THE INFLUENCE OF HEAT DURING SHORT AGEING PERIODS ON THE MECHANICAL PROPERTIES OF CFRP COMPOSITES

J. L. Merino-Pérez[a*], S. Ayvar-Soberanis[b], E. Merson[c], A.Hodzic[a]

[a]*Department of Mechanical Engineering, The University of Sheffield, Sir Frederick Mappin Building, Mappin Street, Sheffield, S1 3JD, UK.*
[b]*Advanced Manufacturing Research Centre with Boeing, The University of Sheffield. Advanced Manufacturing Park, Wallis Way, Catcliffe, Rotherham, S60 5TZ, UK.*
[c]*Sandvik Coromant, Sandvik AB, Advanced Manufacturing Park, Unit 8, Morse Way, Waverley, Sheffield, S60 5BJ, UK.*
** j.merino@sheffield.ac.uk*

Keywords: thermal ageing, heat, CFRP, mechanical properties, composites.

Abstract
In order to evaluate the influence of heat developed during the composites machining process, the effect of heat during short ageing periods on the properties of carbon fibre reinforced polymer (CFRP) composites was investigated in this study. Impact energy absorption (Charpy) and tensile strength tests were carried out on the composite after exposing it to different ageing temperatures during 60, 120 and 180 second intervals. The overall properties of the composite were little affected. The variation of the ageing time showed to have no influence, whereas the viscoelastic properties showed an increase with the ageing temperature increasing up to T_g due to a post curing effect, and a further decrease at higher ageing temperatures due to a subsequent damage in the matrix.

1. Introduction

The use of carbon fibre reinforced plastic composites in the aerospace and automotive industries has increased in the recent years due to their excellent specific properties. As part of their manufacturing processes or in order to ease further assembly processes, these materials are subjected to diverse machining operations under dry environment as milling, trimming, turning or drilling where the machined surfaces and the areas close to these could be exposed to considerable temperatures during short periods that may cause a degradation of the thermoset polymer matrix and/or the interphase. This phenomenon is known as ageing. Early investigations of the ageing mechanisms were carried out, where water absorption by the polymeric matrix was found to be an important factor in the composite degradation [1-6]. A mathematical model was developed to predict the diffusion of water through the CFRP composite thickness, which showed a Fick-type correlation, in good alignment with the experiments [1].

The study of the water absorption on the glass transition temperature of thermoset resins by calorimetric techniques was carried out, and it was observed that high T_g resins exhibited a more significant depression of their T_g, being thus more sensible to water absorption than lower T_g and less cross-linked resins [2]. The water absorption kinetics of glass fibre-reinforced Nylon 6,6 composites and their mechanical properties were studied under controlled humidity and temperature conditions. The authors found that it followed a Fickian pattern, however interestingly this was completely different from thermosets, since for Nylon 6,6 the water uptake increased T_g [3]. Later, the assessment of the thermal ageing on the failure mechanisms under flexural loading of CF-epoxy composites was investigated. The CFRP composite material was subjected to ageing under dry, wet and hot environments during long ageing times. The authors reported that a transition from ductile to brittle failure modes could be observed as the ageing time increased [4]. The viscoelastic creep behaviour of UD glass fibre-reinforced composite was studied where a decrease was observed in the mechanical properties caused by the physical ageing, comparable to the effect of temperature [5]. Further work was carried out to compare the effect of physical ageing on the creep behaviour of thermoplastic and thermosetting composites. Novolac, bisphenol A diglycidyl ether (DGEBA), cyanate ester, polyethylene (PE), polycarbonate (PC), polypropylene (PP) and polyhoweverylene terephthalate (PBT) matrix composites were exposed to physical ageing processes at different ageing temperatures and time intervals. It was reported that the ageing shift rate had little dependence on temperature, however the creep curves were significantly affected by the ageing time [7, 8]. More recent investigations studied the mechanical property degradation during short-term ageing at high temperatures. Contrary to other works, a loss of mechanical properties was reported before the weight loss was measured. This implied that structural changes in the polymer such as chains rupture occurred in the early stage of degradation, indicating a significant influence on the mechanical properties however not on the weight loss. On the other hand, in a later degradation stage, degradation mechanism such as catalytic reaction of gasses was reported, having little effect on the mechanical properties however causing the weight loss [9]. In this work physical ageing was described as a reversible process that involved molecular rearrangement over time, whereas chemical ageing (chain rupture, oxidation, etc.) was described as an irreversible process. The authors stated that in composites exposed to ageing temperatures below T_g, a post curing effect (increase of cross-linking density) existed, whereas in composites exposed to ageing temperatures above T_g, chain rupture, oxidation and thermolysis occurred [10]. The effect of low ageing temperatures during long ageing periods in very humid environments on the mechanical properties of CFRP composites was also studied [11, 12]. Water absorption caused degradation of the interphase, changes in its chemical structure and decreased the mechanical properties of the composite. In addition to this, the authors reported higher level of damage in samples exposed to higher ageing temperatures, despite having the same levels of water absorption.

