INVESTIGATION OF THE MICROWAVE CURING OF AN EPOXY RESIN SYSTEM

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SUMMARY: A commercial resin system, PR500 from 3M, has been cured using microwave heating. For comparison, the same resin has been cured using a conventional oven. The cured resins has been compared using modulated differential scanning calorimetry, dynamic thermal analysis, infrared spectroscopy and solid state NMR spectroscopy. The results show that the reaction path appears slightly different in the two cases. The epoxy-amine reaction occurs to a greater extent in the microwave cured resin than the epoxy-hydroxyl reaction compared to the thermally cured resin. The dielectric properties are not sensitive to this change. Broadening of the glass transition for microwave cured resins has been previously observed and attributed to a difference in network structure.

KEYWORDS: Microwave curing, thermal curing, epoxy resin, reaction path, infrared spectroscopy, NMR, differential scanning calorimetry

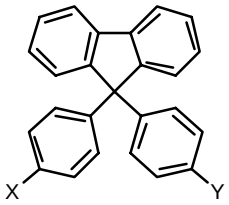
INTRODUCTION

The use of microwave processing could potentially revolutionize the preparation of composites. Typical cure times are reduced from hours to tens of minutes or less through the use of microwave rather than conventional curing. There is thus potential for savings to be made in commercial manufacture through shorter cure cycles and since the microwave energy is largely concentrated on the sample, greater efficiency. This in turn could lead to other savings. For example, the higher throughput reduces the number of facilities required thus leading to a reduction in capital equipment costs.

If microwave processing of resins is to be a useful commercial technique then it is important to understand the structure and properties of the cured resins. Changes in the network structure and detailed chemistry are possible and this could affect moisture uptake and resin degradation properties. This is an area where there has been controversy in the literature [1-3].

In the present work a well known epoxy system, PR500 from 3M, has been cured using both conventional and microwave heating. Comparison has been carried out using modulated differential scanning calorimetry (MDSC), dynamic mechanical

analysis (DMA), infrared spectroscopy (IR), dielectric property measurement and solid state NMR spectroscopy.
The structure of PR500 is known to be:



X, Y = OH

NH_2

$-CH_2-O-CH-CH_2$ (O)

EXPERIMENTAL

Thermal cure

Samples were produced in a conventional oven via isothermal cure at 160 ^{o}C for 90, 100, 130, 160 and 180 minutes.

Microwave cure

The microwave heating was carried out using a conventional multimode commercial microwave oven (Hinari MX717TC). The microwave field within multimode microwave cavities is not uniformly distributed. The variation in the field within this oven was observed by using thin plaques of a room temperature curing epoxy resin system (DER 332/Crayamd 140).[4-5]. Plaques of the resin were cast onto the turntable of the microwave and onto a glass plate which was set to the same height. Following irradiation in the microwave oven variations in the colour of the resin were observed and this allowed selection of a suitable position in the oven where uniform curing of the resins could be expected. Using this information single samples of dimension 50x50x5 mm in silicone rubber moulds were subsequently placed in the centre of the turntable. Initial experiments showed that the power was too high and resulted in a rapid temperature rise in the sample. The rated power of the microwave oven was 800 W. This was reduced by introducing an additional 0.95 μF capacitor between the transformer and magnetron. This resulted in the power, measured using the rise in temperature of a beaker of water, being reduced to 400 W. A further reduction in power was achieved by the use of a load which was 500 ml of 1% sodium chloride solution in water. The power, as measured using water, was then reduced to 30-40 W. This power level is consistent with those reported by others. It must, however, be remembered that the power levels were measured using a water load and not with the resin and are not accurate. The introduction of the water load into the cavity potentially presents the danger of water absorption by the resin during cure. The sodium chloride solution was cooled to a few degrees above freezing prior to use and replaced every ten minutes during cure. The temperature rise observed was approximately 10 ^{o}C, too small to give appreciable evaporation of the solution.
The cure schedule for the PR500 resin in the microwave oven was 180 minutes with the sodium chloride solution load (approximately 40 W) followed by 0, 5, 7.5, 10 and 15 minutes with no load (approximately 400 W). This does not represent a time saving on the thermal cure cycle. It was not the object of the present study to minimize the cycle time for the microwave cure but to produce samples via microwave and thermal cure for comparison.

