

# Micro-heterogeneity of urethane vinylester resin networks

J. Zhang, M.O.W. Richardson\*

*Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire LE 11 3TU, UK*

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## Abstract

The morphological structure of a fully cross-linked vinylester Atac 580 resin has been studied by using modulated differential scanning calorimetry (MDSC). The results show that the networks exhibit a diphasic structure, characterised by the presence of two glass transition temperatures ( $T_g$ ). It is believed that the two phases are composed of a polystyrene-rich phase and a vinylester-rich phase, which results from phase segregation during radical copolymerisation. An annealing process below the glass transition temperatures can make the separated phases readily visible. Furthermore, the results demonstrate that MDSC can offer better resolution and sensitivity than conventional DSC and dynamic mechanical thermal analysis. This enables overlapping glass transitions (with  $T_g$ s closer than 10°C) to be distinguished successfully. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Vinylester resin; Heterogeneity; Phase separation

## 1. Introduction

The structure of a urethane vinylester resin [1] contains both external methacrylate and internal fumarate double bonds (Fig. 1). The curing of the resin can be described as a free radical copolymerisation between these unsaturated groups and styrene monomer molecules, which is similar to cross-linking processes of typical vinylester resins and unsaturated polyester resins (UP). Although it has long been used as a matrix for making fibre reinforced composite materials (because it possesses good chemical resistance and physical properties plus the improved glass wettability and adhesion due to the introduction of urethane groups in its backbone [2]); nevertheless, the morphological structure of the cross-linked vinylester resin has not been studied in detail. This may play a significant role in determining the stress-corrosion and environmental resistance performance of its glass reinforced composites.

A number of workers have investigated the structure formation [3–7] of unsaturated polyester resins. It is generally believed that the cross-linking reaction in these systems results in heterogeneous networks. For example, by examination of the hydrolytic degradation of cured UP resins, Funke [3] found that the final conversion was dependent upon the initial radical concentration, which is not in an agreement with the development of a homogeneous polymer. The assumption of a uniform cross-

linking density cannot explain the disintegration of swollen samples under weak mechanical forces [4]. Jones and Jacobs [5] favoured a two-phase structure for isophthalic UP resin to interpret its non-Fickian water absorption behaviour. Thus, it is assumed that this inhomogeneous system consists of highly cross-linked domains embedded in a loosely cross-linked matrix [5,6].

Experimental evidence [7] showed that micro-gel particles can form at an early stage in the polymerisation of a styrenated UP resin, because of the intramolecular cross-linking amongst pendant polyester C=C bonds. Then interparticle cross-links may occur through the C=C double bonds at or near the surface of the micro-gel particles with styrene monomer acting as chain extender. More recently, Ganem et al. [8] revealed, by the kinetic data of copolymerisation, that the structure of a diglycidylether of bisphenol A (DGEBA) vinylester cross-linked with styrene is a two-phase system. However, this phase separation has not been clearly observed even though the development of heterogeneous structures within vinylester and polyester resins has become increasingly accepted [1,3–8].

Studies of the morphological states of multicomponent polymers can be conducted by a number of methods [9]. Amongst these, determining the glass transition temperature,  $T_g$ , is the most convenient and unequivocal way to judge the homogeneity of such polymers. For amorphous polymers,  $T_g$  can be characterised by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and dielectric relaxation methods. However,

\* Corresponding author.



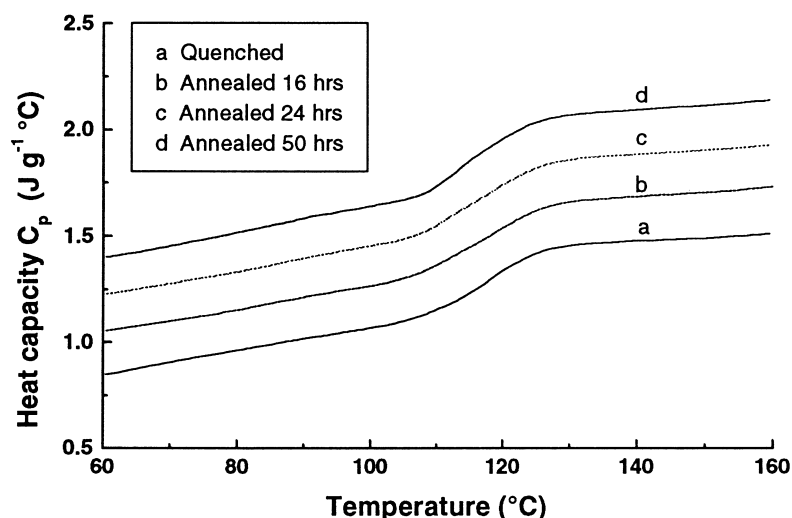


Fig. 3. MDSC heat capacity vs. temperature curves for samples quenched and annealed for different times.

