Glass Fibre Reinforced Polymers (GFRPs) have become increasingly popular materials for use in civil, automotive, marine, sporting and other industries owing to their light weight, high specific stiffness/strength and lower thermal expansion properties [1].

Polymer resins are well known to exhibit thermo-viscoelastic behaviour, meaning that their mechanical behaviour can be time- and temperature-dependent, both above and below the glass transition temperature ($T_g$). In addition, the material properties of polymer resins are cure dependent [2] and have a major impact on the effective mechanical behaviour of final fibre-reinforced polymer (FRP) composite parts [3], given that the resin matrix has the primary structural function of providing bulk stiffness to the composite. Therefore, with respect to design and analysis of structures made of FRP materials, the time/temperature/cure dependent behaviour is an important consideration. This dependence is significantly affected by various conditions (e.g.; environmental condition, processing time and temperature, etc.) [4].

For a viscoelastic material, a relatively slow, progressive deformation under constant load can occur, which is conventionally referred to as creep. As a result, the creep strain is inherently time dependent [5] and can be a source of irreversible dimensional change during manufacturing, as will be shown in more detail later on in the current case study. A schematic representation of the creep and recovery (upon removal of the load) for a typical viscoelastic material is shown in Fig.1.

Processing of thermosetting resins (e.g. epoxy, unsaturated polyester, polyurethane, phenolic, etc.) includes chemical reactions of cure, which involves a network formation through cross-linking of monomers [6, 7]. Such reactions are most often thermally activated and temperature dependent [8].

Curing a polymer resin begins with an increase in its viscosity, followed by gelation, which is the emergent formation of a cross-linked network, and continues to a more developed network [6]. As cure progresses, so do changes in the matrix material properties; e.g., stiffness and the glass transition temperature ($T_g$) [9]. Through the curing process at a given operating temperature, the $T_g$ of the resin increases from the $T_g$ of the unreacted mixture ($T_{g0}$) to that of the final cured resin state ($T_{g∞}$) [4]. Based on the processing temperature, however, the resin matrix may be fully or partially cured after a given processing time. The latter has the potential to introduce permanent deformation in the part after de-moulding, mainly due to the continued mobility of the uncured polymer chains under loads and gradual hardening. This, in turn, can result in dimensional changes in the part after de-moulding and cause a major challenge in subsequent manufacturing stages (e.g., assembly). Creep has been considered to control the dimensional change of the composite parts (e.g., after de-moulding), particularly when they are under stress (e.g., self-weight, or due to the loads applied during assembly, etc) over a period of time [10].

In this study, the effect of degree of cure on the magnitude of creep strain due to storage/operation after de-moulding from a wet lay-up process for a GFRP composite is investigated. Additionally, it is addressed how the creep as well as the associated permanent deformation in its recovery stage can be prevented or controlled by the extent of cure via the temperature during and after the moulding stage. The work is based on an actual case study in the recreational boat industry, yet with a widespread application through other industries where manufacturers may find some parts deform during transport, storage or post-moulding.
operations. The test material, which was scaled from a bulk laminate and characterized via creep and cure experiments, is a thermoset composite composed of unsaturated polyester resin reinforced by three layers of fibreglass mat. The laminate was manufactured in an open moulding process under atmospheric conditions. Practical aspects of the characterization results are given particular attention.

