

High-pressure autoclave curing for a thermoset composite: effect on the glass transition temperature

F. Y. C. BOEY, T. H. LEE, P. L. SULLIVAN

Nanyang Technological University, School of Mechanical and Production Engineering, Singapore 2263

The effect of high-pressure curing within an autoclave on the cured glass transition temperature (T_g) of a thermoset fibre-reinforced composite has been studied. The results indicate that an increase in the T_g value was obtained by a higher curing pressure as well as a lower moisture content. Both results have been related to the reduction in the microscopic free volume and the macroscopic void content of the matrix resin. Using the results obtained, the T_g increase was related to the applied autoclave pressure through equations based on both free-volume and thermodynamic concepts, with the results indicating a significantly higher effect than for homogeneous polymers. This has been attributed to a moisture-dominant diffusion process which has been used to explain the growth and reduction of voids.

1. Introduction

Manufacturing processes for engineering components made from thermoset composites usually involve process parameters which determine two main physical properties, the void percentage and the glass transition temperature T_g . Earlier reports [1–3] have shown that to obtain consistent and maximum strengths, the void content should at least be less than 5%. This is conventionally achieved by using vacuum bagging to obtain vacuum evacuation, and an applied autoclave pressure. More recently, a high-pressure process has been shown to be effective in void reduction [3], which avoids the need for vacuum reduction during the actual curing process. This therefore avoids the requirement for a specific viscosity range within which vacuum evacuation would be effective, and the possible scrap waste due to vacuum bagging leakages.

1.1. Glass transition temperature

The glass transition temperature T_g is the parameter which concerns this paper. T_g is an important physical parameter for polymeric composite materials for various reasons, the most important being that it becomes an upper-bound limit for the service temperature of the material. This is simply because of the considerable drop in the bulk resin modulus, once the material transforms from a glassy to a rubbery phase when it reaches T_g . Whilst the severe reduction in the matrix moduli would not significantly affect a composite with uniaxial continuous fibres aligned in a tensile loading direction, it would have significant detrimental effects on any compressive loads whatever the alignment, since compression failure is known to be matrix-dominant. The significant effect on the compressive load is due to macro- or micro-buckling

failure mechanisms, both of which are dominantly dependent on the matrix shear modulus [4].

The glass transition phenomenon has variously been described in terms of non-equilibrium molecular structural relaxation, or as the beta or second-order transition of the material. Analytically, a thermodynamically related approach and a more qualitative free volume concept have also been commonly used to develop models to relate T_g to other parameters, including the applied pressure [5–12]. An indirect relationship between T_g and the resin or matrix pressure has also been studied using a pressure–volume–temperature (P–V–T) diagram approach [13]. The ability to relate T_g to pressure has a practical and important implication during the processing of thermoset composites. Typically, external pressure by means of an autoclave process is normally applied to the curing composite, which then translates into hydrostatic pressure within the curing matrix resin. Variation of the applied pressure can therefore affect the eventual T_g value achieved.

In the case of the free volume concept, the free volume of the material is defined as the proportional volume not occupied by the polymer substance [8]. This free volume, which is typically a microscopic phenomenon, should be differentiated from the common “void content” or “void percentage” terms used in composite processing. The latter essentially appear as macroscopic gaseous bubbles trapped within the lay-up, and for clarity would be termed the “macroscopic void content”. The free volume within polymers may be considered to be caused by the inefficient and disorderly packing of the long polymer molecules.

Various authors have reported on the correlation of a higher T_g with a reduction of molecular chain-end concentration and the formation of effective crosslinks

[14–16]. Both effects reduce the free volume resulting from disorderly molecular packing, and thus increase the T_g . Whilst these gaps are small relative to the polymer molecules, they can be big enough to be occupied by gaseous molecules such as water or air. In that respect, they do not therefore exist *in vacuo* but are occupied by gases. When the bulk polymer is heated or cooled, the presence of the free volume causes a significantly larger change in its volume than that of the volume occupied by the polymer substance, due to its gaseous nature as compared to the solid nature of the polymer substance. Such a change in volume has been shown to be time-dependent, with the time taken to reach equilibrium controlled by the relaxation time t_r . Several kinetic approaches have been proposed [9, 10], with the rate of volumetric change dependent mostly on the relationship

$$\frac{dV}{dt} = -\frac{V_t - V_e}{b + at_r} \quad (1)$$

where V_t and V_e are the free volume at time t and at equilibrium, respectively, and t_r the relaxation time. a and b are the proportional constants. Equation 1 predicts that should the relaxation time be very small, the rate of volumetric change would be very fast, and equilibrium could be quickly achieved. However, if the relaxation time became significantly long, the rate of volumetric change according to the above equation would become very small and equilibrium could not then be meaningfully achieved.