under a  $N_2$  atmosphere. The oscillation amplitude and period were  $1^\circ\text{C}$  and 60 s, respectively. DSC heat flow signals were directly obtained from MDSC by averaging the modulated heat flow signals. A Polymer Laboratories MK (( DMTA instrument was also used to run the samples from 30 to  $200^\circ\text{C}$  at a heating rate of  $3^\circ\text{C min}^{-1}$  at 1 Hz frequency and  $4\times$  strain level.

### 3. Results and discussion

#### 3.1. DSC and MDSC characterisation

Fig. 2 shows the MDSC total heat flow curves of the samples. They are equivalent to the heat flow graphs from a conventional DSC. Curve (a) was obtained from the quenched sample whilst curves (b), (c) and (d) were from the samples which had been annealed at  $85^\circ\text{C}$  for the various times shown in the figure. From this figure, it seems that

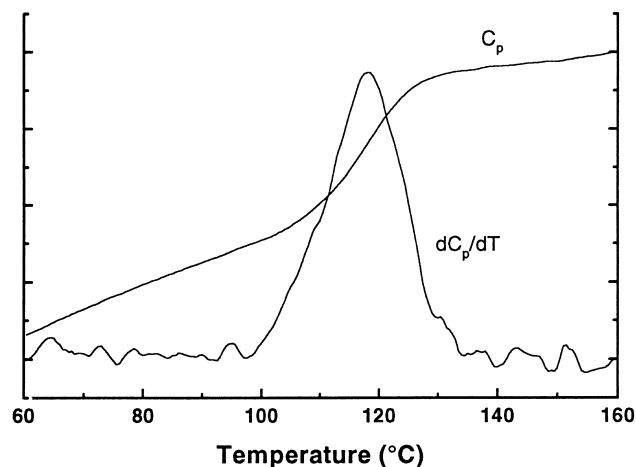


Fig. 4. A comparison of heat capacity and the differential of heat capacity vs. temperature for the quenched sample in MDSC.

only “one step” changes are observed, which indicate a single glass transition. The (b), (c) and (d) endotherms are typical of the normal non-equilibrium behaviour of glassy polymers [11]. They are caused by relaxation of excess enthalpy during the annealing process. The post-curing regime used made it certain that the samples had been fully cured before further investigation started, as indicated in Fig. 2; curve (a) where no exothermic peak occurred. This eliminated the possibility of any further polymerisation in the later annealing and thermal scanning processes.

Studying the miscibility of polystyrene (PS)/styrene-*co*-methyl methacrylate (S-MMA) copolymer blend by DSC, Feijoo et al. [12] comment that it is very useful to ascertain, by physical ageing or annealing, if the polymers are miscible or immiscible. They observed two glass transitions for physically aged PS/S-MMA blends, which were marked by the presence of two “step changes” on heat flow curves. However, this method did not appear to work successfully in the current investigation. Even worse, the  $T_g$ s were obscured by the endotherms, making it difficult to determine the glass transition temperature accurately. This was because DSC measures the sum of all thermal events in a sample.

However, MDSC, by its definition [10],

$$\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t, T)$$

where  $Q$  is the total heat evolved,  $C_p$  the thermodynamic heat capacity,  $T$  the absolute temperature,  $t$  the time, and  $f(t, T)$  the kinetic response of any physical and/or chemical transformation, can separate the thermodynamic events and kinetic responses. Fig. 3 shows that the  $T_g$ s for annealed samples can be clearly derived from the heat capacity versus temperature signal from MDSC without any interference from different thermal histories of the samples. There was still only one  $T_g$  observable for both quenched and annealed samples.