Differential Scanning Calorimetry

Conventional differential scanning calorimetry (DSC) was carried out on the as-received resin in order to determine the enthalpy for cure. Modulated differential

scanning calorimetry (MDSC) was subsequently used to find the residual enthalpy for the cured samples and the glass transition temperature, T_g. A Mettler-Toledo TA8000 system was used. For the determination of residual enthalpy samples with weights in the range 1-20 mg were sealed in 40 ml aluminium pans. The samples were heated from 50 to 350 ^oC at ramp rates of 2, 5, 10 and 20 $^oC\ min^{-1}$. MDSC was performed in the temperature range 50-350 ^oC. An alternating signal of ±1 ^oC was applied to the ramp at 5 $^oC\ min^{-1}$ giving an overall ramp rate of 1.66 $^oC\ min^{-1}$. The glass transition temperature was determined from the onset of the second order change in the storage part of the heat capacity. The enthalpy of residual cure was obtained from the loss part of the heat capacity by integration of the area of the exotherm. A spline baseline was used. From the enthalpy the degree of cure, α, was calculated using

$$\alpha = 1 - \frac{\Delta H_c}{\Delta H_u}$$

where ΔH_c is the residual curing enthalpy of a partial cured sample of resin and ΔH_u is the curing enthalpy of the as-received resin.

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was carried out using a Netzch DMA 242 instrument in dual cantilever mode. The samples were heated from -160 to 300 ^oC at a ramp rate of 5 $^oC\ min^{-1}$. The magnitude of the oscillation was 30 μm and a frequency of 1 Hz was used.

Infrared Spectroscopy

Infrared (IR) spectra were obtained from the cured resin using a Perkin Elmer PE2000 Fourier transform infrared spectrometer. Fine powder was obtained from the cured samples by gently abrading with a fine file. The resulting powder was then pressed into a KBr disc.

Dielectric Measurement

The dielectric properties of the partially cured resin were obtained using a cavity perturbation method. Small cubes of the resin were cut from the cured plaques. These were placed on a polyethylene foam support in a brass cavity. The resonant frequency of the cavity was 2.45 GHz, the same frequency as the microwave source used for curing. The resonant frequency and Q value of the cavity with and without the sample present were recorded using a calibrated Hewlett Packard HP 8753 vector network analyser. From this data the real, ε'and imaginary, ε" parts of the complex dielectric constant were obtained using the following formulae[1]

$$\varepsilon' = 1 + \frac{(\omega_0 - \omega_s)V_{CAV}}{2\omega_0 V_{SAM}}$$

and

$$\varepsilon'' = \frac{1}{4}\left(\frac{1}{Q_0} - \frac{1}{Q_s}\right)\frac{V_{CAV}}{V_{SAM}}$$

where ω_0 is the resonant frequency of the empty cavity, ω_s is the resonant frequency of the cavity with the sample inserted, Q_0 is the quality factor of the empty cavity, Q_s is the quality factor for the loaded cavity, V_{CAV} is the volume of the empty cavity and V_{SAM} is the volume of the sample.

Solid state NMR Spectroscopy

^{13}C NMR spectra were obtained using a Varian Associates Unity 300 spectrometer equipped with Doty Scientific Inc. probes. Approximately 0.5 g of the thermal and

microwave cured resins, with degrees of cure of approximately 90%, were powdered and packed into 7 mm O.D. alumina or zirconia rotors. Spectra were acquired using cross-polarization/magic-angle spinning (CP/MAS) at several spin rates in the range 3.3 to 4.5 kHz to identify chemical shielding anisotropy (CSA) spinning sidebands. The RF field strengths were 36 kHz for cross-polarization and 45 kHz for the dipolar decoupling field. The CP contact time was 1 ms and the recycle time was 5 s. For assistance in spectrum assignment, a spectrum of the microwave cure was run using the dipolar dephasing (DD) technique whereby acquisition of the spectrum with proton decoupling is delayed for a short time to allow the ^{13}C signals to decay under the influence of ^{13}C-^{1}H dipole-dipole-coupling.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

Figure 1 shows DSC traces for the as-received resin, for the resin cured using microwave heating and for the resin cured using conventional heating. The enthalpy for cure of the as-received resin was 210 J g^{-1}. Figure 2 shows the T_g as a function of degree of cure showing that as both the thermal and microwave cured samples become better cured the T_g increases as expected. In the later stages of cure the glass transition temperatures for the microwave samples appeared to be higher than for the conventionally prepared materials. The glass transition could be easily defined for the thermally cured samples. Two separate transitions appeared to be present in the microwave cured samples. The appearance of this double transition is consistent with the previous reports indicating that T_g in microwave cured samples is broadened [4-7].

