The influence of heterogeneous crosslink density on the thermomechanical and hygrothermal properties of an unsaturated polyester resin: 1. Thermomechanical response

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The crosslinking reactions that occur in unsaturated polyester resins result in a heterogeneous structure of highly crosslinked domains separated by less highly crosslinked material. This structure is a result of the formation of gel particles, which are initiated at free radicals during the curing reaction. Controlling the concentration of free radicals present in the system enables the heterogeneity within the resin to be varied, and its influence on the thermomechanical properties to be studied.

(Keywords: morphology; polyester; thermal properties; crosslinking)

INTRODUCTION

The morphological state of a polymeric material may be highly affected by the interaction between the polymerization kinetics and the thermodynamics of phase separation. This is especially relevant to the preparation of high-impact polystyrene from a styrene solution of an unsaturated rubber. An unsaturated polyester resin is analogous except that it consists of a relatively low-molecular-weight polymer dissolved in styrene. In this case, phase separation has not been observed but the development of a microstructure consisting of areas with wide variation in crosslink density is generally becoming accepted[1–4].

The curing of unsaturated polyester resins can be described as a free-radical copolymerization reaction. As there are several double bonds per polyester molecule, the polymerization proceeds with extensive crosslinking and results in a three-dimensional network. Under ideal conditions the radicals that initiate the copolymerization of the polyester with the styrene monomer are randomly distributed throughout the system. This has resulted in a model for the polymer network in which there is a uniform, statistical distribution of crosslinks throughout the system. However, the tendency towards alternating copolymerization in the initial stages in conjunction with the conformational state of the dissolved polyester molecule leads to the development of a heterogeneous crosslinked structure. This was first established by Funke[1], who studied the extent of the hydrolytic degradation of cured unsaturated polyester resins and found it to be dependent upon the initial radical concentration used for the cure. This observation was inconsistent with the formation of a homogeneous network. The disintegration of swollen samples under weak mechanical forces[2] is also inconsistent with a network of uniform crosslink density, as are the light scattering studies of Gallacher and Bettelheim[3].

Funke[2] suggests that a weakly crosslinked primary network results in gelation after a very low degree of conversion. Newly formed radicals quickly react with the network and are, therefore, unable to diffuse freely. Although the translational mobility of the styrene is relatively unaffected at this point, the reduced diffusional mobility of the remaining unsaturated groups on the polyester chains allows for only localized chain propagation and domains form as a result.

N.m.r. spectroscopy has been used by Bergmann and Demmler[4] to study the curing process of unsaturated polyester resins. Since the polyester is randomly coiled in the styrene solution, there is a high probability of an intramolecular polyester reaction, which leads to the formation of gel particles. During post-curing, the material in the interstices continues to polymerize onto the tightly coiled chains, which form the gel particles. Any lower-molecular-weight material present may also diffuse into the particles and subsequently polymerize.

Jones *et al.*[5] could only interpret the enhancement of the linear thermal expansion coefficient of an unsaturated polyester resin by absorbed moisture, and the resultant residual thermal stresses in the glass-fibre-reinforced composite, in terms of a heterogeneous matrix structure. Further evidence was obtained by comparing the moisture absorption of these resins to that of a two-phase polymer[6,7]. It has, therefore, been concluded that, after curing, this isophthalic unsaturated polyester resin consisted of highly crosslinked domains embedded in, or

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bridged by, a matrix of less densely crosslinked molecular chains.

Since the microstructure is established at a low extent of cure, in this study the concentration of accelerator used to cure the resin has been varied in order to modify the free-radical concentration, and hence the number of gel particles. The final size of each particle would then be expected to decrease with increasing accelerator concentration. Assuming that this pre-microstructure is not removed by post-curing, an increase in accelerator concentration should result in a finer microstructure.

