STRENGTH DEGRADATION OF GLASS AND CARBON FIBRES AT HIGH TEMPERATURE

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SUMMARY

Engineering fibres lose strength (carbon, glass) and stiffness (carbon) at elevated temperatures in the range of 300 – 1000ºC due to growth of surface flaws and/or mass loss. The property degradation is time and temperature dependent. Possible kinetic models are investigated for E-glass and T700S carbon fibres.

Keywords: Fire, glass fibres, carbon fibres, property degradation, surface flaws

INTRODUCTION

Fire performance is one of the most significant factors affecting the wider use of composites in engineering structures. Many composite materials, whether reinforced with glass or another fibrous material such as carbon, have a flammable polymer matrix that combusts at high temperature. Composites can smolder or burn with the release of significant heat, smoke and fumes, which may pose a serious safety hazard. Composites may also soften, buckle or collapse in a fire. This is a concern in most structural applications, especially when failure can cause injury and death.

Major advances have recently been made towards modelling the structural response of composites in fire. Recent fire research by Feih et al. [1, 2] has shown that tensile failure of fibreglass composites in fire is dependent on thermally induced strength reduction of *both* the polymer matrix and the fibres. Composites in fire generally retain significant tensile strength after the matrix has fully softened and decomposed because of the strength provided by the glass fibres. However, glass fibres also lose their strength, albeit at a slower rate than the matrix, and eventually fail by thermally induced embrittlement and rupture under certain fire and load conditions. Current work is showing that similar trends are obtained with carbon fibre composites.

The capabilities offered by being able to analyse the fire structural response underpin the need to develop fire models that are robust and mechanistically accurate. Required input parameters include fibre mechanical properties at elevated and high temperatures. The development of kinetic models relating to strength and stiffness loss is preferable to minimise extensive material testing programs. This research paper presents an experimental study into the strength loss and damage mechanisms of glass and carbon

fibres at elevated temperatures. The effects of temperature and heating time on the reduction in tensile strength is determined experimentally, and the data is used to develop kinetic models to predict the softening rates of glass and carbon fibres. The study is confined to determining the property loss of E-glass and T700S carbon fibres. These fibre types were selected because of their widespread use in engineering structures. The strength loss behaviour for the E-glass is expected to be indicative of the behaviour of other types of fibreglass (e.g. S-glass, C-glass). Likewise, the property loss for the T700S fibre and other types of carbon fibres will be similar. Therefore, the results presented in this paper provide general information on the thermal softening behaviour of various glass and carbon fibre types.

EXPERIMENTAL PROCEDURE

Fibre bundles of E-glass (300tex, 111A sizing, Owens Corning) and T700S (24k, FOE sizing, Sigmatex, US) were investigated in the current test program.

Various types of tests are available to investigate fibre strength, with the fibre bundle test and single fibre test being the most widely used. Fibre bundle testing includes the unknown variable of friction, which influences the strength results. Single fibre tests eliminate friction, but are much more time-consuming due to the large number of samples required for statistical data treatment. Both methods were used to investigate the fibres, and comparison of the results highlights interesting differences.

Fibre bundles were heat-treated in air using a muffle furnace. Different exposure times (5 mins to 2 hours) and temperatures ($150°C - 650°C$) were chosen for the strength loss measurements. No load was applied during the heat treatment. The fibre bundles were subsequently cooled in air, prior to separation of fibres and testing.

The fibre bundles were tested under tension using a 10 kN Instron machine. The ends of the fibre bundle were wrapped around circular rollers so that the stress introduced into the specimen gradually via friction. This ensured bundle failure in the gauge section of 150 mm. The maximum force was measured, which can be related to the maximum strength of the fibre bundle through the weight per unit length of the bundle and the density of fibres:

$$\sigma_{max} = \frac{F_{max}\rho_f}{W_f} \qquad\qquad\qquad [1]$$

Single fibres were glued onto cardboard frames with Loctite 406 adhesive. The cardboard frame had an internal cutout of 20mm length, thereby defining the gauge length. The fibre diameters were measured using a Mitutoyo laser scanner, optical microscope and scanning electron microscope (SEM). A 2.5 N Instron 4501 machine operated at 0.5 mm/min (glass) and 0.1 mm/min (carbon) was used to measure the tensile strength of the single fibres. The broken fibres were collected, and their fracture surfaces examined and measured using a scanning electron microscope (LEO 1530VP-21-32) operated at 5kV.

Single fibre testing data were analysed using the two-parameter Weibull distribution with sample sizes of 30 fibres per thermal treatment condition. The failure probability of the fibre at stress σ for a constant length of L=20 mm is then given as

$$P_f(\sigma) = 1 - \exp\left(-\left(\frac{\sigma}{\sigma_0}\right)^m\right) \text{ with } P_f(\sigma_i) = \frac{i - 0.5}{N} \qquad [2]$$

where P_f is the probability of failure, N is the total number of samples tested, m is the Weibull modulus, and σ_0 is the characteristic strength. The Weibull modulus m is an indicator of the amount of scatter in the experimental data.