As a point of fact, the glass transition is thermodynamically

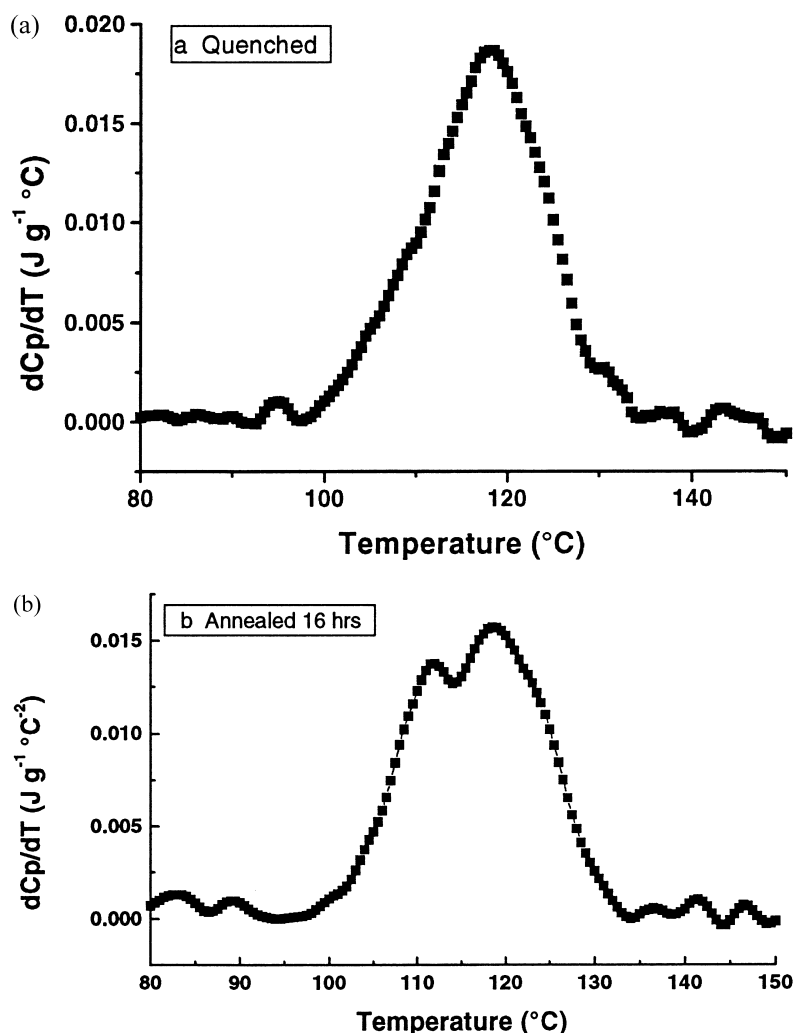


Fig. 5.  $dC_p/dT$  vs. temperature curves for: (a) quenched sample; and samples annealed for (b) 16 h; (c) 24 h and (d) 50 h.

not a true transition but a spectrum that reflects the segmental motions of different lengths [13].  $T_g$  represents the temperature at which segmental motions with an average length begin, which corresponds to the inflection point of the heat capacity versus temperature of the polymer. Alternatively, this inflection point can be measured by the differential of heat capacity with respect to temperature,  $dC_p/dT$  (see Fig. 4). A glass transition temperature at half vitrification measured by the  $dC_p/dT$  maximum is only governed by the time scale of modulation in MDSC [14]. Thus, the glass transition temperature of a polymer can be expressed by the temperature where the  $dC_p/dT$  reaches a maximum. Hourston et al. [13,15,16] have successfully used this technique to study polymer glass transitions, physical ageing and morphology of interpenetrating polymer networks.

Fig. 5 shows  $dC_p/dT$  vs. temperature data for the same samples as those presented in Figs. 2 and 3. It is very evident now that there are two peaks in Fig. 5(b)–(d), which represent two glass transitions. The results strongly suggest

that two phases exist in these networks. However, the glass transition temperatures of these phases are so close that they nearly completely overlap. This is the reason why the separated phases of the vinyl-ester cannot be sensed by the conventional DSC even for annealed samples (Fig. 2), whilst the same phenomenon can be easily observed for aged PS/S-MMA blends [12] using the same method. Conversely, this minor change cannot be discerned from the  $C_p$  signals (Fig. 3). It is the  $dC_p/dT$  signal that is capable of clearly disentangling these overlapping processes.