EXPERIMENTAL

Materials

The isophthalic unsaturated polyester resin Crystic 272 (Scott Bader Co. Ltd) selected was a propylene glycol/diethylene glycol/isophthalic acid/maleic anhydride copolyester dissolved in styrene (40% w/w). The exact composition of such a commercial resin was uncertain, but it was considered that >90% isomerization of maleate to fumarate links occurred. It had previously been used in moisture diffusion experiments, which suggested that the resin exhibited a 'two-phase structure'[6,7]. This resin can be cold-cured using a 50% methyl ethyl ketone peroxide solution (Catalyst M, Scott Bader Co. Ltd) and a 0.4% cobalt octoate solution (Accelerator E, Scott Bader Co. Ltd). In all cases the resin was cured using 2 phr (parts per hundred resin) of Catalyst M and between 0 and 1.0 phr Accelerator E. It has been noted[8] that when >1 phr of accelerator was used a significant exotherm was produced in sections thicker than 20 mm. As all the castings used in this study were 15 mm thick, or less, no exotherm was found to occur and reproducible void-free castings were produced.

Resin specimens suitable for testing in the Polymer Laboratories DMTA (Dynamic Mechanical Thermal Analyser) were prepared by casting the activated resin into polypropylene beakers. Cast resin discs were produced using this technique without the need for any release agents. The discs were ground to a thickness of approximately 12 mm and specimens 2 × 10 × 40 mm^3 were then cut from the discs using a water-cooled diamond saw. All the faces of each specimen were polished to a better than 1 μm finish using cerium oxide.

After cutting and polishing, the specimens were post-cured in an air circulating oven at 130°C for 1.5 h. This schedule was considered to produce a fully post-cured structure, as further post-curing did not change the mechanical properties or the glass transition temperature of the resin[8]. After slowly cooling from the post-curing temperature, specimens were placed in a vacuum oven at 50°C and dried to constant weight. This procedure ensured that the specimens were completely dry prior to testing.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis was used to investigate the effect of heterogeneous crosslink density and hygrothermal ageing on the thermomechanical properties of the resin systems under examination. The instrument used was a Polymer Laboratories DMTA (Dynamic Mechanical Thermal Analyser). All the specimens, both dry and appropriately conditioned, were tested in dual cantilever bending, and all the specimens were of the same dimensions (i.e. 2 × 10 × 40 mm^3) in an attempt to minimize geometric factors. Prior to testing in the DMTA, specimens that had been conditioned were wiped with absorbent paper to remove any excess water or surface contamination and then weighed to determine their moisture contents. Specimens were clamped into the clamping frame of the DMTA using a torque-driver to tighten the clamp bar nuts to a torque of 27 cN m. The torque setting of 27 cN m was found to give the optimum clamping for the resin, and the use of a torque-driver ensured that the specimens were uniformly clamped. A specimen free (unclamped) length of 10 mm, a frequency of 1 Hz and a strain of × 1 were selected.

A heating rate of 4 K min^{-1} was selected and the temperature was scanned from 30 to 150°C. This heating rate enabled accurate and reproducible values of glass transition temperature to be obtained. In the few cases where frequency multiplexing was employed, the heating rate was reduced to 2 K min^{-1}, but the temperature was still scanned from 30 to 150°C. All the other conditions were kept identical to those used in the single-frequency tests, except that instead of a single frequency of 1 Hz the frequency was multiplexed between 0.33, 3 and 30 Hz. All the values of T_g and E' are the average of 2–6 individual tests and the reproducibility was ± 1 K and ± 0.05 GPa respectively.

RESULTS

Dynamic mechanical thermal analysis was used to determine the glass transition temperature (T_g) and dynamic storage moduli of the cured resins. Plots of T_g against accelerator concentration for Crystic 272 polyester resin formulations prior to post-curing and after post-curing at 130°C for 1.5 h are shown in *Figures 1* and *2* respectively. The data from these experiments, and from resin formulations post-cured at 150°C for 1.5 h, are collected in *Table 1*.

