6.31 s^{-1} and at ambient temperature.

Acetone Extraction Measurements

The extraction results at different curing times and temperatures are as expected (see Figure 1 (a), (b), and Figure 2). In general, the degree of cure of phenolic resins increases with curing time up to a maximum. In other words, the weight loss on acetone extraction decreases with curing time to a minimum (i.e., 0% extraction ideally). Similarly, the weight loss decreases with curing temperature.

It is more interesting to notice that the degree of cure increases with curing pH; the same result is also shown by the CH_2/Ar_1 ratios (mole ratios of methylene bridges to phenol residues) determined by solid-state ^{13}C CP-MAS NMR experiments, which are reported elsewhere.² There is clearly a correlation be-

TABLE I
Viscosities of Resoles Used to Make Woodflour Composites

Sample	Viscosity (poise)
<i>Catalysed with: (F/P ratio 1.37, reaction time 5½ h)</i>	
NaOH	19
Ba(OH) ₂	37
Na ₂ CO ₃	56
<i>F/P mole ratio (reaction time 5½ h, Ba(OH)₂-catalysed)</i>	
1.37	37
1.70	83
2.03	113
<i>Reaction time (F/P mole ratio 1.37, Ba(OH)₂-catalysed)</i>	
2 h	15
3½ h	22
5½ h	37
<i>Curing pH (F/P mole ratio 1.37, reaction time 2 h, Ba(OH)₂-catalysed)</i>	
6.5	10
8.3	15
9.5	110
<i>Commercial resole adhesive (neutral pH)</i>	109

tween the content of acetone extractables and the CH₂/Ar₁ ratio (Figure 3) despite the relatively large experimental error in the acetone extraction measurements. Similar correlations are found in the effects of curing time and curing temperature (not shown).

The effects of catalyst type, reaction time, and F/P mole ratio on acetone extraction results are summarized in Tables II, III, and IV. Although the experimental error is relatively large (also see Fig. 1(b)), clear trends are still observable.

If the assumptions mentioned in the Introduction were true for the acetone extraction experiments, there should not have been any weight gain of extracted samples. The IR spectra of those resins which showed weight gains before and after the extraction all indicated that a new carbonyl functional group emerged around wave number 1700 cm⁻¹ (see Figure 4) after the extractions. This might suggest that the curing conditions of the resin could accelerate the thermal-oxidative degradation of the resin during the extraction period. Such degradation has been described elsewhere.¹⁴ It is unlikely that the extraction conditions were severe enough to provoke degradation of the phenolic resin, however, and an alternative, more likely explanation follows.

Acetone that had been used to extract cured phenolics was stripped in a rotary evaporator. A significant residue of a yellowish-brown high boiling liquid was found. This is mainly diacetone alcohol¹⁵ which forms from the aldol con-

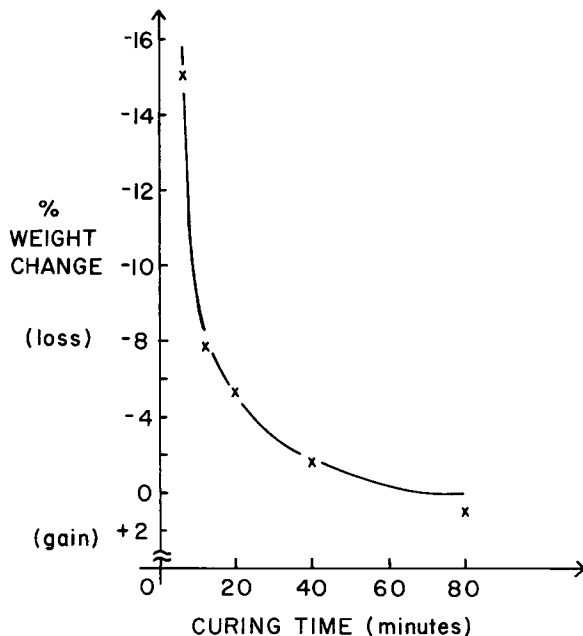


Fig. 1(a). Effect of curing time on acetone extractables. Curing temperature 160°C , condensation reaction time 2 h, $\text{Ba}(\text{OH})_2$ catalyzed resole, F/P mole ratio 1.37, curing pH neutral.