This work investigated the study of the effect of heat during short ageing times in the mechanical properties of CFRP composites. Test coupons of the selected material were exposed to different ageing temperatures below and above T_g during different short ageing periods; and were subsequently tested in order to assess the changes in the mechanical properties of the composites and compared to non-aged material.

2. Materials and Methods

2.1. CFRP

The CFRP system considered for this investigation was MTM44-1 CF0300 manufactured at Composite Centre of the *Advanced Manufacturing Research Centre with Boeing* using prepreg plies supplied by *Cytec Engineered Materials*. MTM44-1 resin is a toughened phenol-formaldehyde (PF) based resin which features a glass transition temperature (T_g) of approximately 210°C. CF0300 is a 2/2 twill carbon fabric, 3K high strength (HS) carbon fibre reinforcement having density of 199 g/cm^2. A 750 x 550 mm plate was manufactured by the vacuum bag method, laying up 11 plies to an approximate thickness of 2 mm and degassing each ply to minimise the concentration of voids. The plate was cured in autoclave at 130°C for 4 hours and then post-cured at 180°C for 2 hours in order to develop full mechanical performance and maximum T_g, as it was specified by the supplier. The manufactured plate was afterwards cut down to 250 x 200 mm plates.

2.2. Ageing

Table 1 shows the ageing conditions considered in this investigation. The ageing temperatures considered ranged from below to well above the T_g of the studied material. Prior to the ageing process, the test coupons were machined from 250 x 200 mm panels, in accordance with ISO 2818, to the size required to perform the mechanical tests described in the subsequent points 2.3, 2.4 and 2.5. Thereby, thermal stresses and deflections that might appear within the material due to the unequal thermal expansion coefficients were minimised.

Table 1. Ageing conditions considered in the study. The non-aged material is represented by Condition 1.

Condition	Ageing temperature [°C]	Ageing time [s]
1	-	-
2	150	60
3	200	60
4	250	60
5	250	120
6	250	180
7	350	60

The furnace used to age the CFRP samples was a *Carbolite 1806/SIRIUS/LEV3* model fitted with a thermocouple located in the middle of the chamber which allowed a better control of the temperature. The composite samples aged in the middle of the chamber where the temperature was measured with higher accuracy. A steel mail fixture helped to introduce and withdraw the samples from the furnace and reduced the temperature fluctuation. The aged samples cooled down to room temperature in air.

2.3. Charpy impact test

The study of the impact energy absorption of CFRP relied on the British Standard BS EN ISO 179:1997 *Plastics — Determination of Charpy impact strength*. The Charpy test impact machine used in this experiment was an instrumented *Hounsfield Plastic Impact Machine No. P221*, fitted with a 2 pounds (approximately 0.91 kg) pendulum and set up at a height of 34 cm. The nominal energy in this configuration was 2.70 joules and the impact velocity 2.60 m/s. The configuration of the impact corresponding to the type of material tested was unnotched flatwise normal. Prior to the testing, the the temperature was recorded, a blank test with no specimen was performed and recorded, accounting for the frictional losses. The number of test specimens used was 13 per condition. The specimens were preconditioned during 24 hours in the same environment as tested. After the tests, the average absorbed impact energy (a_{cU}) and the scatter (standard deviation) for each ageing condition were calculated using MS Excel software