2 Description of the Case Study

Boats made from GFRP composites frequently contain large quantities of random mat or chopped fibre materials and are manufactured in two specific parts (deck and hull), using a separate mould for each part. Each mould is pre-coated with a gelcoat (usually polyester or vinylester resin with filler materials and colour additives) and the rest of the deck/hull components are made by either spray-up or wet lay-up. Each process involves the application of fibreglass (either mat or chopped) and polyester resin, allowing the part to cure before removing from the mould. Due to the high cost of moulds, manufacturers often use one mould per boat design; therefore, profit is maximized by minimizing the hold time of the part in the mould. After de-moulding, each part is normally left to rest on a storage rack/station before the boat is assembled and transferred. In each of these post-moulding stages, the part may experience a load over a period of time (e.g., due to self-weight/sagging, or external loads) and start deforming undesirably. Consequently, it is hypothesized that creep is a non-negligible contributing factor to the process-induced deformation [11] of the GFRP parts, and as a result of that the hull and deck parts may not hold to the pre-specified geometric tolerances to fit together during assembly. Essentially, the creep deformation would occur due to the softening of the material (increase of creep compliance), in conjunction with the load magnitude, degree of cure, and the operating (manufacturing floor) temperature.

From a practical viewpoint, undesired dimensional changes in parts after de-moulding can potentially lead the manufacturer to manage the fit-up process with shimming or part displacements. Next to extra time and cost, this process can induce residual stresses that could lead to cracks, e.g., in the gelcoat of the GFRP parts, which in turn would need to be fixed before the boat is sold, or can make the final product structurally weaker than the original design.

3 Experimental

The creep-recovery behaviour of the boat parts was characterized as a function of the percent cure during moulding, manufacturing floor temperature (mimicking winter versus summer conditions), and a constant applied force after de-moulding.

Fig. 1 Schematic illustration of creep and recovery for a typical viscoelastic material (at a given temperature) [4].

3.1 Sample Preparation

A 300mm × 900mm plate sample was prepared by wet lay-up onto a flat mould. The plate laminate consisted of three fibreglass mat layers and unsaturated polyester resin (Aropol®, Ashland chemicals) initiated with 1.75% Luperox DDM-9 initiator for a total thickness of approximately 2mm. The laminate was left to cure past the gelation point enough to de-mould and then quickly transferred to a freezer to preserve minimal cure. This master plate was then used in subsequent steps of experimentation to cut smaller samples.

3.2 Fibre Fraction Determination

60mm × 60mm specimens of the above master plate were cut and fully cured in a conventional oven (the material was held at 75°C for 90min). Each cured specimen was then weighed immediately and transferred to a muffle furnace for a burn-off test where all the resin material was driven off at high temperature (550°C, 20 min). The remaining fibres were re-weighed, and subsequently the fibre weight fraction of the composite laminate was calculated [12].
3.3 Partial Curing

15mm × 60mm specimens were cut from the master plate using a table saw. Six batches of nine small specimens were then placed into an environmental chamber at different pre-defined temperatures (10, 20, 30, and 40°C) for a set time (180 minutes). A cure plateau was reached by the end of this long heating cycle; therefore, each batch was at a different nominal percent of cure. It has been proven that under an isothermal curing condition, beyond the gelation point, diffusion effects can hinder the resin from further cure reaction and hence the degree of cure reaches a plateau after a certain time at that given temperature [13]. Each batch was then moved back to the freezer to preserve its particular final (plateau) degree of cure.

3.4 Creep Strain Determination using Dynamic Mechanical Analysis

Two specimens from each specific conversion batch were tested using a three-point bending clamp of a Dynamic Mechanical Analyzer (DMA-Q800, TA Instruments) (Fig. ). One temperature condition imitated the summer ambient temperature on the manufacturing floor (30°C) and the second temperature condition imitated the winter condition (10°C) in BC, Canada. Three repeats per temperature (i.e., from each batch) were performed. The DMA was used to monitor the creep rate of each test sample while a constant stress is applied, following ASTM D2990. A corresponding relaxation period of 30 minutes was applied after the loading in order to properly capture the creep behaviour of the material. After this period, the load was removed and the recovery behavior of the samples was monitored. The magnitude of applied force (1.2 N) was chosen based on self-weight and second moments of area scaled from an industrial part to induce the maximum normal stress equivalent to that in the actual manufacturing after de-moulding.