densation of acetone under reflux in the presence of a basic catalyst like $\text{Ba}(\text{OH})_2$. It is unlikely that the increase of weight during acetone extraction is solely due to the oxidation of $-\text{CH}_2-$ or $-\text{CH}_2\text{OH}$ groups of the phenolic resins to carbonyls because the increase is sometimes rather large (i.e., well above 1%). It is more likely that the cured resin may absorb some diacetone alcohol

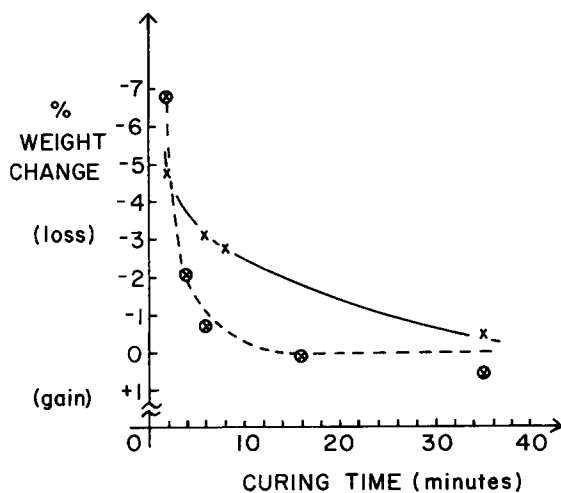


Fig. 1(b). Effect of curing time on acetone extractables. Curing temperature 160°C , condensation reaction time 2 h, $\text{Ba}(\text{OH})_2$ catalyst resole with F/P mole ratio 1.37, curing pH 8.3 \odot 1st trial, \times replicate.

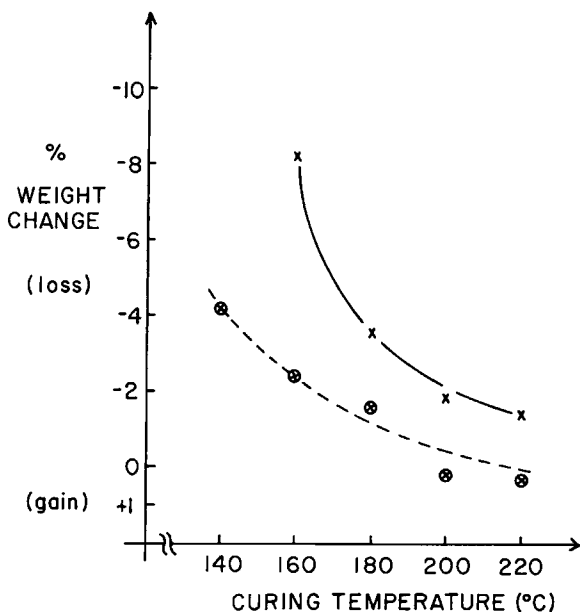


Fig. 2. Effect of curing temperature on acetone extractables. Condensation reaction time 2 h, $\text{Ba}(\text{OH})_2$ catalyzed resole with F/P ratio 1.37, curing pH 8.3 \times curing time = 2 min. \odot curing time = 4 min.

or other condensation products of acetone, causing the weight increase after the acetone extraction experiment, as well as the presence of carbonyl group in the IR spectra. For resins with relatively high degrees of cure (e.g., Table IV, $5\frac{1}{2}$ h reaction time), there is no weight loss at all. The positive values that are observed show that the acetone extraction technique is not a sensitive

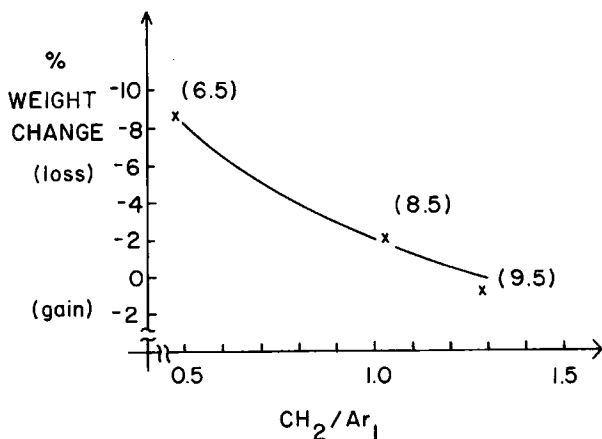


Fig. 3. Effect of curing pH; relation between weight loss during acetone extraction and CH_2/Ar_1 ratio from ^{13}C CP-MAS analyses. Condensation reaction time 2 h; $\text{Ba}(\text{OH})_2$ catalyzed resole with F/P mole ratio 1.37; cured for 4 min at 160°C . Numbers in brackets are the pH's of the resoles.