As mentioned above, the phase segregation results from the inhomogeneous course of the vinyl-divinyl cross-linking copolymerisation such as in styrenated UP and vinyl-ester resins. The primary microgel particles due to intermolecular and intramolecular reactions tend to develop a higher cross-link density than the external regions linking these primary regions [7]. The external regions contain a higher content of styrene-based blocks since the methacrylate copolymerisation in a styrene-vinyl-ester mixture

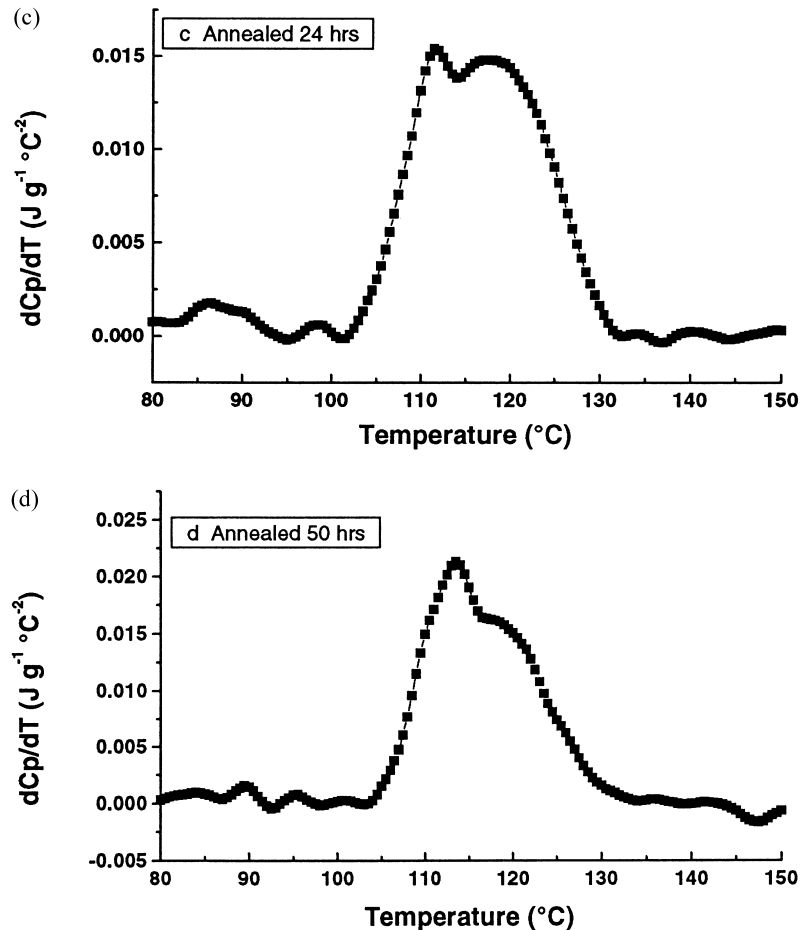


Fig. 5. (continued)

stops long before complete consumption at a certain stage whereas styrene continues to react to form large homopolymer sequences [8].

Atlac 580 urethane vinyl ester may have the same phase segregation mechanism as DEGBA and UP resins since it contains both the fumarate groups which exist in the UPs, and the methacrylate groups which exist in vinyl ester resins generally. This could mean that a higher cross-link density region was formed in a vinyl ester-rich phase whereas a lower cross-link density was formed in a polystyrene-rich phase. It is well known that a glass transition temperature is proportional to a cross-link density. Thus, it is reasonable to assign the lower peak in Fig. 5(b)–(d) to a polystyrene-rich phase with a lower  $T_g$ , and the higher peak to the vinyl ester-rich phase with a higher  $T_g$ .

It should be noted that the difference between the two  $T_g$ s is only about 10  $^\circ C$ . This might imply that the extent of the separation is very limited probably because of the restriction of the cross-linked network on the simultaneously occurring phase segregation process. Additionally, the intrinsic  $T_g$  value of the pure vinyl ester network may be close to that of polystyrene. It is difficult to obtain fully cured vinyl ester homopolymer experimentally and the size of the domains

may be very small as is indicated by the transparency of the sheets.