3.5 Degree of Cure Determination

Two specimens from each batch described above were analyzed using Differential Scanning Calorimetry/DSC (STA 449 F3 Jupiter®, Netzsch) to determine its (partial) degree of cure (also called ‘conversion’). This is done by comparing the residual heat of reaction evolved from the sample ($\Delta H_{\text{residual}}$) to the total heat of reaction of completely uncured raw resin ($\Delta H_{\text{Total}}$) using the following equation [14]:

$$\text{Degree of Cure} = 1 - \frac{\Delta H_{\text{residual}}}{\Delta H_{\text{Total}}}$$

4 Results and Discussion

4.1 Fibre Weight Fraction Determination

From the resin burn-off experiment explained in Section 3.2, the fibre content of the fabricated composite laminate was calculated to be 48 ± 0.35 wt%.

4.2 Dynamic Mechanical Analysis-Creep Tests

The creep representative curves of the composite laminates are shown in Fig. 3, depicting the change in displacement over time under the specified operating temperature and loading conditions. Results in Fig. 3-a confirmed that creep for the given material is temperature-dependent and for the same manufactured/moulded part (cured at 30°C), there is an increase in the creep displacement at the higher temperature; e.g., when the post-moulding operation/in-service loading is applied in summer. This is because of a temperature increase during the storage period after de-moulding, which can lead to a greater degree of mobility of the polymer chains by means of a higher kinetic energy. Also, owing to the greater influence of the viscous component of partially cured resin, the material becomes softer and flows more readily at higher temperatures.

On the other hand, at a given operating temperature, the creep-induced displacement magnitude after de-moulding is seen to considerably decrease by increasing the curing temperature of the resin during the moulding process (Fig. 3-b).
To understand the latter observation, let us recall that material properties of polymer resins change with the degree of cure. As cure progresses, the modulus increases, the material hardens, $T_g$ is increased and cross-linked polymer chains have reduced mobility. Therefore, smaller displacements have occurred under the same applied load for the more cured samples. This can also be realized by the lower rate of creep deflection in Figure 3-c, for higher cure temperatures, indicating an increase in the viscous portion of material behaviour.

After the load removal (recovery stage), it was interesting to note that the magnitude of the elastic recoverable deformation was not similar to the initial elastic displacement, especially at lower curing and higher operating temperatures. Namely, when the DMA (operating) temperature was equal to or higher than the previous curing (moulding) temperature, the specimen continued to cure during the DMA experiment. Therefore, after removing the load, the specimen had developed modulus compared to its original state as a result of cure progression; hence, the elastic deformation was not fully recoverable upon load removal. For the cases when the operating temperature was lower than the curing temperature (i.e., the case of DMA at 10°C with cured sample at 10°C in Fig. 3-a, and the case of DMA at 30°C with cured sample at 40°C in Fig. 3-b), there seems to be also a small portion of unrecoverable displacement. In these cases, the curing may have progressed slightly due to the time factor itself (specially in the case of non-uniformity in cured samples, which can happen at higher curing temperatures [15], or there could be an effect of preloading/measurement error in DMA, as well as the possibility of physical ageing during the storage of the specimens before the DMA experiment or even during the elevated temperatures of the test [16, 17]. Consequently, it can be said that the final recovered displacement in all samples is predominantly a combination of thermo-viscoelastic behavior and cure progression (where the latter contributes to the uncovered deformation portion and makes the material behavior semi thermo-visco-elastic fluid).

The unrecovered-to-recovered displacement ratio when the DMA experiment was performed at 30°C decreased on average from 0.81 for specimens cured at 10°C to 0.45 for specimens cured at 40°C. The above values were found to be 0.37 and 0.17, respectively, when the DMA experiment was conducted at 10°C using a new set of samples. The lower operating temperature resulted in lower uncovered (permanent) deformation portion after the loading is removed.