TABLE II
Effect of Catalyst

Catalyst	1st experiment % weight change	Replicate experiment % weight change
NaOH	-3.2%	-2.3%
Ba(OH) ₂	-2.0%	-1.3%
Na ₂ CO ₃	+4.5%	+6.9%

Note: Reaction time 2 h, curing time 4 min, curing temperature 160°C, curing pH 8.3, and F/P mole ratio 1.37.

TABLE III
Effect of Reaction Time

Reaction time	1st experiment % weight change	Replicate experiment % weight change
2 h	-2.0%	-2.4%
3½ h	-0.2%	-1.1%
5½ h	+0.7%	+0.4%

Note: Curing time 4 min, curing temperature 160°C, curing pH 8.3, F/P mole ratio 1.37, Ba(OH)₂-catalysed condensation reactions.

TABLE IV
Effect of Formaldehyde/Phenol Mole Ratio

F/P mole ratio	1st experiment % weight change	Replicate experiment % weight change
(2 h reaction time)		
1.37	-2.4%	-2.0%
1.70	+5.0%	+1.6%
2.03	+5.8%	+1.4%
(5½ h reaction time)		
1.37	+0.7%	—
1.70	+1.5%	—
2.03	+3.4%	—

Note: Curing time 4 min, curing temperature 160°C, curing pH 8.3, Ba(OH)₂-catalysed condensation reaction.

discriminator between highly crosslinked resins. Despite its inaccuracies, however, the technique is simple and may still be useful as a go/no-go specification method.

Dynamic Mechanical Analysis

The results of forced-torsion and 3-point bending tests are summarized in Tables V and VI. The experimental errors are estimated at 95% certainty, using

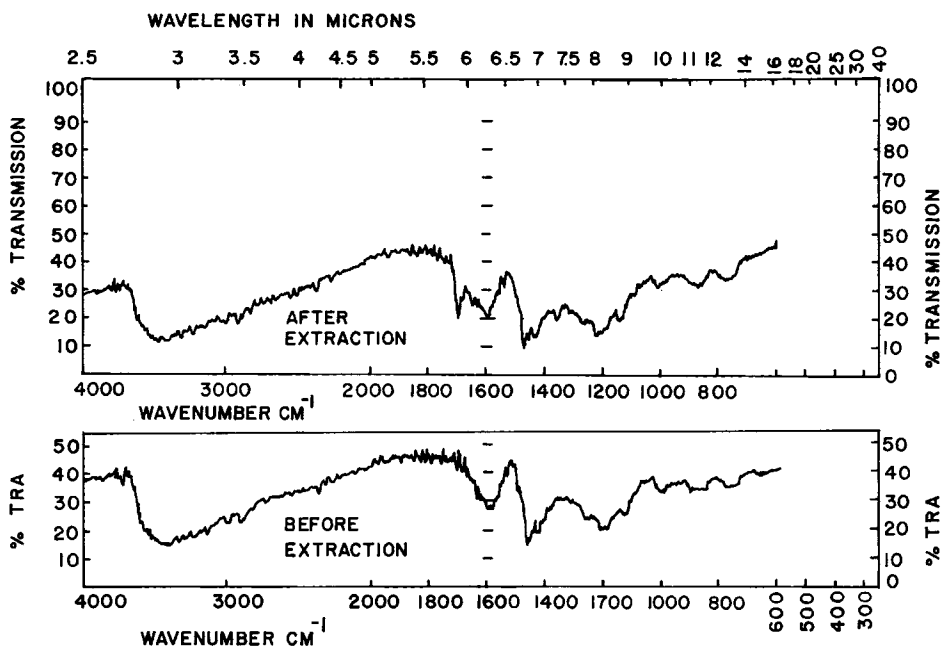


Fig. 4. IR spectra of phenolic resin before and after acetone extraction. $\text{Ba}(\text{OH})_2$ catalyzed resole with F/P ratio 1.37; condensation reaction time 2 h, cured at pH 9.5 for 4 min at 160°C .