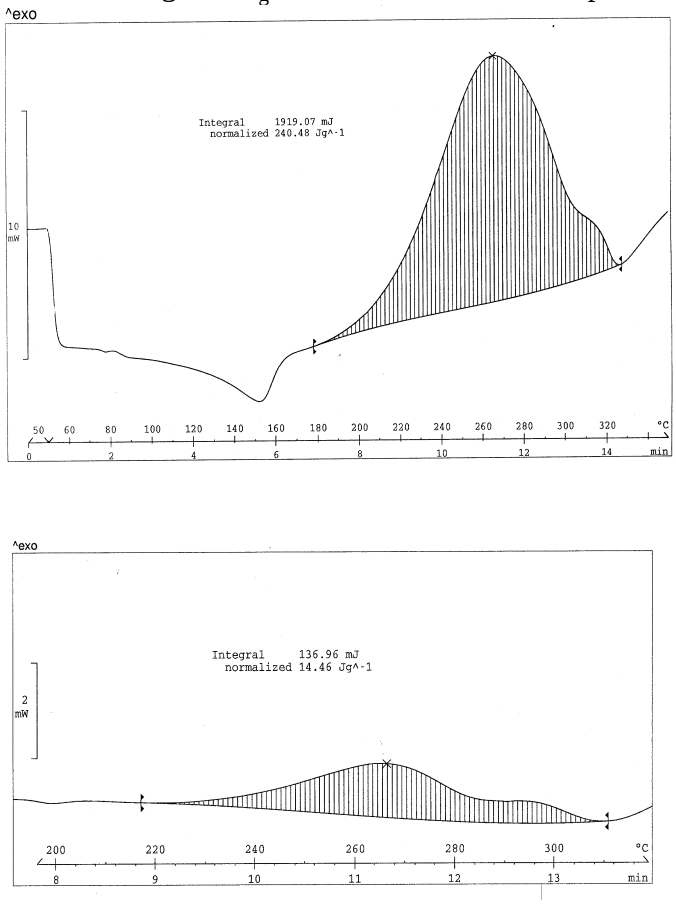


Figure 1 DSC traces for as-received (top) and microwave cured (bottom) samples. The trace for the microwave cured sample shows only the region of the residual exotherm.

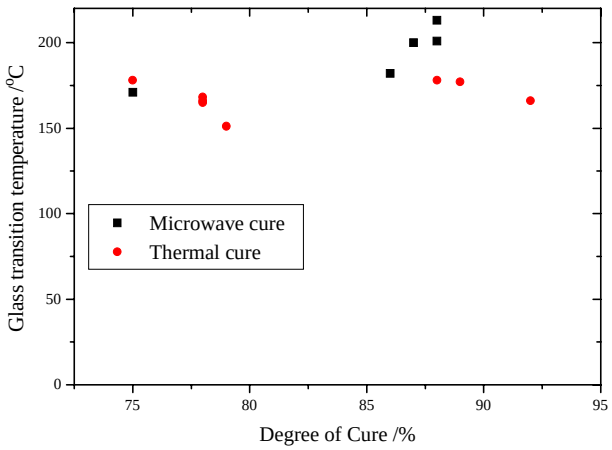


Figure 2 Glass transition temperature, measured by MDSC, as a function of cure for microwave and thermally cured samples.

To illustrate this phenomenon, the difference between the onset and endset temperature of the glass transition is plotted against the degree of cure in figure 3. It can be seen that the width of the transition is always greater for the microwave cured samples than for the thermally cured samples at a given degree of cure and that as full cure is approached the width of the transition decreases for samples cured by both methods.

