Structure of the carbon chain polymer in unsaturated polyesters

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The curing behaviour of thick laminates was simulated by curing thin polyester sections isothermally at various temperatures. Unsaturated polyesters with different ratios of styrene to unsaturations in the polyester were cured with benzoyl peroxide and subjected to hydrolytic degradation. The molecular size and structure of the carbon chain polymer was examined by size exclusion liquid chromatography and high resolution ^{13}C *FT* n.m.r. analysis and was found to depend on the reaction temperature. The overall values of the molecular weights ranged from 12 000 to 36 000, which is a magnitude lower than those reported earlier. There was a similar tendency for molar ratios of styrene to unsaturations in the resin varying between 1.25 and 2.00. In the region 60°C–80°C the molecular weight increased with increasing temperature and then, from a maximum at 80°C–90°C, the molecular weight decreased with cure temperature. For the molar ratio of styrene to unsaturations of 2.25 the molecular weight decreased with increasing cure temperature. The average styrene sequence lengths were not found to deviate from the ratio expected from the stoichiometry in the resin before curing except for temperatures below 70°C and above 120°C.

(Keywords: unsaturated polyester; molecular weight; crosslinking; structure; cure temperature)

INTRODUCTION

Unsaturated polyesters are commonly used as matrix materials in composites. They are based on macromolecules with a polyester heterochain in which a saturated and an unsaturated acid are condensed with a glycol. A three-dimensional structure is produced by crosslinking this polyester heterochain through the unsaturated acid component with a vinyl monomer, the most common being styrene.

The crosslinking process is a free-radical copolymerization in which a carbon chain polymer is formed. The unsaturations in the polyester have been found to react in the proportion estimated by the reactivity ratios for the two types of unsaturations[1].

The curing process is exothermal giving a temperature rise of over 200°C as previously reported[2-4]. The temperature was found to vary with the distance from the surface to the centre of the material.

When the cured polyester is subjected to hydrolytic degradation, a carbon chain polymer is liberated from the network to form a linear poly(carboxylic acid) via a poly(potassiumcarboxylate) as described by Funke *et al.*[5].

Unsaturated polyesters with a low concentration of initiator have been examined after curing at 20°C[6]. By ebullioscopy and viscometry the molecular weights of the carbon chain polymers were detected and found to be over 100 000. In contrast to these values, Mleziva *et al.*[7] found molecular weights one magnitude lower, also determined by ebullioscopy.

The purpose of the work presented here is to describe the dependence of molecular weight and molecular structure on the cure temperature of the carbon chain polymers obtained when curing unsaturated polyester resins and subsequently hydrolysing them. The reaction and products are shown schematically in *Figure 1*. Methods used for the analyses of the carbon chain polymer liberated in this way are high resolution ^{13}C n.m.r. and size exclusion chromatography, SEC.

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EXPERIMENTAL

Materials

Two unsaturated polyester resins were synthesized according to the scheme described by Funke *et al.*[1]. A flexible, aliphatic unsaturated polyester was synthesized from fumaric acid (1 mole), adipic acid (2 moles) and propylene glycol (3.2 moles). A more rigid, aromatic resin was synthesized from fumaric acid (1 mole) and isophthalic acid (1 mole) with propylene glycol (2.2 moles). The temperature was not allowed to exceed 190°C to minimize isomerization of the *trans-* to *cis-*configuration of the unsaturated acid. The acid value for the aliphatic resin was 30 and for the aromatic resin 29. The unsaturated polyesters were diluted with styrene in different molar ratios of styrene to polyester unsaturations. The molar ratios were varied around the azeotropic ratio of 1.8 where the composition remains constant during the curing reaction. The azeotropic ratio was calculated from the reactivity ratios presented by Lewis *et al.*[8] for diethyl fumarate ($r_1 = 0.07$) and styrene ($r_2 = 0.30$). These reactivity ratios were found to also be valid for the unsaturations in the polyester[1]. The values of the molar ratios of styrene to polyester unsaturations were 1.25, 1.50, 1.75, 2.00 and 2.25 for the aliphatic resin. For the aromatic resin the ratio was 2.25.

The styrene was purified by filtering through basic Al_2O_3 before addition to the polyester resin and then hydroquinone (0.02%) was added as stabilizer.

