Investigation of the effects of scale and cure environment on the properties of vinyl ester polymer

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ABSTRACT

This work involves the study of the cure kinetics of a commercial bisphenol-epoxy vinyl ester resin as a function of sample thickness and environment atmosphere. It has been previously suggested that cured vinyl ester polymer is a diphasic material consisting of a lower Tg styrene phase and a higher Tg vinyl ester phase. The cure kinetics of each phase have been observed to have a significant effect on the thermal properties of the system, such as the degree of crosslinking, glass transition temperature and final conversion. DSC, DMA and FTIR were employed to characterize two vinyl ester resin systems and study the material property transferability from macroscale to microscale. The effect of reduced styrene content on resin curing and polymer thermal behaviour was studied. The effect of oxygen interaction during initial cure was investigated at both microscale and macroscale and found to have a significant effect on final polymer performance.

1. Introduction

Vinyl ester (VE) resins are increasingly being used as the matrix polymer in fibre reinforced composites for demanding large applications in the marine, offshore, and civil infrastructure sectors. VE formulations are low viscosity at room temperature and are highly suitable for infusion of a reinforcing fabric preforms to make large parts such as windmill blades. VE systems exhibit short fabrication cycles and ease of processability as well as relatively low cost, high environmental durability and adequate level of cured polymer performance in comparison to more expensive epoxies [1,2]. These VE resins are typically formulated from styrene and a condensation product of methacrylic acid with an epoxy and polymer curing is achieved by free-radical polymerisation [2–7]. The cured VE polymers consist of highly cross-linked methacrylated epoxy compounds surrounded by a lightly cross-linked, styrene-rich region. Monomeric styrene is used as a diluent in the resin and in vinyl ester acts as a cross-linking agent. It has been suggested that cured vinyl ester resin can possess a diphasic microstructure consisting of a lower glass transition temperature (Tg) styrene phase and a higher Tg vinyl ester phase [3,8–11]. The assessment of the polymer morphological state can be carried out by evaluating the Tg using thermal analysis techniques such as DSC and DMA [3,6]. The cure kinetics of each phase have been observed to have a significant effect on the thermal properties of the system, such as the degree of crosslinking, Tg

and final conversion [3–10].

Vinyl ester resin properties are highly dependent on the performance of both the vinyl ester and the styrene phase. A high styrene content can result in reduced cross-link density but can produce increased volumetric shrinkage and therefore enhanced performance of the composite over time as cure continues to increase maximum conversion. In composite systems complete polymerisation may increase degradation rates at both the fibre-polymer interface, and within the matrix itself, since high heterogeneity promotes accelerated moisture induced degradation of the VE polymer [2,4–6,12]. It has been long established that the Tg is proportional to the cross-link density of a polymer. Hence, it has been found that a high styrene concentration can result in a reduced cross-link density and a reduction in the Tg of the material. However, this change in Tg has been reported by some authors to be insignificant [3,6]. Moreover, varying styrene content has been associated with changes in the DMA curves obtained from the polymer: increased styrene concentration can result in a reduction in the breadth of the loss modulus and tan δ curves, without affecting the Tg value. The magnitude of tan δ may also increase proportionally with an increase in styrene content [6].

A significant parameter in the cure kinetics of vinyl ester polymers and their composites is the influence of ambient oxygen in the polymerisation process. Although polymerisation may be achieved under an ambient environment, oxygen interaction with the pre-polymer may result in the formation of additional radicals which may complicate the

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polymerisation and compromise the final properties of the polymer [13]. Albertin et al. have found that the use of a nitrogen environment may not be adequate for oxygen removal from the polymer mix [14]. The presence of oxygen within polymer links has been associated with thermal instability. An increase in styrene has been found to accelerate oxygen diffusion through the structure of the polymer [6]. However styrene evaporation in open systems can also be a concern, especially in systems with a high surface-to-volume ratio. These issues can be of particular influence in the field of micromechanical testing of thin films and adhesion at the fibre-polymer interface in composites, where sample preparation is often limited to take place in an ambient atmosphere.

The microdroplet test is commonly employed to characterize the interfacial shear strength in fibre-reinforced polymers. Dirand et al. [15] reported styrene loss in VE microdroplets on glass fibre, which resulted in poor interfacial adhesion. Laurikainen [16] observed that for a glass fibre-VE system, attempts to cure VE microdroplets were unsuccessful, regardless of post-cure temperature. Incomplete curing was also attributed to styrene loss. Laurikainen also suggested that the effect of styrene evaporation could be countered by curing specimens in a styrene-rich atmosphere. However, Thomason et al. found that curing microdroplets under styrene rich atmosphere did not fully overcome the droplet performance deficiency in their VE resin system [17]. Thomason recently reviewed a number of these potential scaling issues in a range of polymer systems including VE. It was concluded that in many cases the structure and properties of the polymer in such microdroplets is not representative of the same polymer, with the same thermal and environmental exposure history, prepared on the macroscale [18].

Consequently it appears that there are significant potential issues with the preparation and polymerisation of VE resins used in micromechanical testing of fibre reinforced VE. However, direct investigation of the polymerisation kinetics of microdroplets is limited by their extremely small scale, often only nanograms in mass. To obtain a better understanding of these phenomena, in this work, scaling effects on the polymerisation of VE resins have been investigated using thin films with a thickness of the same order of magnitude as the diameter of droplets used in the microbond test [17,18]. Results of a study on the effects of sample preparation scale on the cure kinetics and polymer properties of two VE resin systems are presented and discussed. Curing conditions such as temperature, environment atmosphere and styrene content have been varied. The resulting polymers have been characterised using Fourier-transform Infrared Spectroscopy (FTIR) and thermal analysis techniques such as Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA).

2. Experimental

2.1. Materials

Two different vinyl ester polymers were used in this study. DION 1260 from Polynt is a commercial bisphenol-epoxy vinyl ester with a styrene content of 48–52 % by weight. Designed for vacuum infusion, it has low viscosity and giving good fibre wet-out in composite production, curing to give high toughness and good crack resistance, as well as improved high-temperature stability. DION 1273, a developmental resin from Polynt, is a pre-accelerated, modified vinyl ester resin, primarily based on methyl methacrylate-based (MMA) and styrene (<20 % by weight). This resin was also designed for vacuum infusion in composite production. It is a low viscosity resin curing to give a polymer with very high fracture toughness and exceptional adhesion. Both resins were cured using a PBC-21 UN 3103 Organic peroxide type C initiator from United Initiators GmbH. The initiator was added to the resin at a ratio of 97.5 : 2.5 by weight prior to use.

2.2. Specimens cure conditions

All the polymer specimens and sample preparation conditions used

in this study are described in Table 1. The cure conditions and specimen geometry employed were selected to examine the following parameters, which are known to possibly affect the cure kinetics and thermal behaviour of vinyl esters: polymerisation scale - varying sample thickness, resin styrene content, oxygen intrusion during polymerisation, post-cure temperature. VE polymer plates prepared in a sealed mould (SM) samples were supplied by Polynt. Bulk open mould (OM) specimens were manufactured in a silicone rubber mould fabricated in-house. The manufacturing of thin film specimens was found to be a challenging task and could not be performed in a closed mould. The low resin viscosity made it difficult to obtain a uniform film thickness and high adhesion between cured resin and substrate made it very difficult remove a whole film specimen. Several substrates and manufacturing techniques were attempted, such as spin coating on glass slides, spreading resin on a silicone mould, using a seam roller and manufacturing between metal plates. Nonetheless, not all these techniques resulted in an adequate finish. The most effective manufacturing method for uniform thickness films was found to be the use of a metallic drawdown bar for the application of the film on a nylon substrate, adhered onto a steel plate. Drawdown bars of different thicknesses were used to vary final polymer film thickness. Film thickness was measured using a digital micrometer. The effect of scale on the cure kinetics of the specimens was examined using three different thickness (t) ranges:

- $3.9 \leq t \leq 4.5$ mm *(macroscale – bulk)*.
- $0.1 \leq t \leq 0.2$ mm *(microscale – thin film)*.
- $t < 0.1$ mm *(microscale – thin film)*.