5 to 8 replicate samples. In Table V G is a shear modulus, while E is a tensile modulus in Table VI. The dynamic modulus values vary, of course, with specimen temperature. For present purposes, they are measured at ambient temperature (about 25°C). At a glance, both the dynamic shear and tensile moduli from the two tests provide similar trends of results. The high values of storage moduli of resin-woodflour composites indicate properties of typical glassy polymeric materials, and the very low $\tan \delta$ values show that there is not much molecular mobility within the polymers.

There are slight differences of the modulus values, depending on the effects of reaction time, catalyst and F/P mole ratio (see Tables V and VI). Such results are quite readily explained. Apparently, there is an optimum F/P mole ratio around 1.7 which gives good resin-woodflour adhesion.

The important factors that have significant influences on the moduli of these cured composites are, firstly, curing pH and, secondly, the curing time. The curing rate is very slow at neutral pH and increases with curing pH.

For resoles made with 2 h reaction time, ^{13}C CP-MAS experiments² showed that the degree of crosslinking is higher in $\text{Ba}(\text{OH})_2$ than in NaOH -catalyzed resoles. However, dynamic mechanical measurements do not distinguish between catalysts used to prepare resoles made in $5\frac{1}{2}$ h condensation reactions. This is probably because the molecular weight of the resole with $5\frac{1}{2}$ h reaction time is high enough that a 4 min cure is sufficient to crosslink all composites to a high level (Table VI).

Most resoles used for making the woodflour composites for the dynamic mechanical tests were made with longer reaction times than those used in the ^{13}C CP-MAS NMR experiments.² Therefore, it is not always possible to compare

TABLE V
Summary of Forced-Torsion Dynamic Mechanical Analyses of Phenolic-Woodflour Composites at Ambient Temperature

Sample	$G' \times 10^{-8}$ (dyne/cm ²)	$G'' \times 10^{-7}$ (dyne/cm ²)	$\tan \delta \times 10^2$
<i>Effect of reaction time (curing temp. 160°C, curing time 4 min, curing pH 8.3, F/P mole ratio 1.37, and Ba(OH)₂-catalyzed)</i>			
2 h	8.43 ± 1.4	44.1 ± 1.2	5.2
3½ h	85.4 ± 2.8	43.4 ± 2.3	5.1
5½ h	89.0 ± 1.2	42.5 ± 2.5	4.8
<i>Effect of F/P mole ratio (reaction time 5½ h, other parameters same as above)</i>			
F/P = 1.37	89.0 ± 1.2	42.5 ± 2.5	4.8
1.70	96.8 ± 2.6	39.3 ± 2.9	4.1
2.03	95.3 ± 1.8	38.0 ± 5.1	4.0
<i>Effect of catalyst (reaction time 5½ h, F/P mole ratio 1.37, curing temp. 160°C, curing time 4 min and curing pH in parentheses)</i>			
Ba(OH) ₂ (8.3)	89.0 ± 1.2	42.5 ± 2.5	4.8
Na ₂ CO ₃ (8.6)	91.8 ± 4.0	39.9 ± 2.3	4.3
NaOH (8.4)	92.9 ± 3.5	47.1 ± 3.7	5.1
NaOH (8.4) (12 min cure)	88.9 ± 3.9	42.1 ± 2.5	4.7
<i>Effect of curing pH (reaction time 2 h, curing time in parentheses, other parameters same as in effects of reaction time)</i>			
pH = 6.5 (12 min)	57.6 ± 3.1	90.1 ± 1.9	15.6
pH = 6.5 (26 min)	104.9 ± 3.1	56.2 ± 2.5	5.4
pH = 8.3 (4 min)	84.3 ± 1.4	44.1 ± 1.2	5.2
pH = 9.5 (85 sec)	90.7 ± 1.5	41.5 ± 1.5	4.6
<i>Commercial resole adhesive</i>			
10 min cure at 160°C neutral pH	92.9 ± 7.0	42.7 ± 2.4	4.6

results from these two techniques. The exceptions are those resoles made with different reaction times. There is a good correlation between the degree of crosslinking (i.e., CH₂/Ar₁ ratio) from ¹³C CP-MAS NMR experiments² and the dynamic storage moduli from dynamic mechanical tests are shown in Figure 5.