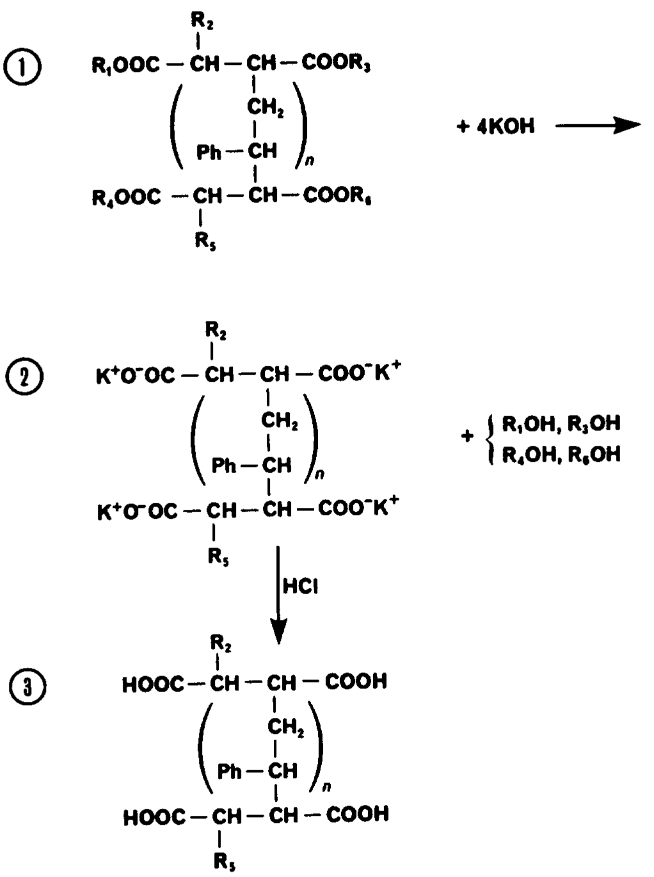

Figure 1 Hydrolysis reaction of the crosslinked polyester. R_1, R_3, R_4 and R_6 are the segments of the crosslinked polyester chain and R_2 and R_5 are the segments of the crosslinked carbon chain polymer. R'_2 and R'_5 are the corresponding segments of the poly(carboxylic acid) after hydrolysis. The index *n* is the sequence length correspondence to the average number of styrene residues between the polyester chains

Differential scanning calorimetry

A Perkin Elmer DSC 2 apparatus was used for the d.s.c. measurements. High pressure cups sealed with D-rings were used to eliminate leakage of styrene. The scanning speed was 10°C/min and the weights of the samples were around 20 mg. Resins, with a series of initiator concentrations (benzoyl peroxide), were analysed in order to find the lowest concentration that could be used without a second reaction occurring at high temperatures.

The times for curing of the resins at each styrene concentration, at different temperatures, were calculated from the d.s.c. experiments as previously described[9].

Temperature rise for unsaturated polyesters in thick moulds

The rise in temperature, when curing the resin in a thick mould, was examined by use of a mould with dimensions 20 x 40 x 40 mm. The mould was heated to 80°C and the temperature in the centre of the slab of resin was recorded (*Figure 2*).

Curing in the mould

The mould was comprised of two aluminium plates covering a frame leaving an inner space of 0.5 x 100 x 150 mm. The frame distance was 0.5 mm wide to minimize exothermic heat build-up from the curing reaction. The mould was heated in the press before injection. The resin was injected into the mould and the excess resin was allowed to flow out from the mould. Curing of the samples then proceeded for calculated times at a series of predetermined temperatures.

Dynamical mechanical analysis

The equipment used was Du Pont 982 DMA interfaced with a computer for the collection and evaluation of data. Cured preparations were cut from the sheets to give samples with dimensions of 18 x 10 x 0.5 mm. The temperature was scanned from 20°C to 120°C.

By measuring the energy absorption as a function of the temperature, the loss factor, tan(δ), of the material was determined. The glass transition temperature was determined as the maximum in the loss factor.

Hydrolysis

From the sheets cured at predetermined temperatures, samples were ground to powder and hydrolysed in benzyl alcohol under refluxing in the presence of KOH as previously described[5] to liberate the carbon chain polymer from the network. The potassium salts of the carbon chain polymers were all converted to poly(carboxylic acids) before analysis.