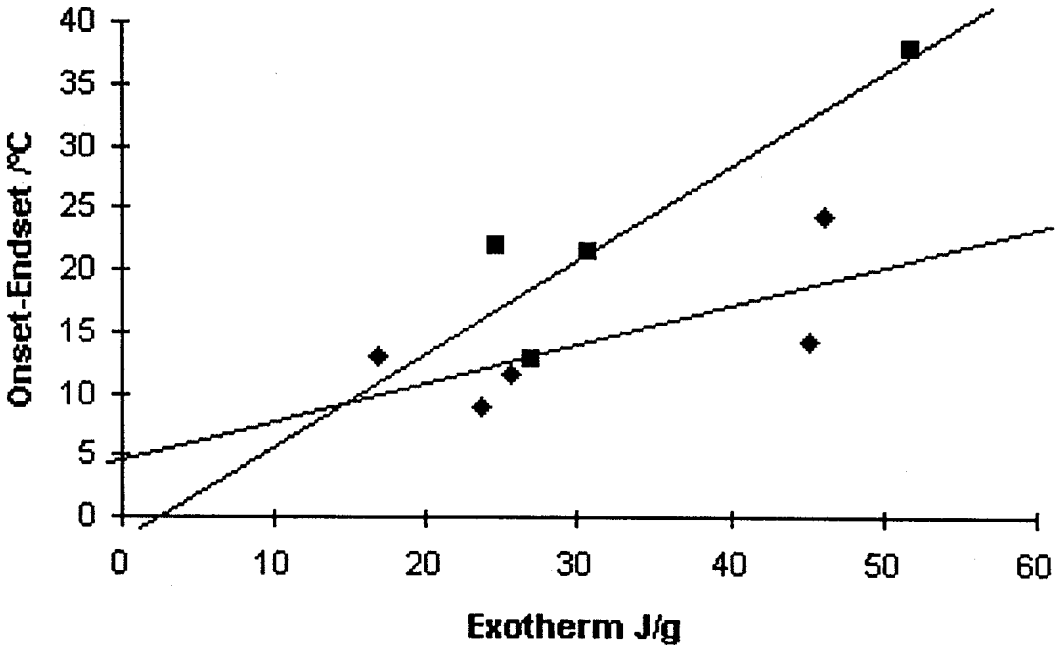


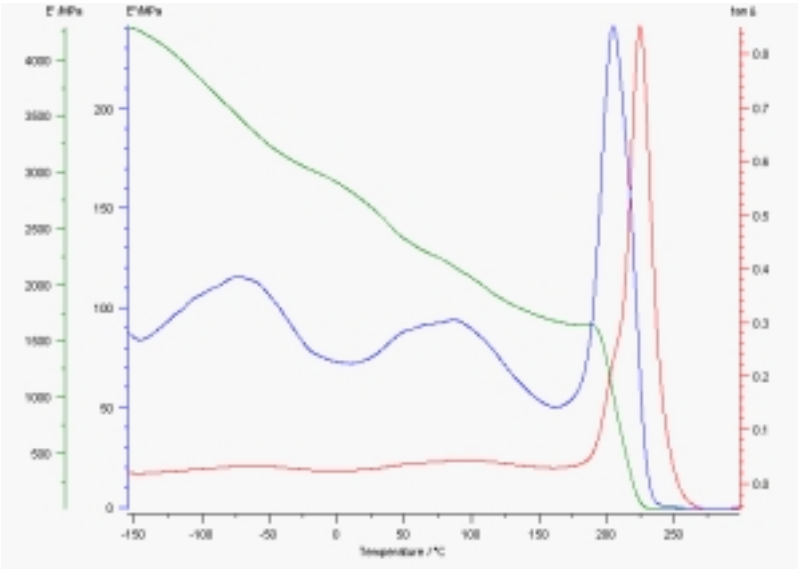
Figure 3 Difference between onset and endset temperatures as a function of degree of cure for microwave cured () and thermally cured () samples.

Dynamic Mechanical Analysis

In order to investigate whether the samples were uniformly cured strips were taken across the width of both microwave and conventionally cured plaques. These showed a variation in the glass transition temperature of ±4 °C for thermal cure and ±10 °C for microwave cure. Visual inspection of the cured plaques revealed that they were of a uniform colour. Typical DMA traces for the microwave and thermally cured resin

are shown in figures 4a and 4b respectively. These reveal further differences in the behaviour of samples prepared using the different heating routes. Figure 4a shows a prominent secondary β peak which is of comparable magnitude to the primary β peak. In the thermally cured sample (figure 4b) the secondary β peak is of much lower magnitude than the primary transition. Comparison of figures 4a and 4b suggests that there is a difference between the network structures of the microwave and conventionally cured resins. The primary β peak is associated with the crankshaft motion of the -O-CH_2-CH(OH)-CH_2- segments which are formed by the reaction between the hydroxyl and epoxy groups [8]. The greater magnitude of this peak in the case of the thermally cured samples suggests that this reaction occurs to a lesser extent in the microwave processed materials. Quantitative analysis of the differences was not undertaken since it is generally accepted that the magnitude of peaks in DMA is not absolute.