2.4. Tensile test

The study of the effect of ageing on the tensile strength relied on the British Standard BS EN ISO 527-4:1997 *Plastics — Determination of tensile properties — Part 4: Test conditions for isotropic and orthotropic fibre-reinforced plastic composites*. The universal testing machine utilised for this experiment was a *Mayes SM 100*, fitted with two bolt-tightened grips and a load cell rated at 100 kN. A click-type torque wrench applied a 100 N·m torque on the bolts to clamp the test specimens. The testing velocity was 2 mm/min. The number of test specimens per condition used in the experiment was five. The data were recorded with a computer attached to the testing machine and fitted with NI's LabVIEW software. After the tests, the average tensile strength and standard deviation for each ageing condition were calculated.

2.5. Dynamic Mechanical Analysis

The machine utilised to investigate the variation of the T_g and the damping coefficient (tan δ) of the selected CFRP samples was a *Perkin Elmer DMA 8000*, which was able to apply a maximum testing force of 10N. The testing arrangement was a 3-point bend test, the optimum dynamic displacement for the thickness of these samples was $8 \cdot 10^{-3}$ mm and the maximum force of approximately 8 N was applied. The frequency of the tests was 10 Hz and the temperature sweep ranged from room temperature to 250 °C.

3. Results and Discussion

3.1. Charpy impact test

Table 2 shows the results of the Charpy impact tests for equal ageing time intervals. The impact energy absorbed by the material did not vary in a great extent and maintained most of its initial ability to absorb energy. The absorbed impact energy was divided in three intervals. Conditions 1-2 delimited the first interval in the trend. Here, the trend showed an increase in the impact energy absorbed by the material. A possible explanation for this increase can be a residual post-curing effect. This possible residual post-curing increased the density of cross-links, enhanced the ability of the resin to transfer the load to the reinforcement and therefore increased its ability to absorb energy. Conditions 2-4 delimited the following interval. This interval showed a pronounced decrease in the absorbed impact energy and reached the lowest value of energy absorbed in condition 3. The structural relaxation (movement and rearrangement) of the polymer chains that form the matrix can explain the drop in the impact energy absorption. This relaxation affected or modified the interphase in a way that reduced its ability to transfer the load to the fibres and decreased the absorbed impact energy. Conditions 3-7 comprised the last interval, which indicated an increase in the impact energy absorption. These conditions were contained within temperatures up to 150°C above T_g. At these high temperatures, the ability of the interphase to transfer the load to the reinforcement would be lower than in the former interval, so the increase of the impact energy absorption could be explained by a different mechanism to dissipate energy. The material aged at these temperatures would have local micro-cracks, delamination, fibre-matrix debonding and voids caused by the decomposition of the matrix. These discontinuities within the material would contribute to dissipation of the energy in the form of heat. However, despite the impact energy absorption in this interval being increased in comparison with the two former intervals, this would be considered an unfavourable impact energy dissipation mechanism since it indicates a severe damage of the material.

Table 2. Results of Charpy impact tests in CFRP samples aged at different conditions.

Condition	Average a_{cU} [kJ/m^2]	Standard deviation
1	72.6	4.7
2	74.1	5.7
3	71.3	5.4
4	72.3	4.9
5	74.3	5.6
6	73.5	7.5
7	74.8	5.8

The ability of the material to absorb impact energy after being exposed to different ageing temperatures during equal ageing time intervals exhibits different behaviour before and after the glass transition temperature. Two different mechanisms would dominate the different ageing temperature intervals: at ageing temperatures below T_g and increased cross-link density of the matrix that enhanced its ability to transfer the load; and above the T_g, the damage created in the material due to the exposition at high temperatures dissipated the energy in the form of heat.