Size exclusion liquid chromatography

The samples were dissolved at room temperature in tetrahydrofurane (THF) to a concentration of 2 g/l, and analysed by SEC in a Waters 200 GPC apparatus with 5 Styragel^R columns separating over a range of 10^3–10^7. The intrinsic viscosities of the polystyrene standard samples were evaluated for a series of molecular weights using an Ubbelohde viscometer at 25°C. From the elution volume and intrinsic viscosity results for the polystyrene standards of known molecular weights, universal and and standard calibration curves were constructed. Intrinsic viscosities of the samples were determined using a Sofica viscometer connected on line to the g.p.c. apparatus. The solvent tetrahydrofurane was distilled immediately before the analyses, which were performed at 25C°.

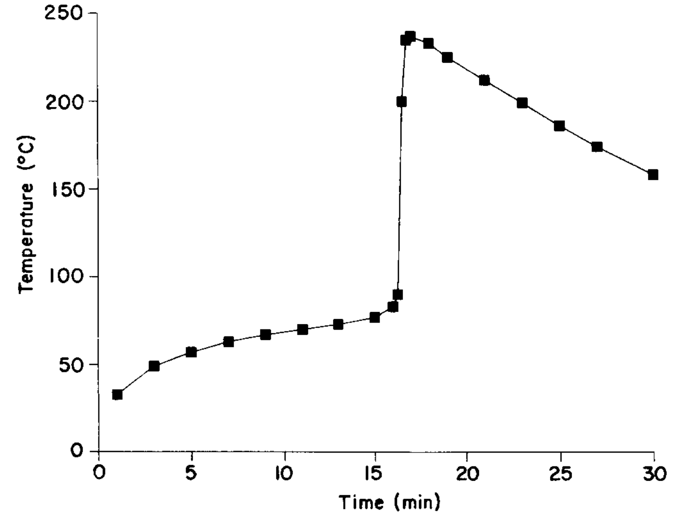

Figure 2 Temperature rise in the mould. Mould temperature, 80°C and dimensions 20 x 40 x 40 mm

^{13}C nuclear magnetic resonance

The dried carbon chain polymers (20% w/w) were dissolved in deuterated dimethyl sulphoxide (DMSO d6) in n.m.r. tubes of outer diameter 12 mm. ^{13}C n.m.r. spectra were obtained at 50.3 MHz in a Varian XL-200 NMR spectrometer at 80°C. The solvent used provided a deuterium signal for field and frequency stabilization. The spectra were obtained with the following spectrometer conditions: spectral width 200 ppm (4000 Hz), acquisition time = 0.8 s, delay time = 1 s, number of transients = 10 000.

RESULTS AND DISCUSSION

In thick sections of unsaturated polyester materials a considerable temperature rise is caused by the heat generated in the curing reaction. This was simulated in thin sections cured isothermally at representative temperatures corresponding to those within a thick laminate. The structure and molecular weight of the carbon chain polymers were examined.

The concentration of the initiator is of importance since, if the initiator is exhausted before the polymerization is completed, then a fraction of the unsaturations will not react. On the other hand, the molecular weight of the carbon chain polymer falls with increasing initiator concentration.

Similarly to Kubota[10], it was found that two peaks appeared at low peroxide concentrations when the resin was analysed by d.s.c. There was one peak in the temperature region 60°C–160°C, which could be associated with the reaction initiated by peroxide decomposition. The other peak at a higher temperature region (150°C–230°C) is associated with the thermally initiated reaction of the residual unsaturations. From d.s.c. analysis, the lowest concentration of benzoyl peroxide necessary for complete reaction was indicated by the absence of a second reaction peak at high temperatures. This concentration was found to be 1.50% which is the same value as found by Cuadrado *et al.*[11]. This concentration was subsequently used throughout this work.

The T_g of a resin, having a ratio of styrene to unsaturations in polyester of 1.75 cured at 90°C, was found to be 75°C when analysed by DMA.

Molecular weights of the carbon chain polymers

The poly(carboxylic acids) formed by hydrolysis and subsequent acidification of the cured samples were analysed by SEC in THF. Considerable differences were found in the elution volumes of samples from resins cured at different temperatures.

Molecular weights were calculated by means of a previously reported computer program[12–14].