The manufacturer recommendations for cure on the two different scales were -

- Macroscale samples, room temperature (RT) cure for 24 h in a closed mould followed by a PC of 24 h at 60 °C.
- Microscale films, RT cure for 24 h under nitrogen (N_2) followed by a PC of 24 h at 60 °C, 3 h at 80 °C, 1 h at 100 °C.

These cure cycles have been identified as standard cure (SC), as shown in Table 1. The N_2 environment used in the initial cure phase of thin films was recommended by the resin manufacturer to prevent probable oxygen interaction and volatile component vaporisation from the high-surface-to-volume ratio film configuration. Moreover, an additional elevated temperature postcure (PC) at 150 °C was recommended to ensure optimum conversion of the thin films. Consequently, some macroscale specimens were also subjected to PC at 100 °C to allow comparison with the standard cured thin films. The assessment of the presence of ambient oxygen during the manufacturing of vinyl ester specimens was carried out at both scales:

Table 1
VE sample preparation conditions.

Designation	1260	1273	Cure 24 h at RT	Postcure (PC)	Max. PC Temp (°C)	Scale
SM, SC, plate	X	X	Sealed Mould		60	Macroscale
SM, PC, plate	X		Sealed Mould		100	
OM, SC, plate	X		Air	Air	60	
AA, SC, film	X		Air	Air	100	Microscale
NA, SC, film	X	X	N_2	Air	100	
NN, SC, film	X		N_2	N_2	100	
NA, PC, film	X		N_2	Air	150	
NN, PC, film	X	X	N_2	N_2	150	

- Bulk neat resin samples fabricated both in a sealed mould (hindering oxygen introduction) and an open mould (allowing interaction with ambient oxygen).
- Thin films were cured and post cured both in an inert nitrogen environment and in an ambient atmosphere. The effect of elevated post-cure temperature of 150 °C was also examined.

The effect of styrene content on the microscale was studied by reducing the styrene content of a "standard" cure film by approximately 67 % by first applying vacuum evaporation to unreacted resin.

2.3. Differential Scanning Calorimetry (DSC)

DSC analysis was carried out using a Q20 differential scanning calorimeter (TA Instruments). The following heating programme was used for each specimen: equilibrate and isothermal for 10 min at −10 °C, ramp at 10 °C/min to 180 °C (cycle 1) and hold isothermally for 10 min, ramp at −10 °C/min to −10 °C and hold isothermally for 10 min, ramp (cycle 2) at 10 °C/min to 180 °C. Nitrogen was used as purge gas at 50 ml/min for all tests. The glass transition temperature was assigned from a clear step change visible on the curve of heat flow plotted against temperature. All specimens were contained in standard aluminium pans sealed with a lid. For bulk specimens, a thin section was cut to give an approximately 20 mg sample. Film specimens had a lower mass (2–3 mg) than bulk specimens, the stacking of multiple layers was avoided to prevent uneven heat transfer between the different layers. The fractional conversion of monomer to polymer for each system was evaluated using Equation 1

$$a = \left(1 - \frac{H}{H_t}\right) \tag{1}$$

where a is the degree of cure, H is the heat of the reaction of the specimen and H_t is the total heat of reaction measured from an unreacted sample (measured as 325 J/g). The unreacted resin baseline specimen was subjected to vacuum for approximately 10 min while in the DSC pan for removal of oxygen prior to testing.

2.4. Dynamic Mechanical Analysis (DMA)

DMA analysis was carried out using a Q800 Dynamic Mechanical Analyser (TA Instruments). Measurements were performed on the thick specimens in 3-point bending mode in accordance with ASTM D5023-15 [19]. DMA parameters used were a frequency of 1 Hz, 0.1 N preload, amplitude 50 μm, and force track of 120 %. The specimen dimensions used were 64 × 13 mm with a thickness of 3.9 ≤ t ≤ 4.5 mm; the span length during testing was 50 mm. All microscale thin film specimens were tested in tension mode according to ASTM D5026-15 [20]. The test parameters for the thin film specimens tested in tension were kept as close as possible to the macroscale testing. However, a significant reduction in amplitude was required as a function of scale. Testing frequency was 1 Hz, no preload, amplitude 10 μm, and force track of 105 %. All specimens were equilibrated at 25 °C for 5 min, then ramped at 2 °C/min up to 150 °C. Tg values were recorded at the peaks of the tan δ and loss modulus curves as taking the onset temperature of the drop in logarithmic storage modulus.

2.5. Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was used to assess the degree of cure of vinyl ester as a function of scale, cure environment and temperature. Spectra were collected using a 4100 ExoScan FTIR with a spherical diamond attenuated total reflectance (ATR) interface. Analysis was performed in the 650 cm^{-1} to 4000 cm^{-1} range with a spectral resolution of 8 cm^{-1} and 64 scans per sample. Background scans were taken every 10 min and the crystal was cleaned with acetone

between measurements. Data processing and normalisation were conducted with OriginPro software. A quantitative analysis was performed through the use of SpectraGryph software using the "integration with baseline" tool. For both matrix systems, the degree of cure was monitored by the depletion of the C═C at 946 cm^{-1} and 910 cm^{-1} for the vinyl ester and styrene monomers respectively. The C–H of styrene and vinyl ester at 695 cm^{-1} and 830 cm^{-1} were used as internal reference. Lastly, the large variation in styrene content of different specimens and the lack of information regarding the molar ratio of the two resins were restrictive parameters for the calculation of the total polymer fractional conversion. The individual styrene (α_{ST}) and vinyl ester (α_{VE}) monomer conversions were calculated using the Equations (2) and (3) derived from the Beer-Lambert law [21].

$$\alpha_{VE}(t) = 1 - \left(\frac{ABS\,(t)945\;cm^{-1}}{ABS\,(t=0)945\;cm^{-1}}\right) * \left(\frac{ABS\,(t=0)830\;cm^{-1}}{ABS\,(t)830\;cm^{-1}}\right) \tag{2}$$

$$\alpha_{ST}(t) = 1 - \left(\frac{ABS\,(t)910\;cm^{-1}}{ABS\,(t=0)910\;cm^{-1}}\right) * \left(\frac{ABS\,(t=0)700\;cm^{-1}}{ABS\,(t)700\;cm^{-1}}\right) \tag{3}$$

3. Results and discussion

3.1. The chemistry and thermal properties of DION 1260

3.1.1. Thermal analysis – effect of scale

The results of the DSC study of cured vinyl ester as a function of material thickness are presented in Fig. 1. The various polymer Tg values
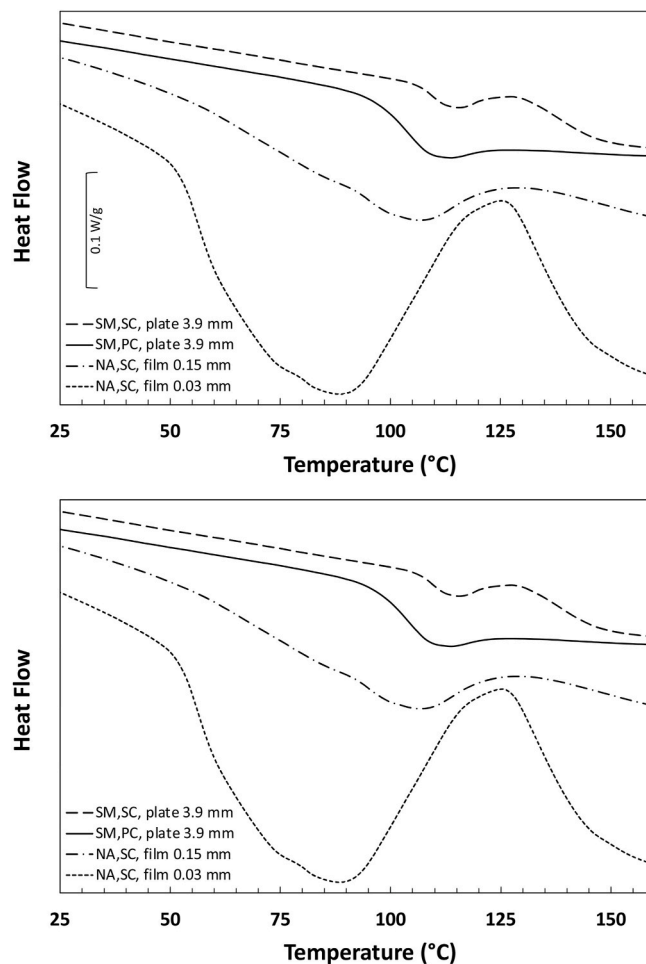