Kinetically, one would expect the relaxation time to be dependent dominantly on the temperature, and this has been shown to be experimentally so [10]. If a polymer was cooled from its melt state at a given cooling rate, because of the continuous reduction in temperature the relaxation time for shrinkage of the free volume would become larger and larger. As long as the relaxation time was small relative to the cooling rate, equilibrium of the volume shrinkage would be achieved very quickly; but once the relaxation time became very large compared to the cooling rate, the equilibrium would need some time to achieve. The glass transition temperature can therefore be defined as the temperature range below which the volume shrinkage relaxation time becomes significantly larger than the rate of cooling, so that the total shrinkage could never be achieved. As a result, the cooled material would retain a volume fraction which for kinetic reasons could not be reduced.

1.2. Effect of pressure

The above explanation is important to polymer composite processing, primarily because of the application of autoclave vacuum and pressure during curing, for the purpose of reducing macroscopic voids within the pre-cured resin–fibre network [1–3]. Consider what happens to the above argument if the resin was to be cooled in a vacuum under applied pressure. Application of a vacuum, usually in the order of 0.1–0.3 bar, would physically transport macroscopic voids out of the resin. However, it would be limited by the driving force, which could achieve at most about 0.9 bar, since

it would be impossible to reduce the vacuum any lower due to the presence of volatiles within the resin. Thus the vacuum would not have much effect on the free volume of the resin. This, however, would not be the case for the applied pressure.

In the case of epoxy resins, curing of the resin will begin when it is in its liquid form, and the applied autoclave pressure could transmit at least a significant fraction to the resin in the form of hydrostatic pressure. For the case of liquid resin which eventually crosslinks to a glassy solid, the void growth or reduction has been shown to be dominantly diffusion-driven [3, 17]. It has also been shown that correspondingly, an applied high pressure during curing of thermoset resins would actually provide a negative driving force for void reduction by dissolution of the moisture back into the matrix resin.

2. Experimental procedure

The matrix resin material used was the diglycidal ether of bisphenol A, with 50 plies of 0/90 continuous cross-woven fibre E-glass. The averaged cured fibre volume fraction for the unpressurized specimen was about 55%, whereas the range was between 63 and 67% for the other pressurized specimens, with the higher volume fraction achieved at higher pressures. Matrix resin starvation due to the high applied pressure was avoided by using a silicone ribbing along with tacky tape to act as a dam against excessive resin outflow.

Measurement of the void percentage was done by using the specifications set out in ASTM D2734. The fibres were laid up on a stainless steel caul-plate measuring 120 mm by 60 mm using rollers, placed in a nylon vacuum bagging and evacuated to 0.2 bar for about 20 min before being placed in an autoclave vessel capable of pressurization up to 20 bar. Curing was then done at 120 °C for 12 h during which the pressure was maintained at the prescribed value, followed by 4 h of post-curing at atmospheric pressure.

The moisture content of the matrix resin was measured using a Perkin Elmer thermogravimetric analyser, by heating at 105 °C. The heating was at a rate which could differentiate between the evaporation of volatiles below 90 °C and that of the water vapour beyond 100 °C.

The T_g values were determined with a Perkin Elmer DMA7 dynamic mechanical analyser (DMA) with a three-point bending load on the cured sample. The heating rate during the DMA test was such that the total time taken to achieve the transition from the glassy phase to the rubbery phase was kept to a minimum, since it was possible that prolonged heating in the DMA itself might help increase the T_g further. Determination of T_g was by plotting the tangent loss value against the scanning temperature, and determining the temperature at which the maximum loss value occurred as the T_g value. It has been shown [18] that this technique gave a more precise and consistent measurement of the glass transition temperature value, in comparison with using the differential scanning calorimeter technique.

3. Results and discussion

Fig. 1 shows the plot of the apparent composite density and the corresponding fibre volume fraction against the applied autoclave pressure. It can be seen that the rate of density increase was high up to about 10 bar, after which the density approached a limiting maximum value. Fig. 2 plots the void content of a fully cured specimen against the applied autoclave pressure. The results for the measured macroscopic void content indicate a parallel trend, since it was only the void reduction within the resin that caused the increase in density, and the fibre remains unchanged geometrically. The results indicate that for this lay-up, pressures in excess of 5 bar have significantly brought the void content down.

Fig. 3 plots the effect of the resin moisture content on the void content at 5 bar, indicating the significant influence of the moisture content on the void content. A significant drop in the void content was obtained at very low moisture content, indicating that the very low moisture content itself helped to reduce the volume of voids existing within the matrix. This is consistent with existing moisture-dominant diffusion models [3, 14], which predict such a behaviour for macroscopic voids resulting mainly from moisture diffusion during the heated curing process.