A series of fixed frequency variable temperature sweeps were performed with resole-woodflour composites in the forced torsion mode. The specimens were cooled and the temperature sweep was repeated. The corresponding storage moduli are plotted in Figures 6 to 10. The open symbols in all figures are for the first temperature sweep; while the solid symbols represent data from the second temperature sweep. The composite samples were not absolutely uniform and the modulus values would thus vary slightly, so that it is not intended to compare the modulus values from one modulus curve to another. However,

TABLE VI
Summary of 3 Point-Bending Dynamic Mechanical Analyses of Phenolic-Woodflour Composites at Ambient Temperature

Sample	$E' \times 10^{-9}$ (dyne/cm ²)	$E'' \times 10^{-8}$ (dyne/cm ²)	$\tan \delta \times 10^2$
<i>Effect of reaction time (curing temp. 160°C, curing time 4 min, curing pH 8.3, F/P mole ratio 1.37, and Ba(OH)₂-catalysed)</i>			
2 h	23.3 ± 0.8	19.0 ± 1.7	8.2
3½ h	23.9 ± 0.8	18.9 ± 0.8	7.9
5½ h	24.3 ± 0.8	18.2 ± 1.3	7.5
<i>Effect of F/P mole ratio (reaction time 5½ h, other parameters same as above)</i>			
F/P = 1.37	24.3 ± 0.8	18.2 ± 1.3	7.5
1.70	27.3 ± 0.6	18.1 ± 0.9	6.6
2.03	25.7 ± 0.9	17.1 ± 1.8	6.6
<i>Effect of catalyst (reaction 5½ h, F/P mole ratio 1.37, curing temp. 160°C, curing time 4 min, and curing pH in brackets)</i>			
Ba(OH) ₂ (8.3)	24.3 ± 0.8	18.2 ± 1.3	7.5
Na ₂ CO ₃ (8.6)	25.1 ± 0.9	16.3 ± 1.5	6.5
NaOH (8.4)	25.6 ± 2.0	18.2 ± 1.3	7.1
NaOH (8.4) (12 min cure)	24.6 ± 1.2	16.4 ± 1.2	6.7
<i>Effect of curing pH (reaction 2 h, curing time in brackets, other parameters same as in effect of reaction time)</i>			
pH = 6.5 (12 min)	18.6 ± 0.7	26.8 ± 0.8	14.4
pH = 6.5 (26 min)	30.4 ± 1.2	19.4 ± 2.4	6.4
pH = 8.3 (4 min)	23.3 ± 0.8	19.0 ± 1.6	8.2
pH = 9.5 (85 sec)	30.0 ± 1.3	21.2 ± 1.0	7.1
<i>Commercial resole adhesive</i>			
10 min cure, at 160°C neutral curing pH	27.4 ± 0.6	17.5 ± 1.5	6.4

qualitative comparisons of the different curves will be useful in understanding the curing reactions of these thermosetting polymers.

It is clear that all the woodflour composites have a relatively high degree of cure, except those with curing pH 6.5. In the latter case, the dynamic storage shear moduli decrease very gradually with temperature. None of the composites were completely cross-linked, since the first and second temperature sweep modulus curves do not overlap exactly.

Figure 6 indicates that the degree of cure of the composite increases with duration of the condensation reaction used in preparing the resole. This supports the findings from the ¹³C CP-MAS NMR and acetone extraction techniques as discussed earlier. Figure 7 shows that a resole made with 1.70 F/P mole ratio achieves a higher degree of cure than one made with 1.37 F/P mole ratio. There is, however, little to choose between F/P mole ratios of 1.70 and 2.03. Figure 8 shows that the modulus curves of different composites made from

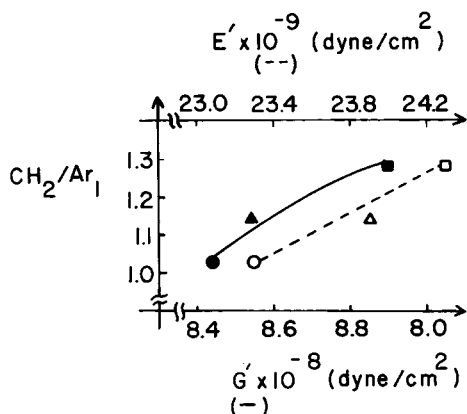


Fig. 5. Relation between dynamic mechanical storage moduli and degree of crosslinking from ^{13}C CP-MAS experiments. The symbols refer to different condensation reaction times: \circ \bullet 2 h; Δ \blacktriangle 3½ h; \square \blacksquare 5½ h.

resoles with different catalysts are very similar, if the molecular weights of the phenolic prepolymers have first been driven to fairly high values in a long condensation reaction.