Fig. 1. DSC 1st heating thermograms of standard cured DION 1260 polymer as a function of sample thickness. Curves are offset and therefore Y axis values are arbitrary.

as a function of specimen thickness from the first and second heating cycles are included in Table 2. Tg (1) and Tg (2) refers to Tg determined from either the first or second heat ramp respectively. Tg_1 and Tg_2 refers to two transition temperatures visible in a single heating ramp. The bulk polymerised samples exhibited a single Tg in both heating scans. However, the film specimens representative of the microscale, feature a broader double transition in the first heating scan. Although the transition of the 0.15 mm film was rather broad, the double transition was still apparent and detectable by the analysis software. In all cases the Tg values were significantly reduced when the material thickness was lower.

It was found that when thin film specimens were re-heated only a single transition was observed at higher temperature. However, the thinnest film (t = 0.03 mm) still only reached a Tg (2) value of 81 °C. The Tg (2) increase was an indication of initial incomplete curing of the specimens and post-curing effects induced by the exposure to higher temperatures in the DSC. Nonetheless, for the thinnest specimen it was shown that the achievement of "bulk scale" cure was still unfeasible, at least when "standard" cure conditions were used. This was a strong indication that the final microstructure of the thinner polymer films may be significantly different from that of "bulk scale" specimens.

No major differences was detected between the Tg values and exothermic reaction energies of the bulk polymerised specimens. The effect of post-curing at a higher temperature was found to be negligible and that a cure temperature of 60 °C was adequate for the specimen to react fully. However, for the film specimens the increase in residual exothermic reaction energy with decreasing material thickness was another clear indication of a reduced level of curing. Based on that observation, a monomer conversion calculation was conducted using Equation (1) and the results are shown in Fig. 2. The results clearly indicate that the degree of conversion of this VE resin is lowered when the material thickness is reduced.

A DMA study of the thermomechanical behaviour of film specimens was also conducted as a complement to DSC study. Storage and loss modulus curves for a cure film (NA,SC) of a thickness of 0.13 mm and a sealed mould plate (SM,SC) of a thickness of 3.9 mm are presented in Fig. 3. The resulting Tg values from storage modulus, loss modulus and tan δ curves are presented in Table 3. It was found that a broad shoulder stretching between 70 °C and 90 °C was apparent in the film loss modulus curve prior to the main peak. Moreover, a slight downward change in the slope of the storage modulus curve can be observed in the same temperature range. This result was found to be in agreement with the first DSC transition at 65 °C (Tg_1(1) in Table 2) of a film in the same thickness range. As shown in Table 3 the Tg range indicated by the various DMA methods ranged from around 88 °C–122 °C, bounded between the first onset of the log of the storage modulus and the maximum value obtained from the tan δ peaks. The Tg range of the macroscale plate was found to be between 99 °C and 115 °C. In this case, a clear single transition is evident in the DMA thermal curves in Fig. 3 and the shoulder apparent in the loss modulus of the film was not present. Moreover, the storage modulus values of the bulk specimen at the viscoelastic range were found to be significantly higher than those of the film ($\approx$1 GPa for film and $\approx$4 GPa for plate at room temperature). This
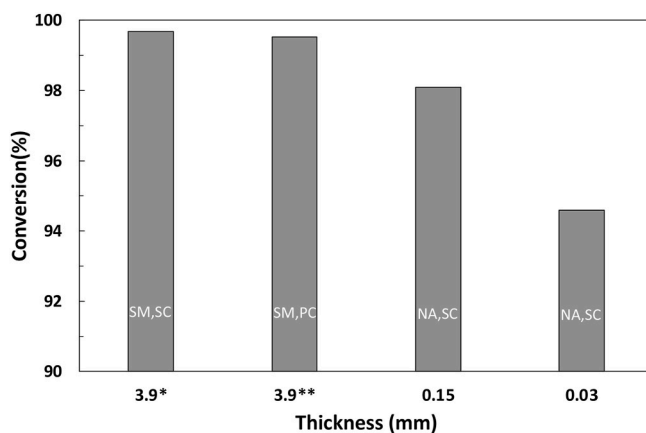

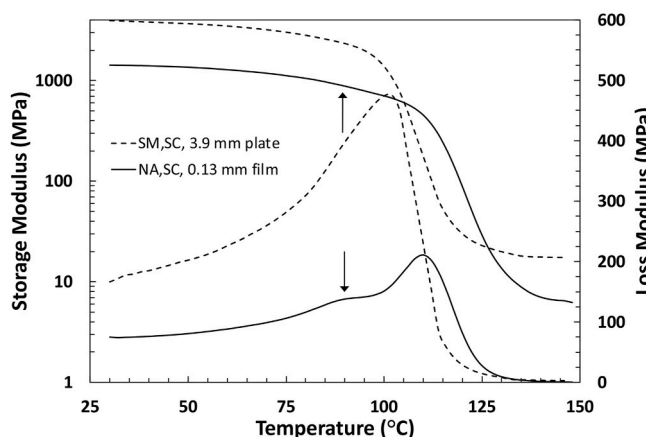**Fig. 2.** DSC conversion calculation for DION 1260 as a function of thickness during cure.

Fig. 3. DMA results for DION 1260 for a DION 1260 NA,SC polymer film of thickness 0.13 mm, and a 3.9 mm thick SM,SC plate.

Table 3
Tg values obtained by DMA for a DION 1260 NA,SC film of thickness 0.13 mm, and a 3.9 mm thick SM,SC plate.

Specimen Type	Storage Modulus - Onset (°C)	Loss Modulus - Shoulder (°C)	Loss Modulus - Peak (°C)	Tan δ - Peak (°C)
NA,SC, film	107	88	110	122
SM,SC, plate	99	N/A	99	115

was indicative of notably higher stiffness for the bulk polymerised specimens and was clear evidence of the effect of scale on vinyl ester polymer properties. As described in the experimental section, different DMA test setups were used for the film and plate specimens and hence some difference was expected between Tg values in the different scales. In theory, so long as the applied strain lies within the linear viscoelastic region for the material at the same frequency, the Tg value should not change. In our case, the strain level chosen for bulk polymer plates (amplitude of 50 μm) was appreciably higher than the one employed in thin film testing (amplitude of 10 μm). Such a change may affect the sensitivity to detect the early stages of the transition – higher strain levels may detect the Tg onset earlier, lower levels later into the transition once softening is more significant. DSC is generally more effective in detecting Tg as a function of sample polymerisation thickness, due to the smaller specimen mass employed (low thermal lag) and the fact that the specimen is sitting directly on top of the thermocouple. On the other

Table 2
Tg change vs thickness of DION 1260.

Cure designation	Original Thickness (mm)	First Heating Scan			Second Heating Scan
		Tg_1 (°C)	Tg_2 (°C)	Residual Reaction Energy (J/g)	Tg (°C)
SM,SC	3.9 ± 0.2	N/A	109	1.5	110
SM,PC	3.9 ± 0.2	N/A	105	1	108
NA,SC	0.15 ± 0.02	65	101	7	110
NA,SC	0.03 ± 0.02	55	81	17	90

hand, with DMA, specimen mass is more significant, the thermocouple is positioned a few mm from the specimen and the specimen is mainly heated by convection of the hot atmosphere of the oven, and not directly via conduction, as is the case with DSC [22]. Thus, DMA is less efficient when it comes to sample temperature uniformity, which is why lower heating rates are usually employed when compared to DSC. It is not uncommon to find reports of Tg values measured by DMA to be higher than those obtained by DSC from the same VE polymer [6,23].