It is worthwhile to point out that in the current investigation the segregation phenomenon is not the result of the isothermal annealing. The annealing process can only result in conformation rearrangement of a polymer, leading to the excess enthalpy and volume relaxation [11]. However, it can be seen that the process can make the overlapping two-phase structure more clearly identified if one compares Fig. 5(a) with Fig. 5(b)–(d). This is because the relaxation rate of the two phases is different. Generally, the width of a glass transition temperature range will become narrower and the peak of  $dC_p/dT$  becomes higher as the isothermal annealing progresses. This is because, the increment of heat capacity,  $\Delta C_p$  in the transition region remain relatively unchanged [15]. As indicated in Fig. 5, whilst the height of the  $dC_p/dT$  peak increases with increase in the annealing time, the width of the  $T_g$  transition decreases from about 30 to 25  $^\circ C$  for the whole network. Individually, the relaxation rate of the polystyrene-rich phase is faster than that of the vinyl ester-rich phase. In other words, if the network were a one-phase structure, there should only be one peak, even after the isothermal annealing (Fig. 5).

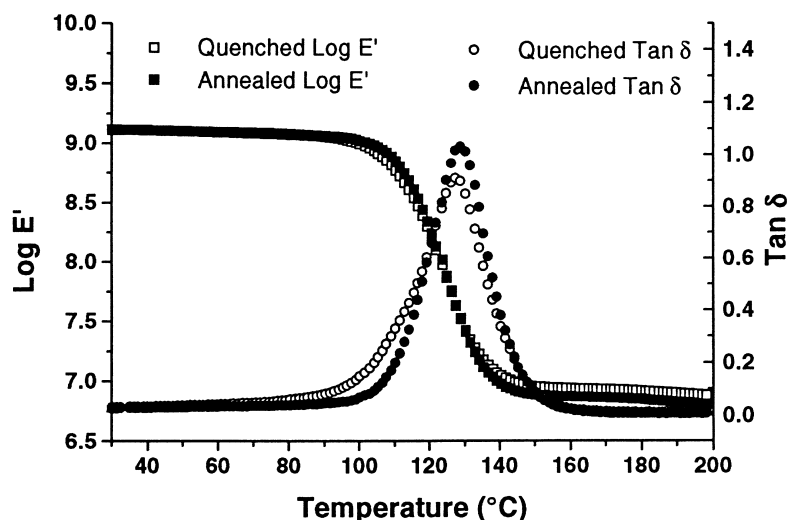


Fig. 6. DMTA data for the quenched sample and the sample annealed for 50 h.

On the other hand, it appears that there is only one peak present in Fig. 5(a) for the quenched sample. However, looking at the asymmetric shape of the curve with the left part being less steep than the right, it may be concluded that a multi-component structure exists and they just simply closely overlap. Experimental evidence indicates that, for pure polymers or miscible polymer systems, the distribution complies with a Gaussian function [16].

The difference in the relaxation rate of the two phases also support the formation of the two domains with the two differing cross-link densities. Because the lower cross-link density domains tend to have statistically more molecular segments which can involve conformation rearrangement due to a less restriction from cross-link joints; whilst the case is reverse for the higher cross-link domains. Accordingly, the polystyrene-rich phase with a lower cross-link density will relax faster as opposed to the vinyl ester-rich phase with a higher cross-link density, which is showed explicitly in Fig. 5.

### 3.2. DMTA characterisation

Fig. 6 shows the DMTA response to quenched samples (open symbols) and the sample annealed for 50 h (solid symbols). The behaviour of the samples annealed for less than 50 h is consistently similar to that of the 50-h annealed sample. It can be noticed from Fig. 6 that the samples after annealing have a higher peak value of  $\tan \delta$ , a slightly higher  $T_g$ , and a narrower width of the transition region, compared to the quenched sample. With the exception of these, however, there is no indication of an existence of two  $T_g$ s, as observed in MDSC, in either the storage modulus  $E'$  or loss  $\tan \delta$  signals. Thus, DMTA may still suffer certain resolution problems, as does conventional DSC but the technique can separate the phases if there is a large difference in  $T_g$ s [9,17].

## 4. Conclusions

It has been found that urethane vinyl ester cross-linked with styrene monomer is a diphasic structure with one phase probably being polystyrene-rich, and the other vinyl ester-rich. This is indicated by the presence of the two characteristic glass transition temperatures associated with the system. The two-phase structure is consistent with the free-radical copolymerisation mechanism proposed in the literature [6–8]. The glass transition temperatures for these two phases are only approximately 10°C apart. The differential of heat capacity signal enables MDSC to resolve micro-heterogeneity of polymers in contrast to DSC and DMTA, which cannot detect such a minor change.

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