Fig. 3 DMA representative curves showing the behaviour of the specimens under creep test at (a) different operating temperatures but the same cure state, (b) different curing temperatures but the same operating temperature, and (c) rate of cure deflection for the specimens shown in (b). At a constant curing state, there are increased total and unrecovered displacements at the higher operating temperature (30°C) compared to the lower operating temperature (10°C). At a constant operating temperature, an increased curing temperature results in considerable reduction in total and unrecovered displacements. 1 and 2 in (a) refer to recovered and unrecovered displacements, respectively, as an example for the
specimen cured at 30 °C, DMA at 30 °C. There was also an increase in the viscosity (lower rate of creep deflection) as the cure temperature increased.

To compare these in a more practical manner, Fig. 4 shows the ‘absolute’ values of the unrecovered displacement for specimens cured at different curing temperatures, and tested in DMA (operation temperature) at 30°C and 10°C.

Statistical hypothesis testing was performed using paired t-tests to check the significance in differences between all pairs of sample means, with a significance level of $p < 0.05$. A statistically significant reduction in the unrecovered displacement was observed in all cases as the curing temperature was increased from 10°C to 40°C, under a given operation temperature. Inversely, there was a statistically significant reduction in the unrecovered displacement at lower operating temperature, given the same initial curing temperature.

4.3 Degree of cure and effect of $T_g$ of the samples

In order to investigate the effect of curing temperature during moulding on the cure progression during post-moulding operation and eventually on the creep response of the specimens, Differential Scanning Calorimetry or DSC was performed on raw resin as well as resin samples cured at 10, 20, 30 and 40°C. Figure 5 shows representative DSC thermographs illustrating the exothermic peak of the curing reaction. The heat of reaction was significantly smaller for the partially cured samples compared to that of the raw resin. Among partially cured samples, as the curing temperature was increased, there was a sequential reduction in the heat of reaction. In fact, as the curing temperature increases, there is a progressive increase in the initial cure extent and, therefore, less un-reacted resin material to participate in the curing reaction during the DSC heating cycle ($4 \, ^\circ\text{C/min}$). The corresponding areas under the exothermic peak ($\Delta H_{\text{reaction}}$) in conjunction with Eq. 1 were used to calculate the degree of pre-cure for each sample.

Based on the results in Fig. 5, Eq. (1) and DiBenedetto’s equation [18], Fig. 6 shows the curing temperature ($T_c$) and $T_g$ versus the degree of cure. There was a linear correlation between $T_c$ and $T_g$, as well as each with the degree of cure; e.g., the degree of cure increases by increasing the curing temperature; similarly there is an increase in the $T_g$ as the cure progresses.

Many properties of the resin, particularly $T_g$, is dependent on molecular mobility and monomer dispersion. As the curing temperature increases, more energy is available to activate the temperature-dependent curing reaction, leading to more cross-linking of the resin monomers; hence, the overall molecular mobility after curing decreases and as a result $T_g$ increases for that given degree of cure. It is interesting to note that there was almost a constant difference (about 25°C) between $T_c$ and $T_g$ at each degree of cure. This is a critical practical threshold value and specific to each given resin type [19]. It has been recognized that cure predominately stops when: $T_g - T_c \geq$ critical value. For a given cure state, raising $T_c$ will lower $T_g - T_c$ below the critical value; cure will then continue and raise $T_g$. For some resins under certain conditions, different from the resin used in this case study, this critical value can
passively take days to reach, so cure continues to progress for extended periods.

Fig. 6 Degree of cure as a function of curing temperature ($T_c$), and glass transition temperature ($T_g$). There was a linear correlation between $T_c$ and degree of cure. The degree of cure was increased by increasing the curing temperature. The $T_g$ also increased progressively, and there was approximately 25°C difference between $T_c$ and $T_g$ once cure progression had ceased. Note: $T_g$ of -67°C, which is the $T_g$ of the raw resin (degree of cure = 0), has also been considered in establishing the regression line.