The appearance of a low-temperature transition in microscale cured vinyl ester specimens may be indicative of the diphasic nature of the resin. Although this effect was not apparent on bulk scale specimens, literature results suggest that a diphasic nature may still be present but cannot be deconvoluted by thermal analysis software [3]. This is due to the two transitions existing within the same temperature region. In this case, it can be assumed that the lower-temperature Tg is exhibited by the styrene-rich region of the resin, considering the volatility of the styrene monomer and the fact that the styrene-rich region is known to have a lower cross-link density than the vinyl ester region.

3.1.2. Effect of reduced styrene – A microscale study

Although it is established that a reduction in the styrene content of bulk vinyl ester specimens has a minor effect on their Tg [7,24], to the best of our knowledge, the transferability of the effect to the microscale involving the preparation and curing of small resin volumes has yet to be examined. The potential for styrene loss during manufacturing and curing of film specimens was considered, due to the volatility of the styrene monomer as opposed to the stable chemistry of the vinyl ester monomer. Nonetheless, it should be taken into account that reducing the amount of styrene of the pre-polymer mix used for films to 67 % of the normal value would simply reduce styrene content further, if styrene was already evaporated during the manufacturing of standard cure specimens. Considering literature evidence regarding incomplete polymerisation of vinyl ester and polyester micro-droplets due to styrene evaporation, it was important to determine whether the lower temperature Tg of vinyl ester films was caused by such an effect. Laurikainen [16] stated that vinyl ester micro-droplet curing could only be achieved under a styrene environment (in air). On that basis, the effect of a styrene-rich environment on the thermal behaviour of film specimens was explored. Fig. 4 shows DMA storage and loss modulus curves for three film specimens which have all experienced standard film cure (Table 1). A reference 1260 formulation film (REF) of a thickness of 0.13 mm, a 0.15 mm film cured under a styrene environment (SE), and a 0.16 mm film with reduced styrene (RS).

All Tg values were found to be within the same approximate temperature range. Nevertheless, the Tg of the film cured under a styrene-rich env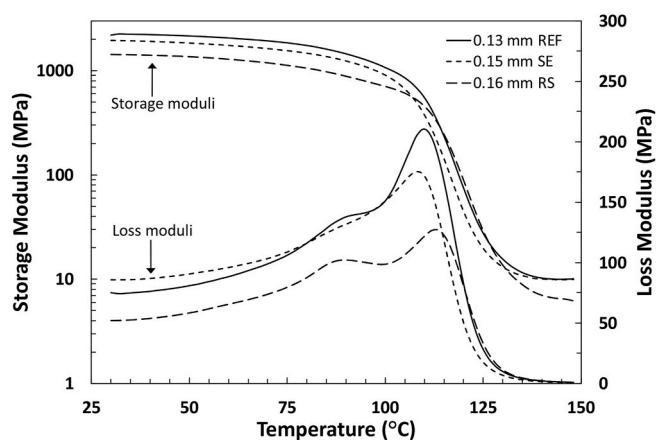ironment did exhibit a slightly lower Tg, while the styrene-poor specimen showed a slightly higher Tg. This was in line with bulk vinyl ester results as a function of varying styrene content reported by Scott et al. [6]. Nevertheless, the DMA results were not in complete alignment with the conclusions of Scott et all who also observed a reduction in the width of the tan δ peak at half maximum (PWHM) when the polymer styrene content was increased. Fig. 5 compares the tan δ peak for the three samples from Fig. 4 with an enlarged temperature scale. The small differences in peak temperature are clearly visible in this Figure. However, unlike the results from Scott et al. there is no significant difference in the peak widths in Fig. 5 (PWHM all 17.5 ± 0.1C). The loss modulus curves in Fig. 4 do show a discernible pattern in the format of the low-temperature transition as a function of styrene content. The breadth of the shoulder increased with increasing styrene content, while a more pronounced shoulder was seen in the case of the reduced styrene film. Moreover, it can also be seen that the reduced styrene film exhibited a slightly lower storage and loss modulus magnitude both below Tg and in the rubbery region above Tg. These are typically taken as indications of a lower cross-link density. This was in line with the observations by Scott et al. [6], who found a reduction in crosslink density with increased styrene content.

In agreement with DMA results, comparative DSC results between reference 1260 formulation and reduced styrene 1260 films in different thickness ranges confirmed the presence of a low-temperature transition. DSC thermograms are shown in Fig. 6 and all Tg values obtained by the styrene content study are contained in Table 4. This transition was within the same temperature range for "standard" cure and "standard" cure, reduced styrene specimens of a similar thickness. For t < 0.1 mm, both reference and reduced styrene films exhibited similar lower temperature Tg's of 55 °C and 54 °C, respectively. A similar effect was observed for films of 0.1 ≤ t ≤ 0.2 mm, whereby an initial Tg between 65 °C and 70 °C was featured by both film specimens. The residual exothermic reaction energies obtained above Tg were slightly higher for the reference films containing the original styrene content, as opposed to the ones of a reduced styrene content. Nevertheless, the differences were not considered significant and most likely unrelated to the change in styrene content after studying the results of a wide range of specimens. It can be concluded that the Tg and cross-linking of styrene-poor films were found to be slightly higher than those of the reference films and films cured under a styrene environment. However, the shoulder in the loss modulus DMA curve was found to be more pronounced for reduced styrene films and was depleted as a function of increasing styrene. Nonetheless, this shoulder was apparent in all tested films, regardless of the styrene content.

3.1.3. Effect of oxygen in vinyl ester polymerisation

Reports suggested that the presence of oxygen during the polymerisation of vinyl ester can compromise the performance of the polymer
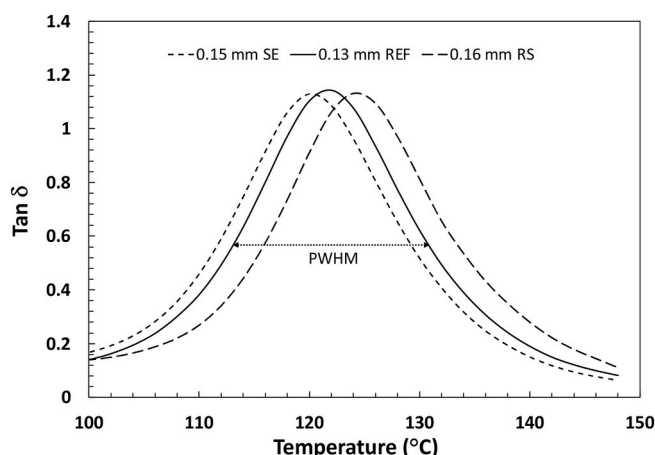

Fig. 4. DMA results from DION 1260 standard cure films of varying styrene content.

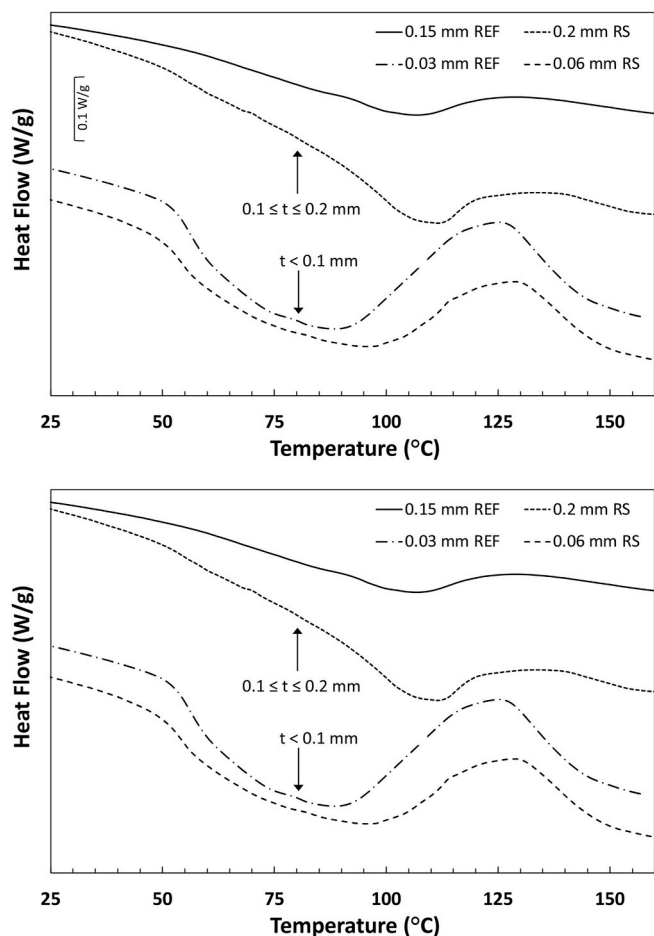**Fig. 5.** Peak width at half maximum of tan δ curves of samples in Fig. 4.