The d.m.t.a. traces produced for the Crystic 272 resin with various accelerator concentrations that were not post-cured show a systematic increase in T_g with increasing accelerator concentration up to a concentration of 0.4 phr. Above this, no further increase was observed, with almost identical curves being obtained from formulations with accelerator concentrations of between 0.4 and 1.0 phr (*Figure 1*). It is interesting to note that some degree of post-curing was found to occur

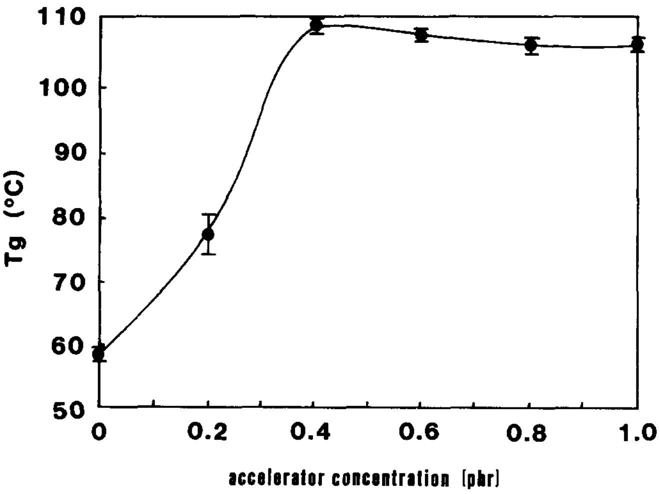

Figure 1 Variation in T_g with accelerator concentration for Crystic 272 polyester resin prior to post-curing

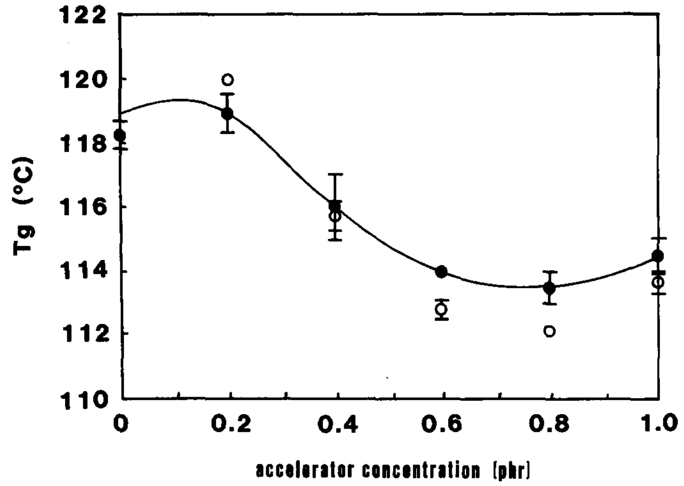

Figure 2 Variation in T_g with accelerator concentration for Crystic 272 polyester resin after post-curing for 1.5 h at 130°C (●) and 150°C (○)

Table 1 Glass transition temperature (T_g) for dry Crystic 272 polyester resin formulations subjected to various post-cures

Accelerator concentration (phr)	T_g (°C) No post-cure	T_g (°C) 130°C 1.5 h	T_g (°C) 150°C 1.5 h
0	58	118	118
0.2	80	119	120
0.4	109	116	116
0.6	108	113	113
0.8	106.5	114	112
1.0	106.5	114	114

during the measurements at temperatures above 90°C in both the 0 and 0.2 phr accelerator formulations. This suggests that, without accelerator, thermal initiation of the free-radical crosslinking reaction occurs above 90°C. A secondary damping peak (tan δ) above the initial T_g and an increase in dynamic storage modulus E' (*Figure 3*) are evidence of the post-curing that occurs in these two cases. This effect is less pronounced in the case of the 0.2 phr accelerator formulation as post-curing begins while the resin is still in the glass transition region of the non-post-cured resin. However, a slight step in the modulus curve and a distinct broadening of the damping peak indicate that some post-curing has occurred. The formulations with 0.4 phr accelerator concentration show the conventional damping peak associated with the glass transition at 107°C.