There are no calibration curves or Houwink–Sakuruda relationships available for the poly(carboyxlic acids). Therefore, when calculating molecular weights from SEC measurements, a comparison between known polystyrene standards and the actual polymer was made with a correction for differences in the hydrodynamic volume between the two kinds of polymers[15]. This comparison was made by using the universal calibration curve, which was constructed for the polystyrene standard samples by the products of intrinsic viscosities and molecular weights *versus* the elution volumes. The elution volumes were determined before the analyses for the set of SEC columns. From these data and the molecular weights of the standard samples a universal curve was constructed.

For the carbon chain polymers the intrinsic viscosity was determined on line and ranged between 0.30 and 0.08 dl/g. From the universal curve, values were taken at the highest intrinsic viscosities, where the relative errors are small. The absolute molecular weights obtained in this way were found to be the same as those calculated directly from the standard polystyrene calibration curve within a standard deviation of 5%. The standard polystyrene curve was therefore used in our evaluation.

Two of the poly(carboxylic acids) were esterified and analysed by SEC. The reaction was performed in a methanol solution with HCl gas being added at room temperature for 1 h. The carboxylic acid groups were thereby esterified to methylester groups in the polymer.The esterified polymers were found to have almost identical molecular weight distributions to those of the corresponding poly(carboxylic acids).

An attempt to use DMF as the solvent in the SEC analyses was not successful, probably because of the strong interactions between DMF and the polymers.

Influence of cure temperature on molecular weight

The influence of cure temperature on molecular weight is presented in *Figure 3* for ratios of styrene to polyester unsaturations ranging between 1.25 and 2.00. The molecular weights increased with increasing ratio of styrene to unsaturations in the polyester at low temperatures. At cure temperatures in the region 60°C–80°C, the molecular weight increased and reached a maximum at 80°C–90°C. Above this range the molecular weight decreased with increasing cure temperature. This result could be expected since the rate of termination increases, and thus the molecular weight becomes lower with increasing temperatures[16].

In *Figure 4* the molecular weights are presented for the ratio 2.25 of the two kinds of polyesters used and no maximum was observed here. However, a monotonic decrease in molecular weight with increasing cure temperatures was observed.

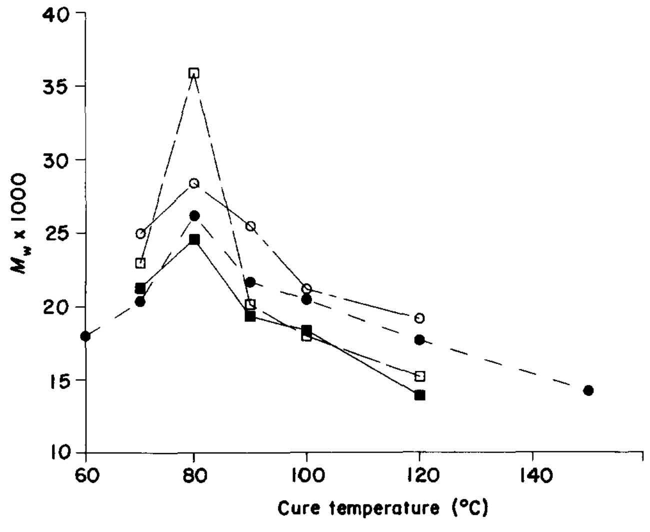

Figure 3 Influence of cure temperature on the molecular weight for ratios (*R*) of styrene to polyester unsaturations: ■, 1.25; □, 1.50; ●, 1.75; ○, 2.00

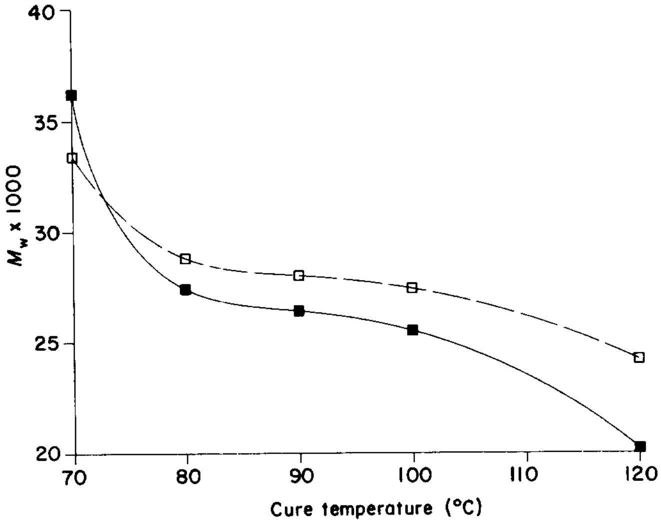

Figure 4 Carbon chain molecular weights in AP (—■—) and GP (—⊟—) resin and ratios (*R*) of styrene to polyester unsaturations 2.25 with the cure temperatures