3.2. Tensile test

Table 3 and Figure 1 show the results of the tensile test experiments for equal ageing time intervals. The variation of the tensile strength only showed a small variation for all the conditions considered and the material maintained most of the original tensile strength. However, it showed a trend in its evolution that needs to be considered. This trend, depicted in Figure 1, could be split in two intervals. The first interval, which included conditions 1-3, described an increase in the tensile strength that reached its maximum at condition 3, close to T_g. This increase can be explained by a post-curing phenomenon that increased the cross-linking density within the composite and enhanced its ability to transfer the load to the fibres. The second interval involved conditions 3-7 and showed a considerable decrease in the tensile strength, having its minimum value observed in condition 7. This behaviour can be explained by a degradation phenomenon in the polymer matrix and the interphase, at distinct levels, influenced by the heat: at temperatures around the T_g the structural relaxation phenomena affected the structure of the interphase, reduced its ability to transfer the load and decreased the tensile strength.

Table 3. Results of tensile tests of CFRP samples aged at different conditions.

Condition	Tensile strength [MPa]	Standard deviation
1	686.5	41.5
2	717.8	49.2
3	739.2	41.8
4	717.9	35.6
5	721.4	76.6
6	714.9	46.2
7	648.6	58.5

In the case of the composites exposed to temperatures higher than T_g, the beforehand mentioned degradation of the interphase was worsened by the decomposition of the matrix that subsequently initiated localised microscopic damages within the composites. These discontinuities acted as stress concentrators and precipitated the failure of the composite.

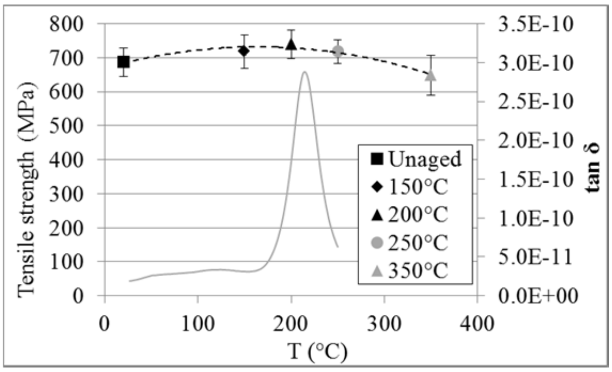

Figure 1. Tensile strength of CFRP samples subjected to different ageing conditions. The value represented for each condition is the average of 5 measurements.

3.3. Dynamic Mechanical Analysis

Figure 2 shows the results of the damping coefficient (tan δ) obtained in the 3-point bending tests for the samples considered: unaged, 200°C and 350°C. At temperatures below T_g, despite the data being slightly scattered, differences in the damping coefficient were observed as tan δ_{unaged} > tan $\delta_{350°C}$ > tan $\delta_{200°C}$.

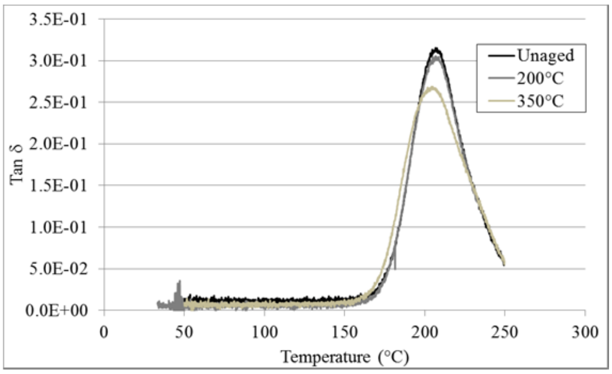

Figure 2. Results of the damping coefficients obtained in DMA tests (3-point bending configuration) for the three considered conditions, unaged, 200°C and 350°C.