After post-curing at 130°C, there is a monotonic decrease in T_g with increasing accelerator concentration up to a concentration of 0.6 phr, while at higher accelerator concentrations there is a slight increase in T_g. The 0 and 0.2 phr accelerator concentration resin formulations both have a T_g of 119°C, but the formulation with no accelerator has a lower, broader damping peak than the one with 0.2 phr accelerator.

Specimens that were post-cured at 150°C for 1.5 h were found to exhibit almost identical post-curing behaviour as those post-cured at 130°C. The formulations with accelerator concentrations of 0.2 to 0.8 phr again showed a systematic decrease in T_g with increasing accelerator concentration (*Figure 2*), while the 1.0 phr formulation showed a slight increase in T_g. This is in agreement with the data obtained for the material post-cured at 130°C, and the probable reasons for this are described above.

It should be noted that the values of T_g measured for the various accelerator concentration formulations post-cured at 150°C are the same (within the limits of experimental error) as those measured for the same formulations post-cured at 130°C. This indicates that no further post-curing occurs at temperatures above the standard post-cure used, and confirms that fully post-cured specimens were used in all the investigations.

The values of E' in both the glassy and rubbery states were also measured for the various formulations post-cured at 130°C. The glassy modulus was measured at T_g − 70°C, while the rubbery modulus was measured at T_g + 30°C. As in the case of T_g, the glassy modulus decreases with increasing accelerator concentration up to an accelerator concentration of 0.6 phr before increasing again (*Figure 4*). As shown in *Figure 5*, the rubbery modulus also shows a decrease with increasing accelerator concentration up to 0.6 phr. However, at accelerator

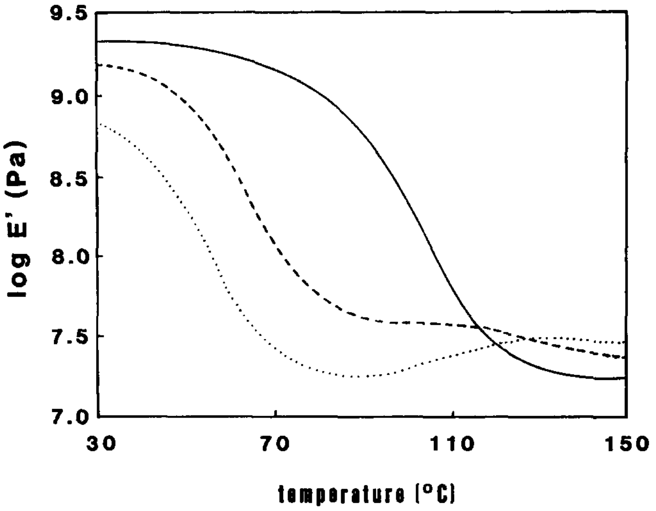

Figure 3 D.m.t.a. traces of log E' against temperature for Crystic 272 polyester resin, of various accelerator concentrations, prior to post-curing: (······) 0 phr, (– – –) 0.2 phr and (——) >0.4 phr accelerator concentrations

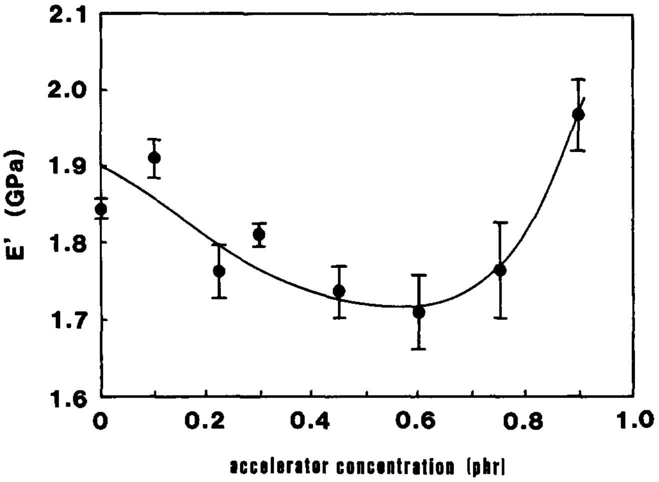

Figure 4 Variation in dynamic storage modulus with accelerator concentration, in the glassy state, for Crystic 272 polyester resin after post-curing at 130°C for 1.5 h