The most striking feature is observed in the effect of curing pH (Figure 9). Composites cured at pH 6.5 show a drastic decrease and then an increase in the modulus-temperature relation during the first sweep. This suggests that the composite initially has a very low degree of cure. The subsequent increase in the modulus is characteristic of further crosslinking. The physical appearance of this composite supports this suggestion. The material changes from soft to

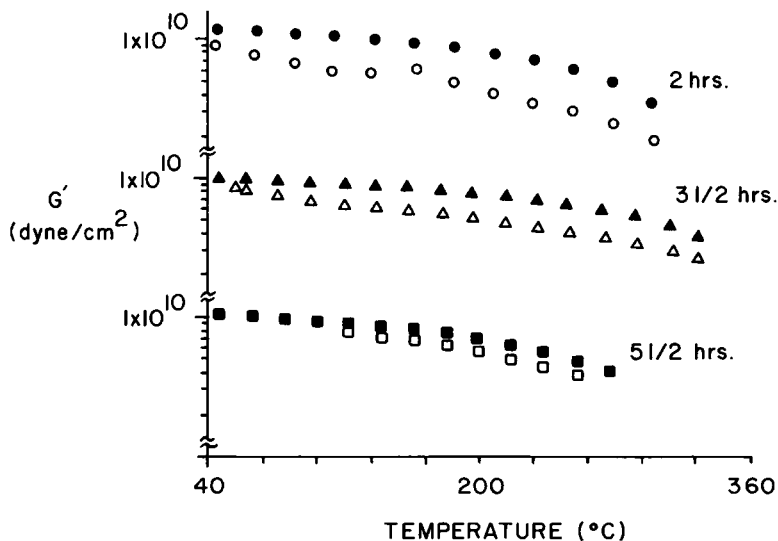


Fig. 6. Effects of duration of resole condensation reaction on storage shear modulus in forced-torsion dynamic mechanical test. $\text{Ba}(\text{OH})_2$ catalyzed resole with F/P mole ratio 1.37; cured at 160°C for 4 min at pH 8.3.

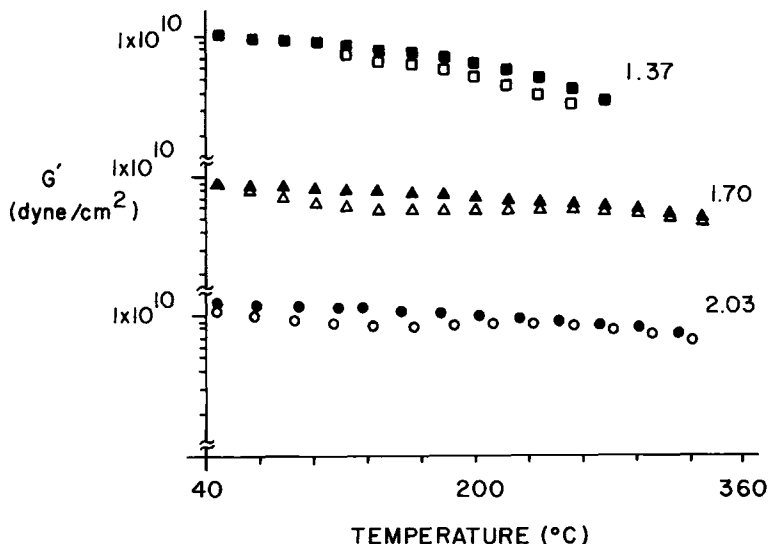


Fig. 7. Effects of formaldehyde/phenol mole ratio of resole on storage modulus of cured resole/woodflour composite. $\text{Ba}(\text{OH})_2$ catalyzed resole with indicated F/P ratios; $5\frac{1}{2}$ h duration of condensation reaction; cured at 160°C for 4 min.

hard during the first temperature sweep. In addition, the modulus curves are generally shifted to higher values after the first sweep.