a)



b)

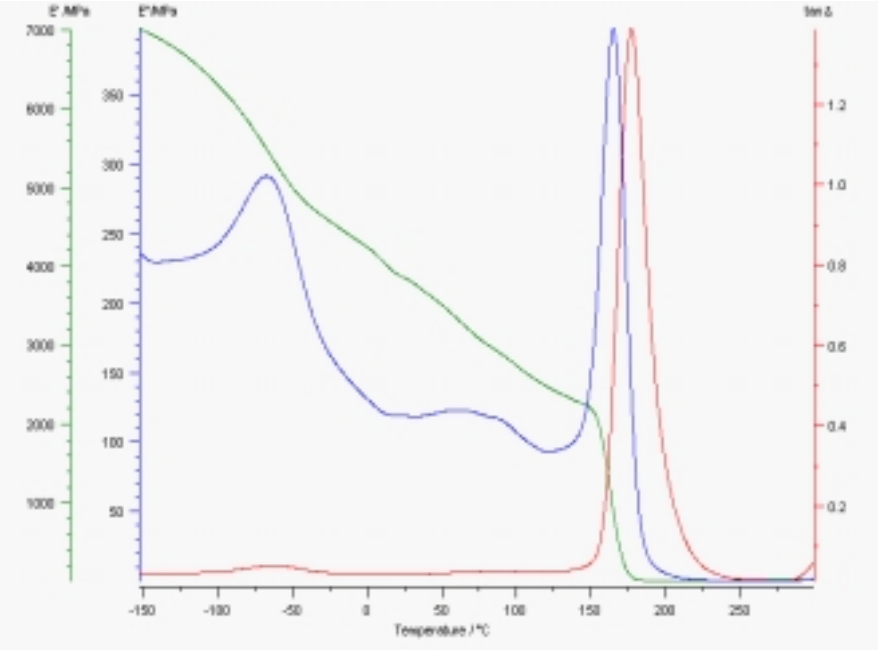


Figure 4 DMA traces for a) microwave and b) thermally cured resin

Infrared spectroscopy

Figure 5 shows the infrared spectra obtained from a thermally cured and microwave cured sample. The extent of cure in each case was approximately 90%. The spectrum obtained from microwave cured samples appeared similar to those of the thermally cured samples. Careful analysis of these spectra revealed that there were some differences in the heights of peaks corresponding to the amine and hydroxyl groups, suggesting the there were chemical differences between the thermally and microwave cured resins at this degree of cure. The results are tabulated in Table 1. The intensities have been rationed against those for an aromatic CH band at 3036 cm^{-1} since the aromatic bonds do not take part in any of the reactions known for epoxy-amine systems. The peaks associated with the amine and hydroxyl groups have a greater height for the thermally cured sample than for the microwave cured one. This suggests that the reaction between the epoxy and amine groups is relatively more dominant in the microwave curing process than the epoxy- hydroxyl reaction.

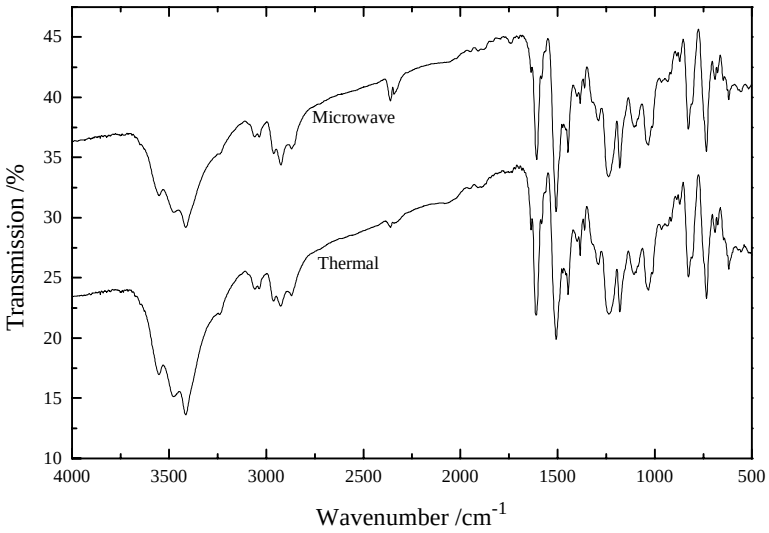


Figure 5 Infrared spectra of thermally and microwave cured samples. The degree of cure was 90%. The spectrum of the microwave cured sample has been displaced upwards by 10% for clarity.