Fractured surfaces of the broken single fibre specimens were examined using SEM after testing to investigate the damage mechanisms. Figure 1 shows the fracture surface of glass fibres which is characterized by a smooth region called the mirror zone and a hackle region. Similar fracture mirrors have been reported for carbon fibres [3]. The mirror zone (bounded by the dashed line) shows the area of sub-critical crack growth in the fibre prior to failure whereas the hackle region indicates unstable crack extension. The fracture mirror can be used to determine the size and location of the original flaw which initiated fibre failure.
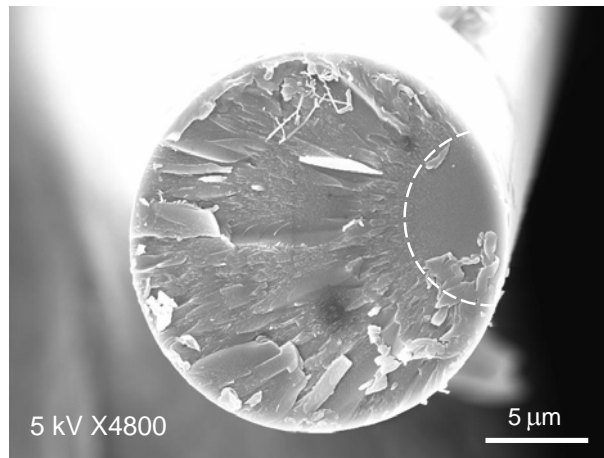

Figure 1: Fracture mirror size on E-glass after high temperature exposure

It has been demonstrated that the tensile strength of polycrystalline or amorphous ceramics is related to the mirror depth d_m through a mirror constant A_m [4]:

$$\sigma_{TS} = A_m(d_m)^{-1/2} \qquad (3)$$

The depth of the surface flaws can be estimated from fracture mechanics based on the mirror measurements. A planar crack perpendicular to the fibre axis is the simplest

idealization of the crack shape, and the dependence of fibre strength on flaw size (*c*) is governed by the well known relationship:

$$\sigma_{TS} = \frac{1}{Y(c,R)} K_{Ic} (\pi c)^{-1/2}$$ (4)

K_{IC} is the fracture toughness. The difficulty lies in defining this value for fibres, but it has generally been found that bulk property measurements can be applied. The fracture toughness for glass fibres is therefore estimated as $K_{Ic} = 0.76$ MPa m$^{1/2}$ (borosilicate glass [5]) and for carbon fibres as $K_{Ic} = 1$ MPa m$^{1/2}$ (polycrystalline graphite and polycarbosilane SiC fibres [3]). *R* is the fibre radius and *Y(c,R)* is a factor generally dependent on the crack geometry and its size in relation to the fibre radius. Assuming small and semi-circular flaws, *Y* can be considered constant with a value of $Y=2/\pi$.

RESULTS: GLASS FIBRES

Previous work by Feih et al [1,2] has led to fundamental research advances for the strength characterization of glass fibre bundles in the temperature range of 100 – 650ºC, and the results have been successfully related to the fire performance of composites. Glass fibres appear inert during high temperature exposure in that no mass loss was measured during heat treatment apart from the sizing removal. Previous research into E-glass fibres reveals that the strength loss is strongly dependent on heating time and temperature (see Figure 2). Unexpectedly, even exposure to moderate temperatures of around 350ºC – which is well below the fibre annealing and softening temperatures - led to significant strength loss.
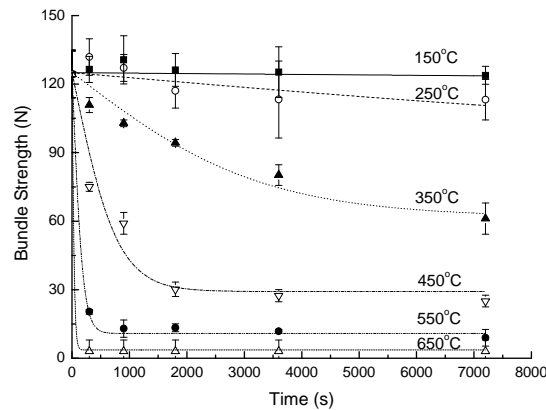
Figure 2: Fibre bundle strength loss of E-glass at high temperature

Extensive single fibre testing at elevated temperatures was undertaken to compare the results to the fibre bundles. Figure 3 (a) shows the strength distributions for four temperatures with the same exposure time of two hours. As expected, higher

temperature leads to higher strength loss. Compared to room temperature, the characteristic fibre strength (as determined from Weibull statistics, see Eq. (2)) reduces by 20% at 350°C, 50% at 450°C and 65% at 550°C. Time-dependent behaviour in strength loss was also observed, but at much shorter time scales than expected from the fibre bundle test results in Figure 2. Strength loss was found to depend on time for exposure times of less than 15 mins only, as shown in Figure 3 (b).