It can be seen clearly that a longer curing time (e.g., samples with curing pH 6.5) yields composites with relatively higher degrees of crosslinking, as indicated by the modulus curves in Figure 10. For a 26 min cure, the "valley"

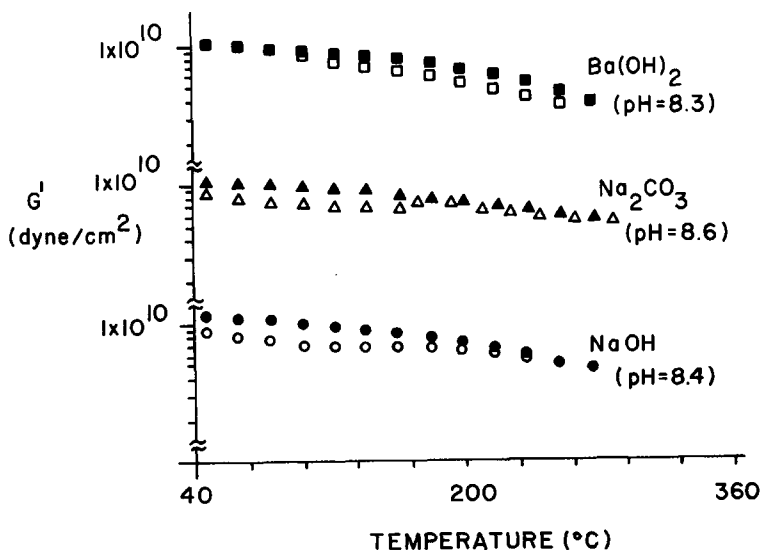


Fig. 8. Effects of catalyst on storage modulus of cured resole/woodflour composite. Resoles made with F/P mole ratio 1.37 and $5\frac{1}{2}$ h condensation reaction time; cured for 4 min at 160°C .

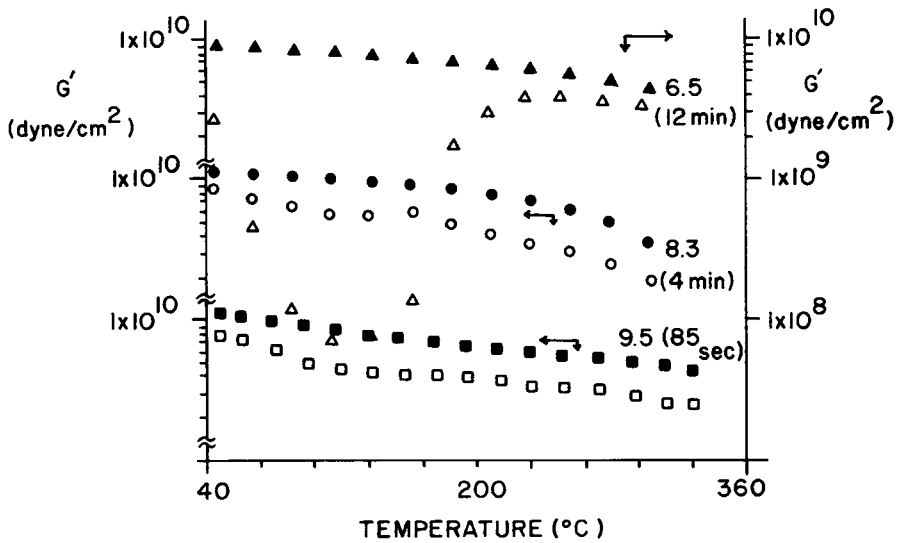


Fig. 9. Effects of curing pH on storage modulus of resole/woodflour composites. $\text{Ba}(\text{OH})_2$ catalyzed resole made with F/P mole ratio 1.37 and 2 h condensation reaction time; pH values are shown on each curve along with curing time, in brackets.

in the modulus curve is smaller. The modulus curves for the composite made from a commercial resole adhesive are also shown in Figure 10. The curing conditions involved 10 min at 160°C and neutral pH; therefore, the curves have similar behaviour to those with curing pH 6.5 (i.e., a small "valley" in the modulus curve in the first temperature sweep). It is known from ^{13}C CP-MAS