Table 1. Relative intensities of infrared peaks in thermally and microwave cured resin

Peak /cm^{-1}	Assignment	Relative height Microwave	Relative height Thermal
3552	OH	4.67	5.69
3475	OH	6.44	7.65
3415	OH	6.33	9.50
3236	NH	1.67	1.88
2963	aliphatic CH	2.50	1.96
2925	aliphatic CH	3.61	2.42
2869	aliphatic CH	2.61	2.00
2854		2.33	1.50
3062	aromatic CH	0.89	0.88
3036	aromatic CH	1.00	1.00

Dielectric measurements

The dielectric properties obtained for samples of resin cured using conventional heating and microwave heating are presented in figure 6. The dielectric behaviour of the curing resin will depend on the change in the dipoles present as the reactions take place. The decrease in epoxy groups leads to a reduction in the dielectric constant. The changes in the amine groups lead to a reduction in the relaxation from high to low frequencies and thus a reduction of the dielectric constant. On the other hand formation of hydroxyl groups leads to an increase in the dielectric constant. Thus potentially a change in the reaction path could lead to difference in the dielectric behaviour in the microwave and thermally cured materials. As can be seen from figures there is little difference between the samples produced by the two heating routes, nor with cure over this range. Changes of dielectric properties with degree of cure tend to follow an exponential form with initially a large decrease in the loss and then a comparatively small change at higher degrees of cure. As a consequence it is not surprising that there is little change in the dielectric properties with degree of cure since the data has only been obtained for samples with degrees of cure above 75%. Since other techniques show that there is a difference in the reaction path, the reason for the microwave and thermally cured materials having similar properties could be that change in dielectric properties is smaller than the error in the measurements.

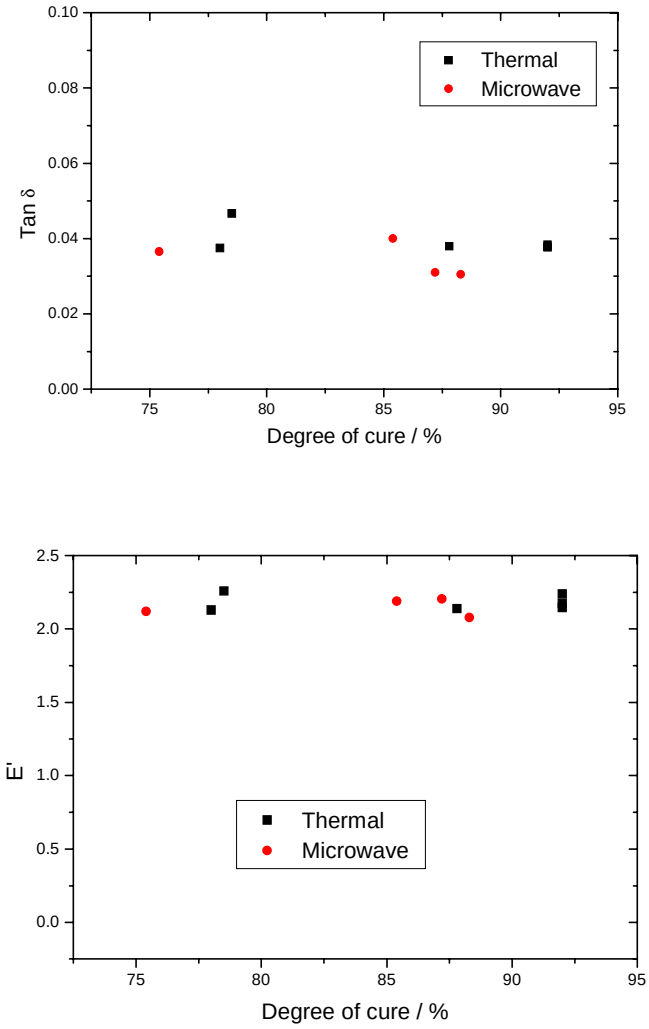


Figure 6. Variation of (a) loss tangent, tan δ and (b) dielectric constant with degree of cure for microwave and thermally cured samples.