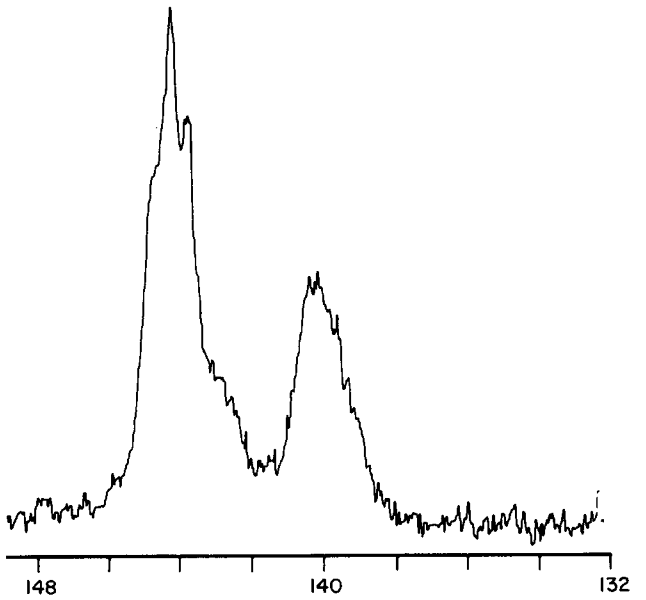

Figure 5 A spectrum in the 130–180 ppm region of the quaternary carbons. Ratio of styrene to polyester unsaturations is 2.25. The quaternary carbons in the phenyl groups show a peak A centred near 140 ppm and a peak B centred near 144 ppm representing the carbons described in *Table 1*

The fact that the molecular weight decreased at temperatures below the maximum at 80°C–90°C for values lower than 2.25 cannot be explained at present. A similar trend was found by Mleziva *et al.*[7].

SEC gives the molecular weight distribution, number- and weight-average molecular weights. The average molecular weights are of importance since they are related to the mechanical properties. The ratios between the weight-average and the number-average molecular weights were in the range 3–4. The molecular weights obtained here were an order of magnitude lower than the values reported by Funke *et al.*[6] after curing at 20°C. Our results were more in accordance with those found by Mleziva *et al.*[7].

Average sequence length

Solutions of the poly(carboxylic acids) in DMSO (d6) were analysed by high resolution ^{13}C n.m.r. A typical spectrum of the 130–180 ppm region, where the quaternary carbons occur, is shown in *Figure 5*.

Birley *et al.*[17] have assigned the quaternary carbons in the phenyl groups, as shown in *Figure 6*, to the peak A centred near 140 ppm and peak B centred near 144 ppm representing the carbons described in *Table 1*.

The area under the absorption peak is proportional to the amount of the species responsible for the absorption, since the quaternary carbons are chemically very similar. The contribution to peak A comes from C_1, C_3 and C_6 and to peak B from C_2, C_4 and C_5. The contribution from peak A is proportional to the total amount of styrene sequences. Since the sum of the areas of the peaks A and B is proportional to the total amount of styrene units, the number-average sequence length L_n can be described by $L_n = (A + B)/A$.

The average sequence lengths calculated from ^{13}C n.m.r. spectra of the carbon chain polymers, as a function of the cure temperature, are presented in *Figure 7*.

All samples had almost constant values for the average sequence length over a wide temperature range (80°C–120°C). Deviations from the values expected from the molar ratio of styrene to polyester unsaturations before curing, indicate incomplete reaction of at least one of the two types of unsaturations. For samples cured below 70°C there is a tendency toward the expected values at the azeotropic ratio for all concentrations of styrene in the resin. This can be interpreted as a consequence of the curing reaction not being complete due to formation of a glassy phase. At temperatures from 120°C and above, the