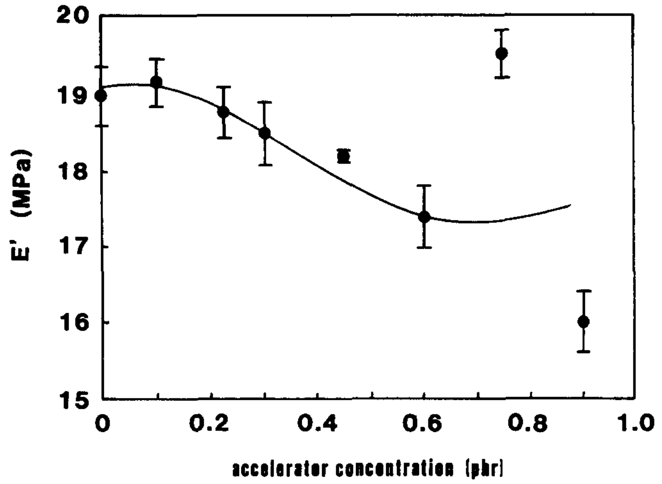

Figure 5 Variation in dynamic storage modulus with accelerator concentration, in the rubbery state, for Crystic 272 polyester resin after post-curing at 130°C for 1.5 h

Table 2 Glass transition temperature (T_g) for dry Crystic 272 polyester resin formulations measured at various frequencies

Accelerator concentration (phr)	T_g (°C)			Activation energy (kJ mol^{-1})
	0.33 Hz	3 Hz	30 Hz	
0	109	116	125	350 ± 50
0.1	108	115	124	360 ± 50
0.3	111.5	118	127	360 ± 50
0.75	108.5	116	124.5	350 ± 50
0.9	106	113	121.5	360 ± 50

concentrations in excess of 0.6 phr, the wide scatter in the results prevents any firm trend being established. The modulus of the resin, and in particular the modulus in the rubbery region, is indicative of the crosslink density within the system. These results show that the average crosslink density of the resin is at a minimum for resin formulations with around 0.6 phr accelerator concentration, which is consistent with the T_g data presented above.

Frequency multiplexing was used in an attempt to compare the activation energies of the main-chain relaxations for the various accelerator concentration resin formulations. As can be seen from *Table 2*, the activation energies for the main-chain relaxation at T_g for these resin formulations are essentially identical.

DISCUSSION

Heterogeneous crosslink morphology

The results of the studies into the effect of morphology in unsaturated polyester resin (*Table 1*) indicate that the critical factors which determine the final properties of the resin (i.e. after post-curing) are the distribution in crosslink density of the resin in the cold-cured state, and the concentration of radicals trapped within the network. Formulations with low accelerator concentrations have a more loosely crosslinked structure prior to post-curing, and this facilitates conformational rearrangement and the diffusion of low-molecular-weight material into the structure, leading to an increase in final crosslink density.

Shibayama and Suzuki[9] consider that a broadening of the damping peak and a decrease in its height are associated with increased crosslink density, as is an increase in the modulus of the resin in the rubbery plateau (measured at T_g + 30°C). It is evident, therefore, that a decrease in crosslink density occurs in the more highly accelerated resin formulations (*Figure 5*). Shibayama and Suzuki[9] suggested that for lightly crosslinked systems the crosslink density (ρ_E) can be evaluated from the rubbery modulus (E') from the equation:

$$\rho_E = \phi E'/3RT$$

where ϕ is the specific volume, R is the gas constant and T is the temperature. For high degrees of crosslinking, Gaussian statistics are invalid, and so the applicability of this equation is open to question. These authors, therefore, suggested that the number of moles of fumarate group per unit weight of cured resin could be used as a relative measure of crosslink density. This, of course, assumes that the conversion of fumarate groups in the polyester chains into crosslinks is quantitative. The results of the present study show that the crosslink density may vary with accelerator concentration, independently of the number of fumarate groups in the polyester chains. The reason for the observed variation in crosslink density with accelerator concentration is not clear, but the heterogeneous structure of the resin cannot be excluded.