These damping properties exhibited by the aged CFRP material were in good agreement with the results of the Charpy impact tests, where $a_{cU350°C} \approx a_{cUunaged} > a_{cU200°C}$. The behaviour around the glass transition temperature was quite different. The maximum value of the damping coefficient corresponded to the unaged material, with a similar value for the material aged at 200°C. However, the material aged at 350°C exhibited a considerable drop in the maximum damping coefficient of about 15% compared to the unaged material. The variation of the damping coefficients can be attributed to the changes in the storage and loss moduli in a different extent. Figure 3 shows the variations of the storage and loss moduli. Whereas the values of loss modulus, that represented the viscous part of the material, exhibited the same behaviour than the one observed in the damping coefficient at temperatures below the T_g, the storage modulus, that represented the elastic part, showed a very different variation. The samples aged at 200°C and 350°C showed an increase in the storage modulus of about 23% and 20% respectively, compared to the unaged material. This supported the argument of a post curing effect after exposing the material to elevated temperatures [9, 10]. This observed behaviour of the storage modulus can explain the results obtained in the tensile tests, where $\sigma_{u200°C} > a_{cUunaged} \approx \sigma_{u\,350°C}$. A post curing effect increased the cross-linking density, enhanced the ability of the matrix to transfer the load to the reinforcement and therefore its ability to store energy.

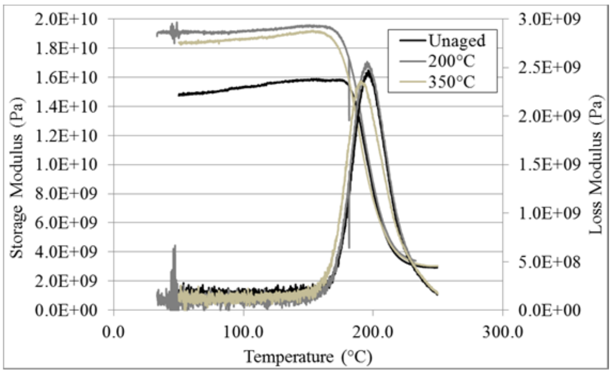

Figure 3. Storage and loss moduli results obtained in DMA tests (3-point bending configuration) for three considered conditions.

Both values of the storage and loss moduli for the material aged at 200°C increased in respect to the unaged material, which indicated a net improvement of the viscoelastic properties of the material. Nonetheless, although the material aged at 350°C showed a storage modulus higher than the one corresponding to the unaged material, this was lower than the one observed for the samples exposed to 200°C. Moreover, at higher temperatures the loss modulus was lower than those of the unaged material and the material aged at 200°C. This indicated that, after the post curing effect, the material suffered further damage due to very high temperature exposure. This damage reduced the ability of the matrix to dissipate energy in the form of heat and, therefore, reduced the damping properties of the composite.

4. Conclusions

This study presented the effect of different ageing conditions on the mechanical properties of CFRP composites by varying ageing temperature and time. The following conclusions can be extracted from the results and their analysis:

– The influence of the short high-temperature ageing intervals showed to have no influence on strength and impact energy absorption in CFRPs. The previous literature in long-term ageing of composites reported that the degradation of the mechanical properties in CFRP composites was associated with water absorption in the polymeric matrix. This study was concerned with the parameters that may influence the composites during the machining process.

– The influence of the ageing temperature had a very small influence on the absorbed impact energy. However, the trend indicated a small decrease at ageing temperatures around the T_g, followed by a further increase. DMA tests (3-point bend test) revealed that the measured damping coefficient and loss modulus of the considered samples at temperatures below the T_g varied in good agreement with the obtained results of the impact energy absorption. In addition to this, a decrease in the maximum damping coefficient (tan δ peak) with the increased ageing temperatures was measured.

– The effect of temperature ageing had a significant impact on the tensile strength of CFRP composites. The tensile strength increased with ageing up to T_g followed by a further decrease at higher ageing temperatures. This increase can be attributed to the post curing effect that incrementally increased the cross-linking density and enhanced the viscoelastic properties of the material. The subsequent decrease indicated further damage caused by the high ageing temperatures. DMA results supported this explanation.

– CFRPs aged at temperatures below T_g showed varied storage moduli (related to the elastic part of the material and to the ability of the matrix to transfer the load to the reinforcement), in agreement with the tensile strength results. However, these ageing temperatures scarcely affected loss modulus (related to the viscous part of the material). In order to measure the extent of the damage through the thickness of the composite, further investigation with nano-indentation techniques will be performed in the future study.

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