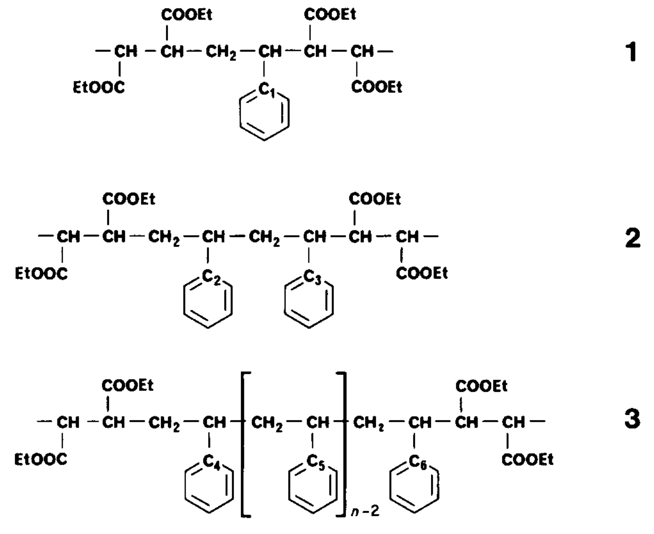

Figure 6 Assignments of the quaternary carbons in the carbon chain polymer

Table 1 Chemical shifts for quaternary phenyl carbons

Quaternary phenyl carbon	Chemical shift (ppm)
C_1	137.5
C_3+C_6	139.1
C_2+C_4	142.5
C_5	144.0

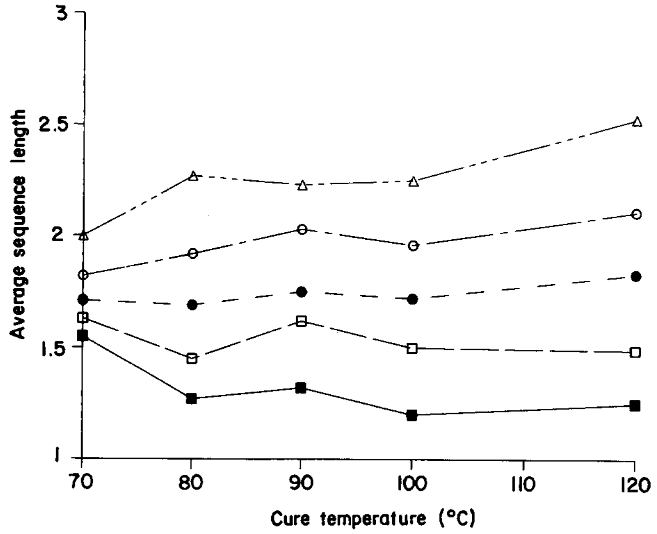

Figure 7 Average sequence lengths calculated from ^{13}C n.m.r. spectra of the carbon chain polymers as a function of the cure temperature: ■, $R=1.25$; □, $R=1.50$; ●, $R=1.75$; ○, $R=2.00$; △, $R=2.25$

sequence length was found to deviate from the stoichiometrically expected values.

An interesting observation is that an extra peak appears at 135.5 ppm in the ^{13}C *FT* n.m.r. analysis. An explanation for this could be that the benzoyloxy radicals form the end groups in the carbon chain polymers. Analyses show a chemical shift at 135 ± 0.5 ppm for a similar quaternary carbon in poly(ethylene terephthalate)[18].

The trend found for the molecular weights with a maximum in a temperature interval also appeared in the ^{13}C n.m.r. analysis of spin-lattice relaxation times for an unsaturated polyester in the solid state[19]. Similar tendencies with a maximum in the same cure temperature region have also been observed for reaction energies[20], *E*-modulus and glass temperatures (T_g)[21].

CONCLUSIONS

Simulation of the consequences of the exothermal temperature rise in thick laminates by curing thin samples isothermally at representative temperatures shows structural variations in the material. The results showed that this variation depends to a considerable extent on the molecular weights of the carbon chain polymer as determined after hydrolysis of the cured resin. The molecular weights were found to be an order of magnitude lower than those reported earlier[6].

The temperature of curing that gives the highest weight-average molecular weight seems to be the temperature region just above the glass transition. At higher temperatures the molecular weight decreases with increasing temperature.

The average styrene sequence length did not deviate appreciably from the stoichiometric values in the resin before curing, with the exception of small changes in the temperature region 60°C–70°C and above 120°C.

In a thick laminate the thermal history varies with distance from the mould surface. We have shown that these differences cause changes in the chain length of the carbon chain polymer and in turn the network structure. A consequence is differences in mechanical properties inside the laminate which, in turn may cause mechanical failure and delamination. In any event, the overall properties will deteriorate with these highly exothermic reactions in thick laminates.

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