Fig. 6. DSC thermograms of DION 1260 standard cure films in two thickness ranges with original and reduced styrene content.

Table 4
DSC Tg values (first heat scan) from standard cure DION 1260 film of original and reduced styrene content for different thickness ranges.

Thickness (mm)	Designation	Tg_1 (°C)	Tg_2 (°C)	Residual Exotherm (J/g)
t ≤ 0.1	1260 Reference	55	81	17
	Reduced Styrene	54	83	11
0.1 < t ≤ 0.2	1260 Reference	65	101	7
	Reduced Styrene	70	101	6

and is likely to be catastrophic when vinyl ester specimens of a high surface-to-volume are employed [25,26]. In this work, the effect of the interaction of polymerising vinyl ester with atmospheric oxygen has been studied using DMA. The DMA thermal curves for several vinyl ester specimens on the microscale and macroscale cured under different cure environments and temperature regimes are presented in Figs. 7 and 8.

A low-temperature shoulder was present in the loss modulus curve of cured vinyl ester specimens regardless of the scale when, during the specimen preparation, there was exposure to ambient atmosphere at some point in the curing process (see Fig. 7). Although some film specimens were cured under a nitrogen environment for the first part of the cure cycle, their particularly high surface-to-volume ratio makes them more susceptible to oxygen introduction during the second stage of the cure in a convection oven under an air atmosphere. On the other hand, when an inert nitrogen atmosphere was used for the initial room temperature cure and elevated temperature post-cure, the shoulder in
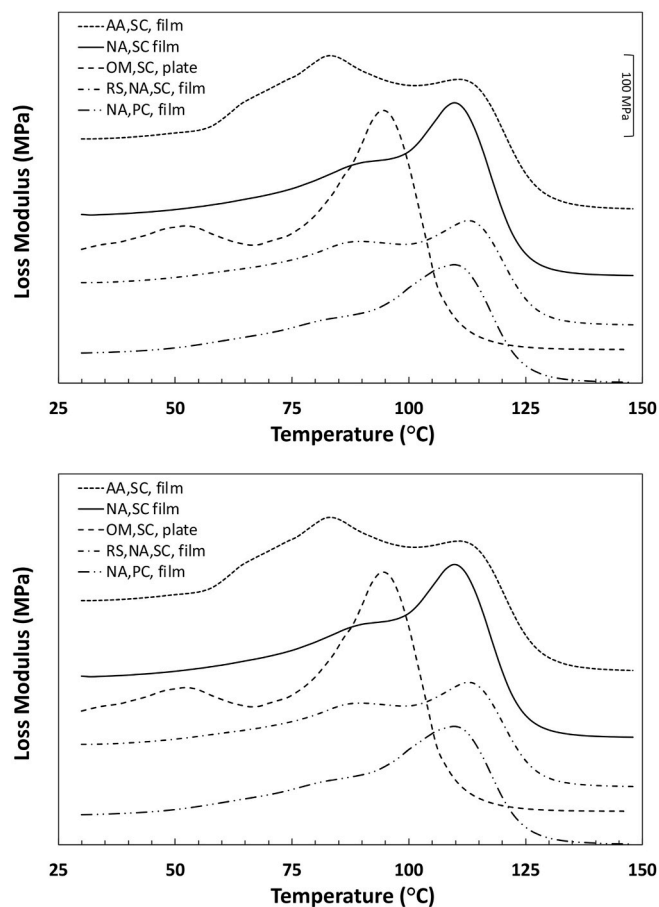

Fig. 7. DMA thermal curves of DION 1260 specimens cured allowing interaction with oxygen during the cure and, or, post-cure phases (curves have been offset for clarity).
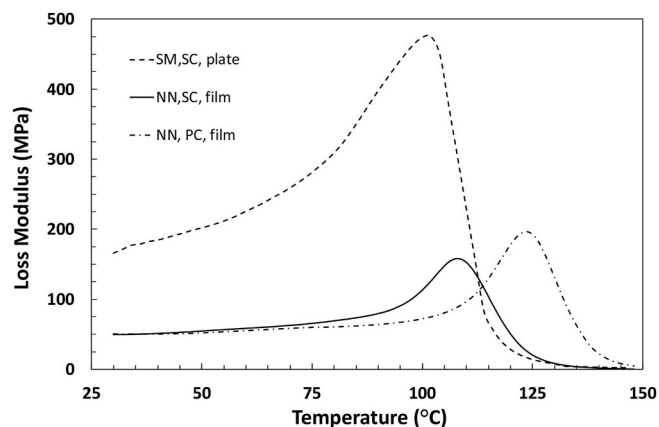

Fig. 8. DMA thermal curves of DION 1260 specimens cured with no interaction with oxygen during the cure and P–C steps.

the loss modulus was no longer apparent (see Fig. 8). The effect of cure temperature was also found to be clear in the case of thin films; post-cure in an inert nitrogen atmosphere and a higher temperature of 150 °C (NN, PC) resulted in a significantly higher Tg of 124 °C, while inert post-cure at 100 °C (NN, SC) resulted in a Tg of 106 °C. If the post-cure temperature was set at 150 °C but nitrogen atmosphere was not used, the shoulder in the loss modulus was still apparent (NA,PC). This is further evidence that the only case where the shoulder was present was when the vinyl ester resin had an interaction with oxygen, either in the initial

or post-cure stages of the matrix.

In the previous section, it was observed that a styrene-rich environment resulted in a less pronounced shoulder in the loss modulus curve. It is also possible that a nitrogen environment may prevent potential retardation of styrene upon interaction with oxygen [14]. The fact that it is not solely styrene evaporation that causes the decrease in the Tg of one of the vinyl ester phases, presumably the styrene-rich phase, was that the loss modulus shoulder remained apparent regardless of the styrene content. Moreover, styrene loss is facilitated prior to solidification of the resin, whereas in this case interaction of the polymer with oxygen, even during the post-cure phase, was enough to result in the appearance of a lower temperature Tg. It is noteworthy that the film which was cured under the influence of oxygen at both cure stages (AA, SC), featured two clear peaks in the loss modulus curve (see Fig. 7). The first peak was highly pronounced and broad, while the second peak, presumably indicative of the Tg of the vinyl ester phase remained at the same temperature level as the other film samples. This is expected since vinyl ester monomer conversion is completed before that of styrene [6], and the vinyl ester monomer is not a volatile component. It is therefore likely that styrene loss and oxygen inhibition acting in combination results in reduced copolymerisation between styrene and vinyl ester, and in turn phase deconvolution, reflected in the double loss modulus peaks.

Although research around oxygen inhibition of vinyl ester polymerisation remains limited, the following information was obtained by studying the literature. Oxygen has been associated with the formation of an inhibited layer on the surface of the free radically polymerised resins in contact with ambient air. The thickness of this layer has been found to be related to monomer composition and activating systems. Materials which possess lower viscosities have been found to have a greater thickness of non-polymerised resin, and lower exothermic heat releases during cure. This observation is in correlation with the DSC conversion results in Fig. 2 which showed that as vinyl ester thickness was reduced, the exothermic reaction peak of the cured material was increased. This inhibited layer has been reported to still possess the capacity of being polymerised further. This was in fact shown in the Tg (2) values presented in Table 2; when vinyl ester films were subjected to a second heating cycle, the Tg obtained was increased [27]. According to Nouranian et al. [25], the diffusion of oxygen into the free surface region of air-cured vinyl ester specimens can result in gradients in the inhibited layer, due to its lower cross-link density. As previously mentioned, such effects may be amplified when sample thickness is significantly reduced [25,26].