Fig. 4 shows the results for the T_g values obtained through the dynamic mechanical analyser, plotted against the applied autoclave pressure. The T_g value showed a small but significant increase in its value as

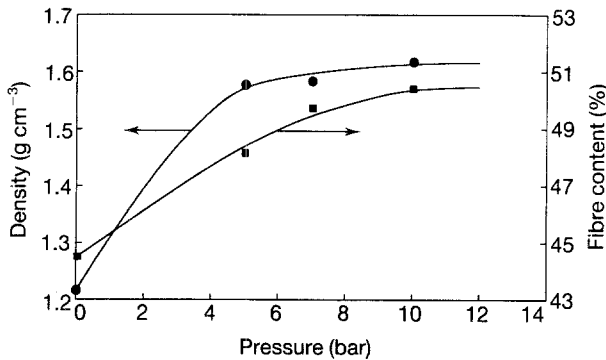


Figure 1 Plots of (●) composite density and (■) fibre content against applied pressure.

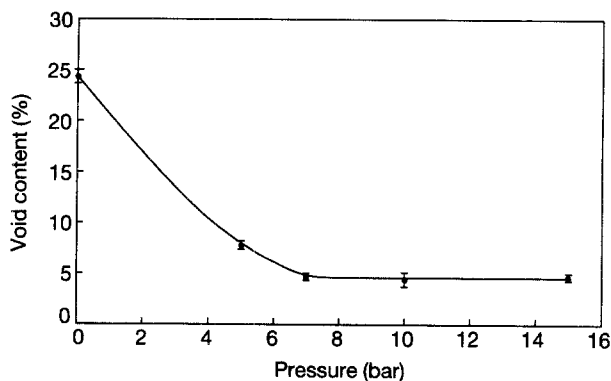


Figure 2 Plot of the void content of a fully cured specimen against applied autoclave pressure.

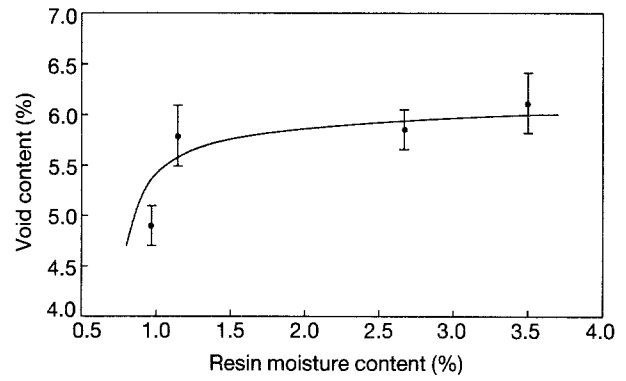


Figure 3 Plot of the effect of resin moisture content on the void content at 5 bar pressure.

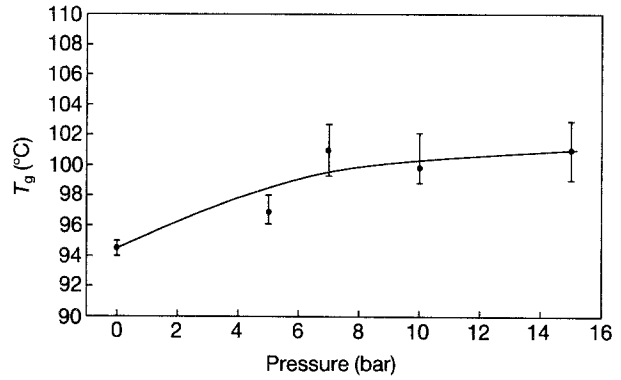


Figure 4 Plot of the measured T_g value against the resin moisture content at 5 bar autoclave pressure.

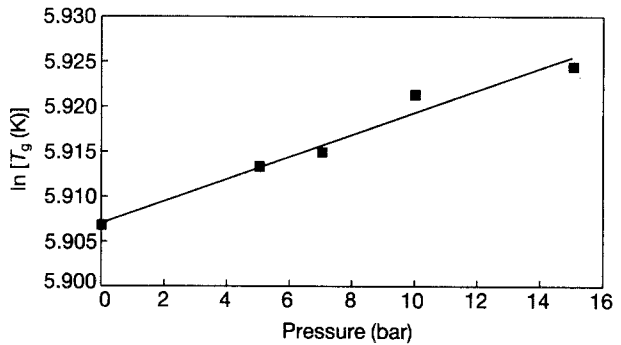


Figure 5 (■) Logarithmic plot of experimental data from Fig. 4 and (—) the corresponding straight line for Equation 5.

the applied pressure increased. The possibility exists that the increase in the T_g value was due to the existing macroscopic void content during cure, particularly when Fig. 2 is compared with Fig. 4. However, no physical mechanism or model has so far been suggested to relate both parameters.