The change in free-radical concentration that arises from a variation in [Co^{2+}] from 0 to 6×10^{-6} M cannot explain the reduction in average crosslink density shown in *Figure 5*, in terms of an increased rate of primary termination in the formation of a uniform network. This is especially so, since during post-curing the overall radical concentration will only be minimally affected ([peroxide] $\gg$ [Co^{2+}]). During the initial stages the true free-radical concentration will also be influenced by added and adventitious (i.e. O_2) inhibitors. Furthermore, the crosslink density is essentially determined by the reactivity ratios for fumarate and styrene copolymerization and the statistical conformation of the unsaturated polyester. Thus the formation of an increasing number of gel particles, which grow by diffusion-controlled processes, is more likely to lead to a reduction in average crosslink density as the interstitial component increases.

At accelerator concentrations of >0.4 phr, the cold-cured structure of the resin already shows a high degree of crosslinking, as indicated by a T_g in excess of 100°C. This reduces the chain mobility and restricts the diffusion of low-molecular-weight material and, hence, post-curing is less effective. However, with increasing accelerator concentration the number of radicals present in the network increases, and this partly compensates for the reduction in chain mobility. From the results of this investigation it would appear that the average crosslink density prior to post-curing has a greater influence on the final crosslink density than the concentration of radicals trapped within the network.

It was found that an accelerator concentration of 0.6 phr resulted in the lowest T_g for the post-cured resin (*Table 1*). As shown by the cold-cured T_g, this formulation has sufficient accelerator concentration to generate a 'high' average degree of crosslinking in the cold-cured state. However, the impingement of the gel particles, which restricts the formation of the less densely crosslinked material, and the entrapment of the network radicals, which reduces their mobility, decrease the degree of further crosslinking that occurs during post-curing. There is also the possibility that the number of incomplete crosslinks present in this system is greater than in the other systems. The presence of incomplete crosslinks in the network also results in an increase in the free volume of the system and, hence, a lower T_g.

Variation in accelerator concentration was found to result in very little difference in the activation energy (E_a) of the relaxation process, as calculated from the multifrequency data. In spite of the limited multifrequency data, the Arrhenius-type plots of log frequency against the reciprocal of maximum damping temperature revealed similar activation energies for the various resin formulations investigated (*Table 2*). It would appear, therefore, that the activation energies obtained from multifrequency data are not sufficiently sensitive to detect small changes in the structure of the polyester resin.

CONCLUSIONS

The microstructure of the cured isophthalic unsaturated polyester resin Crystic 272 has been studied during the course of this work, and it has been found that this resin exhibits a heterogeneous structure of the type described by Bergmann and Demmler[4] and others[1–3,5,7]. This heterogeneous structure consists of highly crosslinked domains surrounded by less highly crosslinked areas, and arises as a result of the statistics of the free-radical cure of the resin.

The change in T_g of both cured and uncured Crystic 272 gave further insight into the structure–property relationships of free-radical-cured unsaturated polyester resins. Prior to post-curing, T_g increases with increasing accelerator concentration up to a maximum value, whereas on post-curing this relationship is reversed. This is considered to be a result of the resin formulations, which are less highly crosslinked in the cold-cured state, having a higher probability for conformational rearrangement and diffusion of low-molecular-weight material during post-curing. This in turn results in a higher final average crosslink density. At high accelerator concentrations the reduction in chain mobility is thought to be compensated for by the increased number of free radicals in the system. However, the final T_g for these formulations is still lower than those with very low accelerator concentrations.

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