3.1.4. Fourier-transform infrared spectroscopy on DION 1260 vinyl ester

To obtain a more thorough understanding of the cure kinetics of vinyl ester as a function of scale FTIR investigations were carried out as a complement to thermal analysis results. Although a quantitative assessment of the degree of conversion was not possible for all specimens, qualitative indicators were sufficient to provide a clear picture regarding the evolution of cure as a function of scale. Figs. 9 and 10 present spectral comparisons between unreacted resin and cured film and bulk samples respectively.

Individual styrene and vinyl ester monomer conversions for the SM, SC, plate casting and the NN,PC, film are presented in Table 5. A quantitative conversion calculation could not be achieved for film and bulk specimens which were cured allowing air interaction during either part of the cure process. This was attributed to two primary reasons. Firstly, excess styrene evaporation confounded the calculation and resulted in inconsistencies. The reduction in the styrene content of the resin was identified by studying the C–H backbone of styrene at 695 cm^{-1}. It is clear that the decrease in styrene was least for the sealed mould plate (SM,SC Fig. 10) followed by the full N$_2$, 150 °C post-cured film (NN,PC in Fig. 9). On the other hand, styrene evaporation reached a maximum for the open mould plate (OM,SC Fig. 10) and the full air cured film (AA,SC in Fig. 9), where in both cases interaction with the
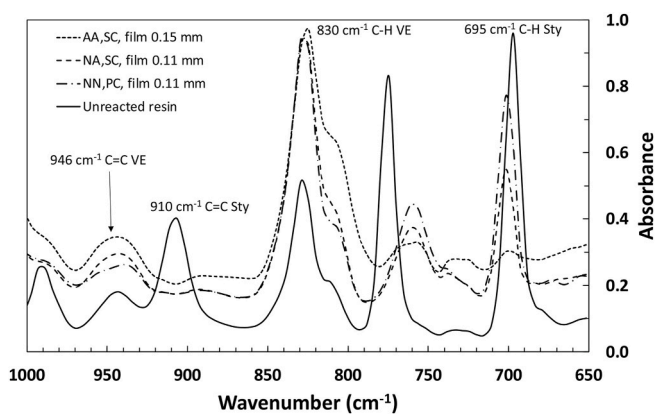
Fig. 9. FTIR spectra of unreacted DION 1260 and film specimens cured under different conditions.
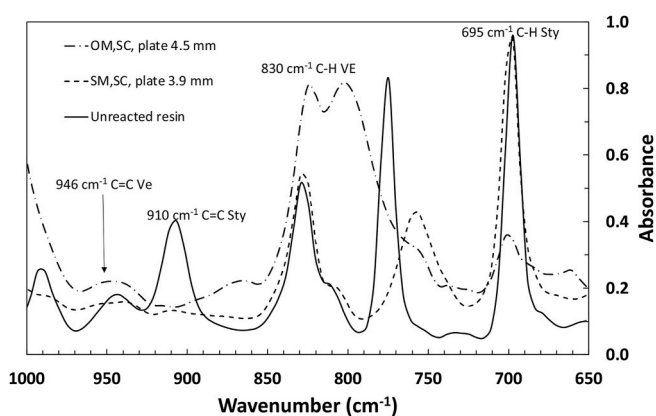
Fig. 10. FTIR spectra of unreacted DION 1260 and bulk specimens cured under different conditions.

Table 5
DION 1260 vinyl ester (VE) and styrene (St) monomer conversions obtained from FTIR.

DION 1260 Specimen	Thickness (mm)	VE Conversion (α_{VE})	St. Conversion (α_{St})
SM,SC, Plate	3.99	0.38	0.94
NN,PC, Film	0.11	0.17	0.91

ambient atmosphere was allowed in both phases of the cure. Significant styrene evaporation was also evident in the standard cure film specimen (NA,SC in Fig. 9), with the spectral area at 695 cm^{-1} being found between the specimens cured for both phases under an ambient and an inert N$_2$ environment. Thus, a pattern for increasing styrene retention in the polymer as interaction with oxygen was minimised is evident in these results. The depletion in the C=C of styrene at 910 cm^{-1}, indicative of styrene monomer reaction, increased as the cure became more rigorous. Notable depletion of this spectral band was featured with specimens in which the largest styrene evaporation occurred (OM,SC and AA,SC). Nonetheless, it should be taken into account that there was only a very small portion of styrene left to react and thus an overprediction of the cure degree of the specimen could be made. A similar observation was made by Scott et al. [28], who stated that at low styrene levels, the copolymerisation does not need to proceed very far before most of the styrene is consumed, and so high styrene conversions are observed.

The second reason why a quantitative analysis was not possible was that a different chemistry could be identified for the specimens affected

by the presence of oxygen when compared to specimens cured by minimising oxygen interaction during cure. More specifically, an unexpected increase in the C=C of vinyl ester at 946 cm^{-1} was of particular interest. In fact, instead of the spectral band being depleted with cure, the measured spectral area exhibited by oxidised specimens was higher than the spectral area of the unreacted resin. It is uncertain whether this increase also took place for the NN,PB, film, but it was less apparent. Generally, the effect was more discernible on film specimens, which have a higher surface-to-volume ratio. Similar results have been reported by Arrieta et al. [29], who showed an increase in the spectral area of C=C for vinyl ester films oxidised at different temperatures. Such a small shoulder was also present between 1730 cm^{-1} and 1775 cm^{-1} for specimens affected by oxidation. This shoulder is indicative of the build-up of carbonyl products and in particular the conversion of an ester into an anhydride [29]. The shoulder was found to be more significant for specimens cured under air for both phases of the cure, whereas it was least apparent for the bulk closed mould and the films with full cure under nitrogen.

A notable increase of the C–H backbone of vinyl ester at 830 cm^{-1} was also observed for all specimens except for the SM,SC plate sample. Thus, it should be noted that since the peak was used as internal reference for the conversion calculation of the vinyl ester monomer, it is likely that there was an under-prediction in the vinyl ester conversion of the NN,PC, film. The increase was largest for the bulk open mould specimen (OM,SC in Fig. 10) where the formation of two clear peaks was also observed. The reason for the latter, as well as the increase in the spectral area, was believed to be either interaction with oxygen or styrene evaporation. However, such an effect could not be identified in the literature. The increase at 830 cm^{-1} was found to start from the manufacturing stage but was exaggerated in the presence of oxygen during curing. On that basis, the following experiment was conducted; unreacted resin spectra were compared with spectra of unreacted resin which had been spread as a thin film and degassed for 10 min to resemble the procedure carried out in film manufacturing. A spectral comparison between unreacted and degassed resin is shown in Fig. 11. It can be seen that the increase in C=C took place upon the processing of the unreacted resin, while the C–H of styrene at 695 cm^{-1} remained the same (hence no significant styrene evaporation). Although it is still uncertain what can cause such a change in chemistry, the effect of oxygen is suggested, since it is the only variable parameter in the experiment, upon the spectral indication that the styrene content remained at a similar level after the degassing of the resin. It is likely that an oxygen-inhibited layer discussed in the previous section [24,25] started to develop when the resin was spread onto the substrate and subsequently degassed, as the surface-to-volume ratio of the resin layer increased. Further investigation of the interaction of oxygen with VE resin, before and during polymerisation, in combination with samples at different scales, could possibly yield more insight into this phenomenon.
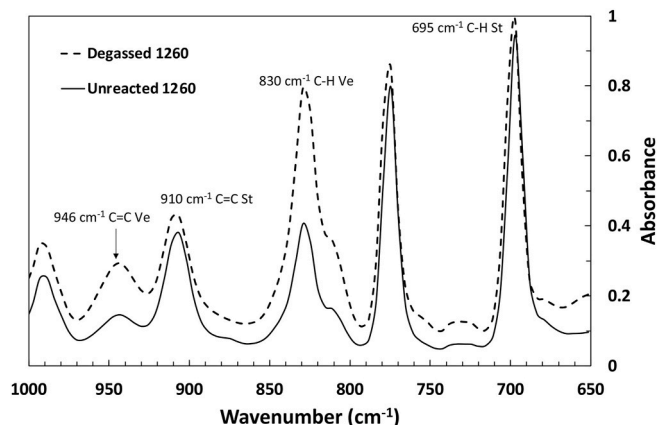
3.2. The chemistry and thermal properties of DION 1273