Fig. 5 plots the measured T_g value against the resin moisture content, when cured at an applied autoclave pressure of 5 bar. The increase obtained in the T_g value by reducing the moisture content from 3.5% down to 1% was about the same amount as that achieved by increasing the pressure in Fig. 4. The increase obtained in the T_g value in Fig. 5 could again be explained by the earlier mentioned moisture-dominant diffusion mechanism. A higher moisture content in the resin accelerates void growth and possibly

increases the free volume of the resin before and during full curing, thereby decreasing the T_g value.

Aside from reducing the macroscopic voids within the composite network, the pressure also reduced the effective microscopic free volume within the resin material. Curing at a higher pressure results in a higher T_g , since the additional pressure in effect helped to reduce the volume shrinkage relaxation time.

Thermodynamically, for irreversible processes such as a curing thermoset system, the relationship between the pressure and T_g can be given as [5]

$$\frac{dp_g}{dT_g} = \frac{Q}{T_g V} \quad (2)$$

where Q and V are respectively the enthalpy of the process and the accompanying volumetric change during the transition. It has been shown [19] also that based on a free-volume approach, the same differential quotient is given as

$$\frac{dp_g}{dT_g} = \frac{e_v}{T_g V_v} \quad (3)$$

where e_v and V_v are the energy required for the formation of a fluctuating void of minimum size of volume V_v . The values for Q , V , e_v and V_v pertain to the properties of the liquid phase during the vitrification process. Both approaches yield the differential equation in the form

$$\frac{dp_g}{dT_g} = \frac{k}{T_g} \quad (4)$$

which, on solving for T_g as a function of p , gives the equation

$$T_g = \exp\left(\frac{p - p_0}{k}\right) \quad (5)$$

where p_0 is a correlating pressure constant and $k = Q/V = e_v/V_v$. The logarithmic plot of Equation 5 therefore should yield the value of k as the slope. This is done in Fig. 5, which yields the value of $k = 814$ bar. Comparison with the data collected by Gibbs *et al.* [5] for various polymers indicates that the value obtained was significantly lower by at least a factor of five, although those data were for significantly higher pressures. A lower value for k indicates a greater effect of pressure on the value of T_g . This is indicated in Fig. 6, which plots the logarithmic value of T_g against the pressure for various k values, at a given p_0 value of 4800 bar (estimated from Fig. 5).

Two possibilities exist which may account for the variation, both of which assume that microscopic free volume within a polymer acted physically as a microscopic void, occupied by volatiles such as moisture, similar to the macroscopic voids. The first possibility is thus the effect of a higher moisture content. At a given pressure, the value of T_g is increased when the moisture content is decreased. Correspondingly, assuming that the effect of pressure was to have reduced the macroscopic and free volume of the curing matrix resin, since a lower moisture content would lead to a lower void content and free volume, it also results in a lesser effect of the pressure on the T_g value. The other

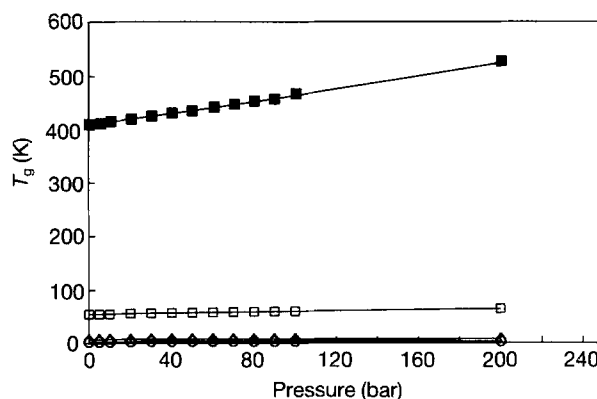


Figure 6 Plots of Equation 5 with $p_0 = 4800$; $k =$ (■) 800, (□) 1200, (△) 2400, (○) 4000.

possibility is that the presence of fibres during cure, which was the case for this work, significantly increased the effect of pressurization on the change in T_g . The availability of a large number of heterogeneous nucleation sites for both the microscopic free volume and the macroscopic voids in the matrix-fibre interface regions would have resulted in a greater effect of an increased moisture content. The high pressure thus actually helps to reduce this adverse effect.

4. Conclusion

Using a high autoclave pressure curing process, the T_g value obtained in a thermoset fibre-reinforced composite was shown to increase with the curing pressure, and decrease for a lower moisture content within the pre-cured matrix resin; both results have been related to reductions in both the free volume and the macroscopic void content of the matrix resin. Using the results obtained, the T_g value was related to the applied pressure through an existing differential equation based on both free-volume and thermodynamic concepts. A moisture-dominant diffusion process which has been earlier used to explain the growth and reduction of voids was used to explain the phenomenon.

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