Solid State NMR

Figure 7(a) and (b) show the ^{13}C CP/MAS NMR spectra of the thermally and microwave cured samples respectively. The chemical shift scale was referenced by setting the most intense aromatic peak to 128 ppm as found in the solution-state spectrum of PR500 in $CDCl_3$. The spectra of both samples were similar in form but there were differences in detail. In $CDCl_3$, the original PR500 resin showed intense peaks at 45 and 50 ppm arising from the epoxide CH_2 and CH carbons respectively. These peaks were very much reduced in the cured sample spectra indicating substantial opening of the epoxide rings. However the residual epoxide peaks appeared somewhat larger in the thermal cure than in the microwave cure. On curing, new peaks appeared in the region 55 to 75 ppm, a broad peak at 70 ppm and a narrower peak at 64 ppm. These were assigned to open-chain CH_nO and CH_nN groups formed by epoxide ring opening. The peak at 70 ppm included a contribution from the glycidyl CH_2O carbons. Further information relevant to the assignment of the NMR spectrum was obtained from the DD spectrum of the microwave cure shown in Figure 7(c). This technique discriminates in favour carbons with relatively weak dipolar interactions because of either remoteness from protons or high mobility. Comparison with the standard CP/MAS spectrum in Figure 7(a) showed that the peaks at 31, 42 and 64 ppm were relatively more intense in the DD spectrum. By comparison with the liquid-state spectrum of PR500, the first was assigned to the quaternary carbon at the centre of the aromatic system. From its chemical shift, the peak at 64 ppm was tentatively assigned to a CH_2OH side-group, a product of the epoxy-hydroxyl reaction. This peak has a lower intensity in the spectrum obtained from microwave cure suggesting that this reaction is less prevalent in this case. The peak at 42 ppm remained unexplained, though a small peak was observed at this chemical shift in the PR500 solution-state spectrum.

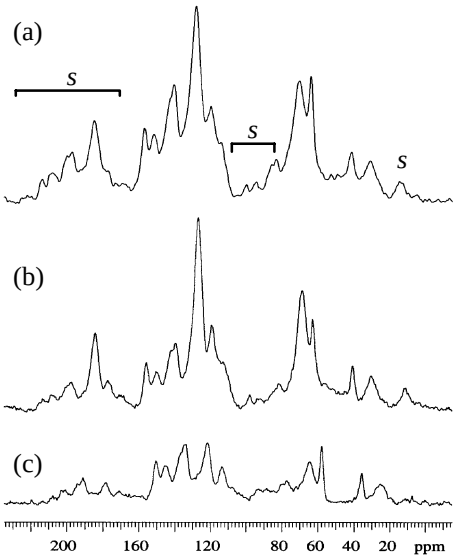


Figure 7. ^{13}C CP/MAS NMR spectra of PR500 resins. (a) thermal cure; (b) microwave cure; (c) DD spectrum of microwave cure. The spinning rate was 4.3 kHz for all spectra. Figures (b) and (c) have been plotted on the same vertical scale. the label *s* indicates a CSA spinning sideband; a sideband of the aromatic peak at 128 ppm underlies the peak at 64 ppm.

CONCLUSIONS

The infrared and solid state NMR spectra indicate that the epoxy-amine reaction is comparatively more dominant in the microwave cured samples than the other possible curing reactions. In the case of the infrared spectrum the evidence is the greater intensity of the hydroxyl and amine bands in the thermally cured sample than in the microwave cured sample at the same degree of cure. In the amine-epoxy reaction, amine groups are consumed. Thus the lower intensity of the amine groups in the microwave cured samples indicates the amine-epoxy reaction to be more dominant. The evidence in the case of the solid state NMR spectra is the presence of a greater number of $-CH_2OH$ groups in the thermally cured sample. This group is formed in the epoxy -hydroxyl reaction and thus this reaction must be relatively more dominant during the thermal curing process. It must be concluded that the dielectric properties do not vary sufficiently with any changes in the chemical path to allow distinctions to be drawn. This is because a number of groups are involved and the dielectric properties depend upon these in a different way.

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