3.2.1. Thermal analysis – effect of scale and effect of oxygen on polymerisation

A more preliminary study was conducted for DION 1273 sufficient to allow a basic comparison with the standard DION 1260 polymer. DSC thermograms of cured DION 1273 as a function of specimen thickness are shown in Fig. 12. Tg values from both heating cycles are tabulated in Table 6. In a similar fashion to the DION 1260 polymer a significant Tg reduction was observed between the bulk scale sealed mould resin casting (SM,SC) and the standard cure films (NA,SC). However, despite a notable Tg difference between the microscale and macroscale, the two film specimens with different thicknesses exhibited a single transition Tg of 68 °C similar to that of DION 1260 in the thickness range 0.1 < t < 0.2 mm (see Table 2).

Fig. 13 presents DMA results for various thick and thin DION 1273 polymer samples. These results enable a comparison of the thermal behaviour between thin film and bulk plate specimens, as well as the effect of the cure environment on Tg between films of a similar thickness. The compiled results for Tg determined by the various DMA methods is shown in Table 7. Although a clear difference in Tg values for the different scale samples is evident in these values it is likely a major contribution to this difference comes from the use of different strains and test methods (film tension vs 3-point bending) in the DMA study.
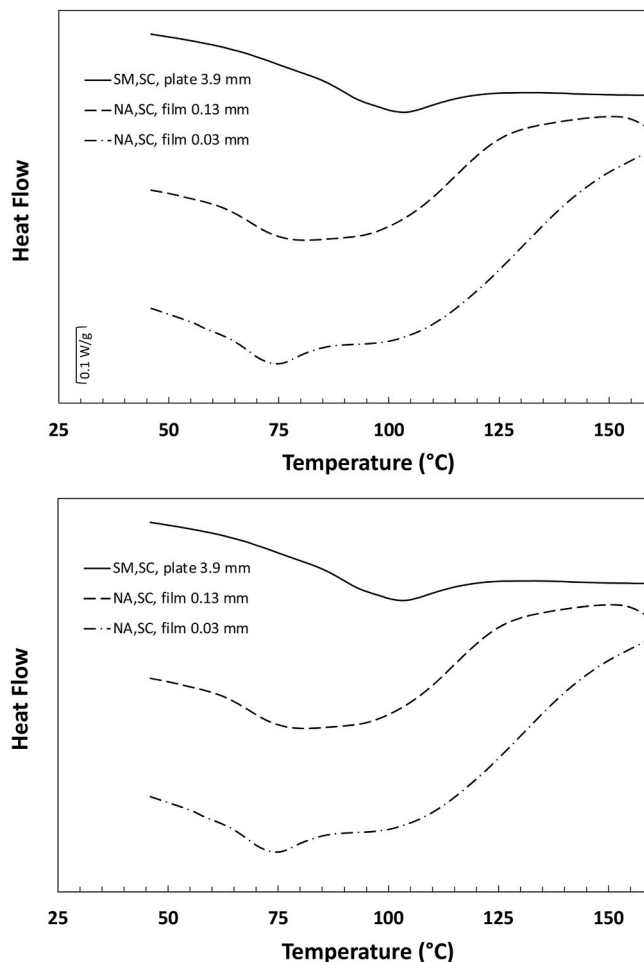

Fig. 12. DSC 1st heating thermograms of standard cured DION 1273 polymer as a function of sample thickness. Curves are offset and therefore Y axis values are arbitrary.

Fig. 11. FTIR spectra of unreacted vs degassed DION 1260 resin.

Table 6
Tg values obtained by DSC for DION 1273 samples.

Specimen	Tg (1) (°C)	Tg (2) (°C)
SM,SC, plate t = 3.9 mm	90	96
NA,SC, film t = 0.13 mm	68	94
NA,SC, film t = 0.03 mm	68	92
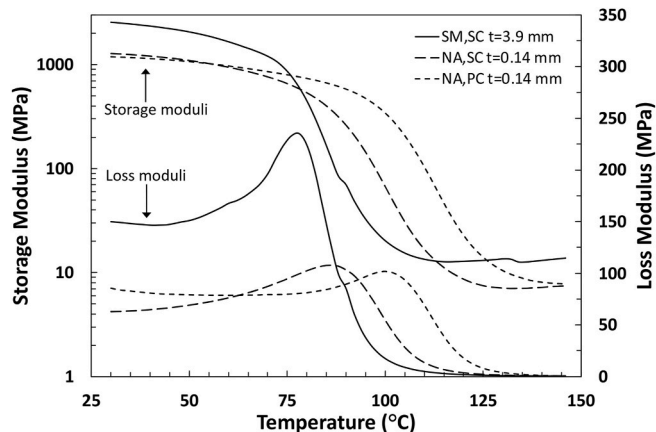
Fig. 13. DMA results for DION 1273 polymer samples.

Table 7
Tg values obtained by DMA for a DION 1273 polymer samples.

Specimen	Storage Modulus Onset (°C))	Loss Modulus Peak (°C)	Tan δ Peak (°C)
SM,SC, plate t = 3.9 mm	75.0	77.5	92.0
NA,SC, film t = 0.14 mm	87.0	85.8	105.0
NA,PC, film t = 0.14 mm	98.0	99.2	114.5

The DMA Tg of a 0.14 mm thick DION 1273 film of 87 °C was notably lower than the high-temperature Tg obtained for DION 1260 of a similar thickness (107 °C) but similar to the low-temperature Tg of the DION 1260 loss modulus shoulder at 88 °C (see Fig. 6). It should be noted that this result was obtained using DION 1260 and DION 1273 films of a similar thickness as well as the same DMA input parameters, thus a direct comparison is acceptable. Post-curing DION 1273 under N₂ and a higher temperature resulted in significantly higher Tg of 98 °C. This was nonetheless notably lower than the Tg of 124 °C obtained by DMA for its DION 1260 counterpart. It can be deduced that DION 1273 possesses a lower Tg than DION 1260 on the microscale, but such a statement is not definitive given the presence of the low-temperature transition for DION 1260.

In Fig. 13 it can also be seen that the loss modulus peak in the transition region of the standard cure film (NA,SC) is broader than that of the full N₂ and post-cured film (NN,PC) and that of the bulk sealed mould sample (SM,SC). This broadening of the loss modulus curve of the NA,SC film sample may be a hint of a secondary (low temperature) transition starting to appear. Overall, DION 1273 showed a lower Tg than DION 1260 on the macroscale. This is probably also the case on the microscale if one compares the Tg of DION 1273 to the high-temperature Tg of DION 1260. Nonetheless, DION 1273 exhibited a more stable thermal behaviour on the microscale than DION 1260 since the 0.13 mm thick film and the 0.03 mm thick film exhibiting a similar Tg. This was not the case in DION 1260 (see Table 4). Moreover, although there was broadening of the loss modulus curve of standard cure films, a pronounced shoulder was not apparent, as was the case in DION 1260.

Oxygen inhibition during DION 1273 polymerisation was considered when the surface-to-volume ratio of the material was increased, and despite the employment of an initial N₂ cure step. Although probable oxygen inhibition did not result in a profound Tg deconvolution between the styrene and the vinyl ester phases of the polymer, as in DION 1260, based on DSC results they led to Tg depression.