Next, unrecovered creep displacement values in Fig. 4 were plotted versus $T_g$-$T$ in Fig. 7 (where $T$ now replaces $T_c$ as the new temperature due to the DMA condition; i.e., post-moulding operation temperature). It was found that both the initial curing temperature, which directly alters $T_g$ right before de-moulding, and the operating temperature influencing the creep displacement, affect $T_g$-$T$ and result in a concomitant reduction in the unrecovered (permanent) displacement. For example, if parts are not cured enough in the mould, then $T_g$ will be too low before de-moulding. In this case, parts that after de-moulding are stored, transported or generally operated at high temperatures may get too close to $T_g$ and become soft enough to undergo a notable deformation under a given load (Fig. 8). Therefore, in manufacturing of composite parts, transportation, storage and operating temperatures of the parts must be considered based on the $T_g$ of the parts dictated by the curing temperature. In addition, when $T_g$-$T$ is lower than the critical value, for example at low $T_g$ and high operating temperature, the cure can still progress and the resin would be in the vitrification stage. Consequently, as the cure progresses, the elasticity of the part increases and hence the elastic displacement that had occurred upon loading will not be fully recoverable (or in other words the modulus will increase over time during post-moulding operation).

When $T_g$-$T$ is high (i.e., above the critical value), for example at higher $T_g$ values and lower operating temperature, there is a significant reduction in the unrecovered displacement, nearly approaching zero. However in these samples with high degrees of cure and hence with high $T_g$, creep can still occur (though to much smaller extents) as the part still exhibits a viscoelastic behavior particularly in the vicinity of $T_g$. As addressed also before in Fig. 3, the minor negligible unrecovered displacement (about 12 µm) observed at the last data points with a high ($T_g$-$T$)>40°C could be due to physical ageing, experimental errors (e.g.; the effect of preloading), as well as possible inhomogeneous micro-structure in the cured resin. With respect to the latter, there might be isolated regions in the polymer network that allows sufficient mobility despite the bulk network having insufficient energy to move due to the high degree of cross-linking.

Fig. 7 Unrecovered displacement dependency on $T_g$-$T$. Ultimate unrecovered displacement was dependent on both curing temperature of samples (affecting $T_g$) and operating temperature ($T$). As the $T_g$-$T$ increases, there is a continuous reduction in the unrecovered displacement. Numbers correspond to same numbers specified in Figure 4 for different curing and operating temperatures. As can be seen both curing and operating temperatures contribute to the unrecovered displacement.

The concepts explained throughout the above discussions have been summarized in Fig. 9 showing the contribution of $T_c$, $T_g$, and operating temperature on curing, viscous portion and elastic portion (recovery/spring back) of a typical polyester resin based composites.
Fig. 8 Illustrative schematic of elastic modulus change versus temperature for different degrees of cure. At a lower degree of cure (i.e., when the sample is cured at a low temperature), $T_g$ will be low. Therefore, at a high operating temperature after de-moulding, $T_g-T$ may become lower than the critical value. In that case, the part becomes soft and potentially deforms under a given load. At the same time, there is a possibility for further curing and eventually permanent deformation upon unloading. However, if the part is cured enough during moulding, and consequently $T_g$ is high enough so that $T_g-T$ will be above the critical value, at the same operating temperature, the part is then stiff enough to not deform much and will be preserved from significant further curing and permanent deformation.

Raising the temperature increases the degree of cure alongside an increase in viscous portion, and a decrease in elastic portion. In addition, progression of cure develops higher elastic modulus. Therefore, the manufacturer should make sure that the curing temperature is selected in a way that the part is cured enough to prevent high deformation and creep during transportation, storage or generally post-moulding operations, and also that the part will not further cure and its $T_g$ will no longer change at the operating temperature. Thus, for a manufactured part, the curing temperature, and temperature to observe viscous behaviour should be pushed to higher temperatures so that at the targeted (nominal) operating temperatures, the part would not undergo curing or exhibit viscous behaviour, and only remain elastic in nature. In this case, the unfavourable displacements due to creep and concurrent cure progression can also be avoided, and any elastic displacement occurring during handling or storage would be recoverable upon load removal.