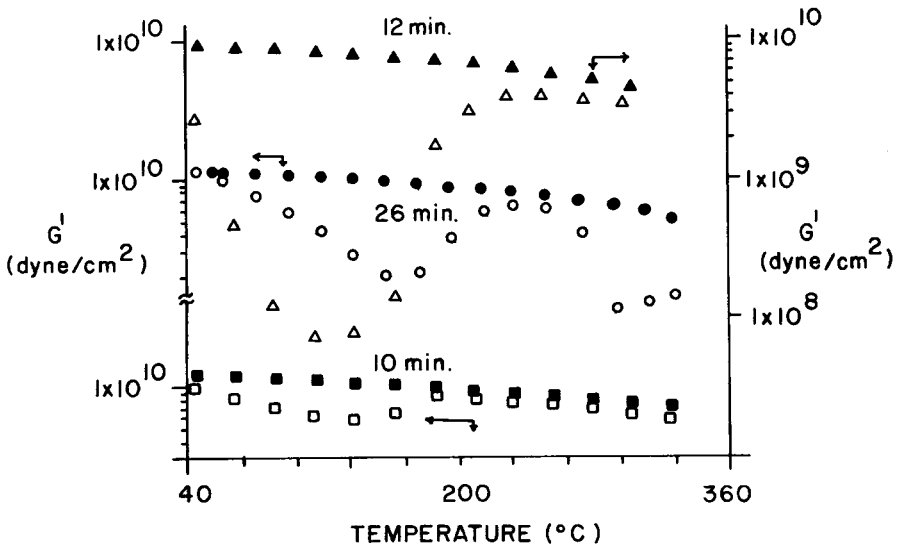


Fig. 10. Effects of curing time on storage modulus of resole/woodflour composite. Δ and \circ refer to $\text{Ba}(\text{OH})_2$ catalyzed resole made with F/P ratio 1.37 and 2 h reaction time, curing pH > 6.5 ; \square refers to commercial resole adhesive with neutral pH, cured at 160°C .

experiments² that at curing pH's near neutral ether linkages are predominantly formed. These will convert to methylene linkages as the curing reaction is forced further by increasing the curing time or curing temperature. Thus, it is likely that the "valley" in the modulus-temperature curves of composites that have been cured at neutral pH is due to the conversion of ether linkages to methylene linkages. Composites cured at other pH's showed no significant "valley" which means that these materials do not have significant amounts of ether linkages.

Finally, we note that the thermal degradation of cured phenolic resins may occur before the glass transition temperature of the material. It is not feasible, therefore, to measure T_g by dynamic mechanical analyses. The composites examined after the second temperature sweep were very dark in color and brittle and were likely degraded to some degree.

CONCLUSION

Acetone extraction is shown not to be sensitive to the state of cure of resole phenolic resins with relatively high degrees of crosslinking. In addition, the acetone solvent is not totally inert. Fortunately, despite the large, inherent experimental errors, this solvent extraction technique can provide useful information that correlates well with results from solid-state ¹³C CP-MAS techniques.

Dynamic mechanical analyses on resin-woodflour composites are generally reliable for both quantitative and qualitative results. The results also correlate well with other techniques. Dynamic mechanical analyses are, therefore, recommended to study the degree of cure of resin composites. It should be remembered that the affinity of resin for the reinforcement (e.g., wood, fibreglass) could also have an important effect on composite behaviour. The results of dynamic mechanical analyses are probably a reflection of both the resin-substrate affinity and the degree of cure of the resin.

Based on the results from acetone extraction, dynamic mechanical tests, and solid-state ¹³C NMR techniques, it does not appear to be crucial how resoles are made (i.e., catalyst, F/P mole ratio, and reaction time); so long as the resoles are of relatively high molecular weight. The final degree of cure depends heavily on the curing conditions (i.e., curing pH, curing time, and curing temperature) if the effect of any reinforcing substrate on the resin is ignored. At a fixed curing temperature, curing pH has more effect on the degree of cure than does the curing time. Experimentally, it is of advantage to cure the resin at temperatures not higher than 180°C (to prevent thermal degradation).

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