3.2.2. Fourier-transform infrared spectroscopy on DION 1273

Due to the higher complexity and the confidentiality of the DION 1273 formulation only a preliminary ATR-FTIR study was conducted as a complement to the thermal analysis investigation. A spectral comparison between unreacted matrix and polymers cured under different conditions is presented in Fig. 14. Despite the complexity of the DION 1273 formulation, some general conclusions can be drawn. The spectra confirm the variation in the degree of cure between standard cure bulk and thin film specimens. Substantial styrene evaporation was confirmed from the standard cure film by monitoring the C–H of styrene at 695 cm⁻¹. The use of N₂ atmosphere reduced styrene evaporation and enhanced the overall degree of cure. This was confirmed by monitoring the C=C of styrene and vinyl ester at 910 cm⁻¹ and 940 cm⁻¹, respectively. In a similar fashion to FTIR results on DION 1260, a shoulder appeared around 1730 cm⁻¹ and 1775 cm⁻¹ for thin film specimens, as shown in Fig. 15. The appearance of this shoulder has previously been associated with the formation of carbonyl products and in particular the conversion of an ester into an anhydride in vinyl esters [29]. Furthermore, an increase in several band intensities was observed for both NA, SC and NN,PC film specimens, which was believed to be due to oxidation effects. In particular, a notable increase in the C–O stretch of ester groups between 1040 cm⁻¹ and 1115 cm⁻¹ was observed. Similar results have been reported by Namouchi et al. [30] for oxidised polymethyl methacrylate (PMMA) specimens. The intensity increase was observed to be greater for the standard cure film, which was post-cured in air. There is also clear variation in the shape of the peaks for the standard cure film, but the reason for this change remains unknown. Other significant band intensities between bulk and the film specimens were seen at the spectral regions between 1184 cm⁻¹ and 1220 cm⁻¹, and 1465 cm⁻¹ and 1565 cm⁻¹. Even though a band assignment for these was challenging due to the confidential polymer network of DION 1273, oxygen inhibition was considered, as per the observations of Namouchi et al. for an intensity increase in all IR bands for oxidised PMMA [30]. On a qualitative basis such pronounced changes between film specimens and the bulk sealed mould sample confirm variation in the chemistry between microscopic and macroscale specimens.

A conversion calculation was conducted for the styrene and vinyl ester monomers for all specimens and the results are shown in Table 8. As opposed to the DION 1260 polymer, the calculation could be
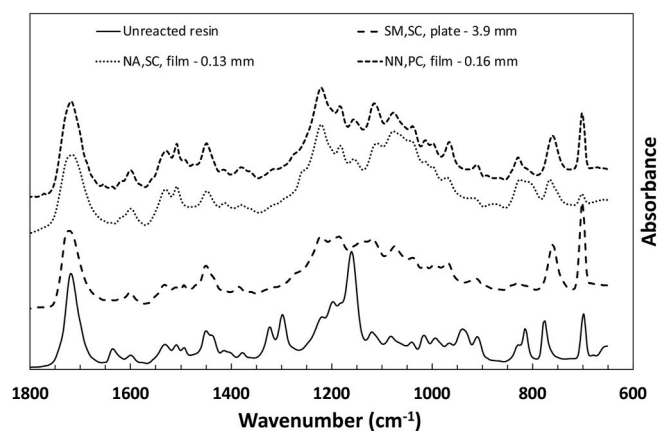
Fig. 14. FTIR spectra of unreacted DION 1273, bulk and film polymer specimens cured under different conditions.
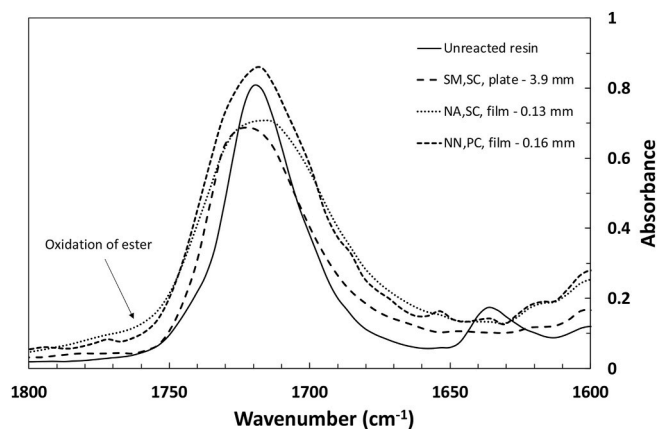
Fig. 15. FTIR spectra of unreacted DION 1273 film specimens cured under different conditions revealing oxidation of ester group.

Table 8
DION 1273 vinyl ester (VE) and styrene (St) monomer conversions obtained through FTIR.

DION 1273 Specimen	Thickness (mm)	VE Conversion (αVE)	St Conversion (αSt)
NA,SC, film	0.13	0.8	0.03
NN,PC, film	0.16	1	0.57
SM,SC, plate	3.9	1	0.64

achieved even for the standard cure film, which underwent styrene evaporation. It should be noted that the DION 1273 formulation already contained an appreciably lower styrene content than the DION 1260 and so potential styrene loss may have a smaller impact on the cross-linking of the final polymer. The conversion calculation showed a rather low styrene conversion for the standard cure film, which nonetheless reached a level close to the bulk polymer when N_2 atmosphere cure was employed. The vinyl ester monomer conversion remained at a relatively high level for the latter specimen and was fully reacted when an N_2 environment was used in the post-cure phase. Hence, FTIR analysis was useful in confirming variations in chemistry between a fully cured bulk specimen, a standard cure film and a post-cured in N_2 at a higher temperature. Effects of oxygen inhibition of the curing polymer and excess styrene evaporation were detected in DION 1273 films by FTIR. In a similar fashion to DION 1260, such effects were promoted by the particularly high surface-to-volume ratio of the films. A conversion calculation was achieved for DION 1273, showing rather poor curing for "standard" cure films and improved curing when matrix films were post-cured in N_2 at a higher temperature.

4. Concluding remarks

This study aimed to provide a better understanding of the cure kinetics and thermal behaviour of vinyl ester as a function of scale. DSC and DMA investigations showed clear evidence of a multiphase polymer morphology in sub-millimetre thin film specimens of a polymerised commercial bisphenol-epoxy vinyl ester with a 50 % styrene content. Whereas bulk polymerised specimens exhibited only a single glass transition, indicative of a more homogeneous microstructure. The nature of the heterogenous microstructure on thin film VE polymers was found to be sensitive to the resin styrene content and the presence, or absence, of oxygen in the polymerisation environment. The presented data clearly suggest that styrene loss from high surface-to-volume ratio specimens and exposure to atmospheric conditions, even during a post-cure phase, reduced copolymerisation of styrene and vinyl ester monomers, and resulted in lower polymer glass transition temperatures. Regarding the deconvolution of the diphasic network in vinyl ester thin

films, the lower temperature Tg was attributed to the styrene-rich phase of the matrix, given the excess monomer evaporation and knowing that the cross-link density of the styrene-rich phase is lower than that of the vinyl ester phase.

Regarding the chemical nature of VE resin a MMA based VE resin with a significantly lower styrene content showed a lower Tg on both the macroscale and microscale. Nevertheless, MMA based resin exhibited a more homogeneous morphology on the microscale with only a single glass transition detected regardless of film thickness. FTIR results confirmed excess styrene loss from VE films during polymerisation and suggested that oxygen inhibition effects can already start to take place at the resin mixing and handling stage prior to polymerisation. Nevertheless, the use of a nitrogen environment throughout the full cure of VE films results in a higher degree of conversion, closer to that of the bulk specimens.

Overall, these results confirm that one must be very wary when making the extrapolation from a macroscale to a microscale regarding vinyl ester curing and material property transferability. However, despite the complicated change in the vinyl ester network between the two scales, an encouraging indication was shown regarding the design of a cure environment, which will prevent degradation effects during curing of specimens with a high surface-to-volume ratio. In particular, oxidation and styrene loss effects may be significantly reduced by the use of more rigorous cure conditions.

CRediT authorship contribution statement

James Thomason: Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Georgios Xypolias:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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