Fig. 9 Schematic graph illustrating the effect of temperature on curing, viscous portion and elastic portion of a typical partially cured polyester resin composite material. Raising temperature increases the degree of cure. It has also been established that raising temperature will increase the viscous deformation portion and decrease the elastic portion, yet cure also develops elasticity. Therefore, curing and operating temperatures must be selected in a way that the part cannot further cure (change in $T_g$) at operating temperatures after de-moulding.

4.3.1 Workflow suggestion for the case study

If we consider the environmental and part conditions in this case study regarding the sagging problem after de-moulding of parts, we can conclude some simple manufacturing bounds. In winter, when the manufacturing floor temperature is approximately 10°C, the whole or some parts of the laminate during open-moulding may not experience a temperature much higher than this, possibly in the order of 15°C. This could be due to the laminate being thin (not able to generate and retain substantial internally generated heat due to curing), low resin content in starved regions, among other factors. In this case, having the $T_g-T$ critical threshold in mind, the storage, transport or operation temperature of the laminate after de-moulding should be limited to approximately 15°C. If this operational limit is not adhered to, the structure may experience dimensional consequences outlined in this manuscript, resulting from the thermo-viscoelastic behaviour and the advancement of cure. Conversely, knowing a specific operating temperature, for instance in summer, can define a lower bound in the
manufacturing process in the form of peak curing temperature.

Since creep is a time-dependent behaviour, a future study can consider actual times for which the parts are transported or stored and subsequently deformation can be prevented/minimized during additional stages of the part lifecycle. This can include the change in material modulus due to physical ageing, independent of cure progression or conventional viscous behaviour. Similarly, the actual time that parts remain in the mould prior to removal should be considered (here a period of 180 min was assumed), for varying processing temperatures and degrees of cure. Future work can also include dimensional measurements of the parts on the actual manufacturing floor, in order to take into account the large size of the boat parts (scaling problem), as well as the variability in the production stages. Incorporating this with other established knowledge areas of residual stress of composite structures, originating from various sources such as cure shrinkage or tool-part interaction [20], can help build an increasingly holistic understanding of dimensional control issues affecting composite structures.

5 Conclusions

Characterizing creep as a function of the percent degree of cure, factory temperature, and force on the part will allow GFRP manufacturers to optimize the length of time that a given part needs to be in the mould and/or the storage condition before assembly. This manufacturing optimization can in turn yield higher quality parts, and reduced waste and repair works. DSC and DMA equipment can be effectively used to characterize, respectively, the degree of cure and its effect on deformation in moulded GFRP parts. Eventually such characterization case studies can lead to new guidelines for manufactures of large GFRP open-moulded parts.

It was found that there is a direct relationship between the curing, glass transition, as well as operating temperatures and the unrecovered displacement that may occur during transportation, storage or operation of composite parts. This unrecovered displacement was hypothesized to be mostly attributed to a combination of cure progression and creep, resulting in partial recovery of the total displacement. The former leads to the development of stiffness that retains the elasticity, whereas the latter can cause irreversible viscous flow. Undesired dimensional changes occur when the manufacture removes the part from the mould after partial curing and transport or store it at a temperature that is close enough to the Tg of the part. This softens the part to the point at which it has the potential to undergo creep under the applied loads (e.g., its own weight when stored on a storage structure). In the case of Arapol® unsaturated polyester resin, it was found that there is about 25°C difference between the curing temperature and the resulting Tg. At temperatures within this window, the part has the potential to become soft and also further cure and change the Tg. Therefore, the operation temperature (including storage) would be ideally low enough (compared to the curing temperature) to make sure that the part neither further cures, nor exhibit a notable viscous behaviour.

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