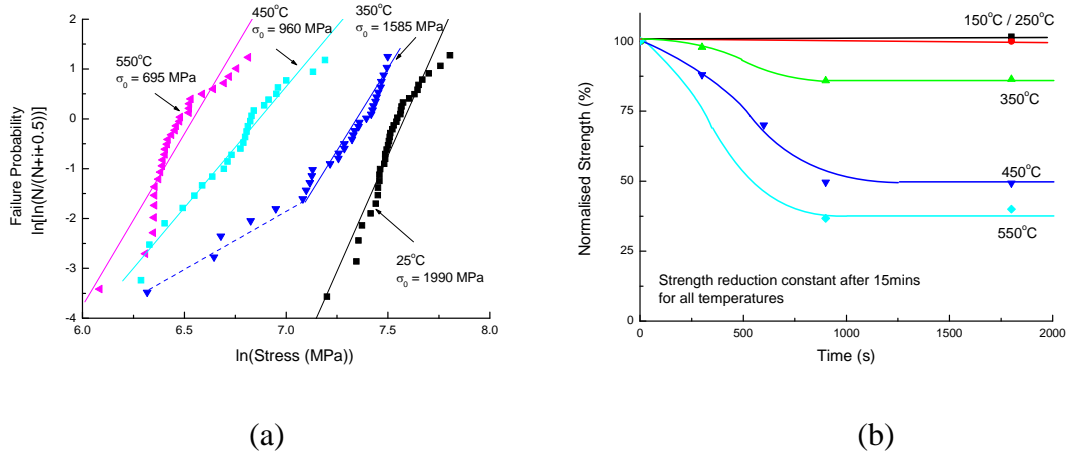(a)   (b)

Figure 3: (a) Single fibre strength loss of E-glass after two hours exposure to given temperature and (b) effect of heating time and temperature on strength loss of E-glass.

In the case of the bundle data, time dependency was found to occur for up to two hours for the lower temperatures. As demonstrated by single fibre testing, this time-dependency cannot be related to the fibre strength reduction, but must be due to another factor. To investigate the issue of time-dependency further, Figure 4 shows the normalized tensile strength values of single fibres and fibre bundles in the as-received and heat-treated conditions. The strength values were normalized to their room temperature (as-received) strength to allow a direct comparison between single fibres and bundles of fibres. Despite the scatter, the results show that the bundles experience significantly greater percentage loss in strength after heat treatment than the single fibres. More interestingly, above 350°C, the percentage difference approaches 30% and appears independent of the heat treatment temperature.

The difference in results is currently attributed to the removal of organic sizing from the filaments, which decomposes during heat treatment above ~350°C. The size provides lubrication between fibres during bundle testing, so its removal will result in greater frictional forces. These forces are believed to create fine-scale damage on the fibre surface which lowers the bundle strength. Up to 40% variation in room temperature bundle strength has been previously observed for identical glass fibre bundles (i.e. the same tex and fibre diameter) with different commercial sizings [6]. This theory will be further investigated by testing glass fibres with different sizings in both bundle and single fibre test mode for one selected heating condition.
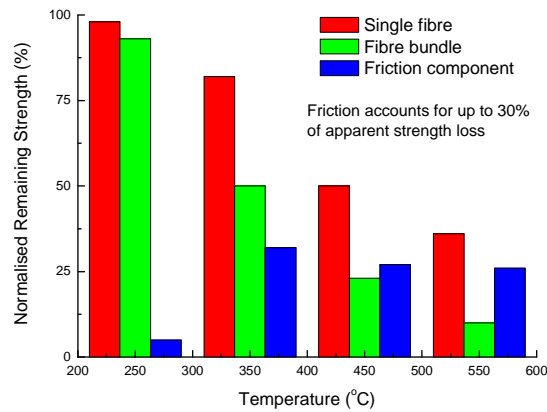
Figure 4: Single fibre and bundle strength loss of E-glass at various temperatures

Kinetic Model Approaches for E-Glass Fibre Strength

The cause of strength reduction needs to be resolved prior to development of a possible kinetic model. This issue has been much-debated, and fully satisfactory conclusions have yet to be drawn. The loss in strength has been attributed to several mechanisms [7], which may include (1) annealing of compressive residual stresses, (2) re-orientation or loss of orientation of a silica network structure, (3) presence of a surface layer with different properties to the fibre core, and (4) development of surface flaws due to high temperature attack, probably involving water. Mechanism (1) has now been discredited, but mechanisms (2)-(4) are still regarded as plausible, despite little evidence of either network orientation or differences between the surface and core properties of the fibre.

Previous work by Feih et al [2] has led to fundamental insights into the origin and size of flaws causing the strength reduction. All fracture surfaces obtained from single fibre tests showed the failure initiated at pre-existing surface flaws. No development of internal flaws was observed. Secondly, the fracture mirror depth was analysed as a function of fibre strength (see Figure 5 (a)). A linear relationship was observed independent of heat treatment, thereby indicating unchanged fracture toughness (see Eq. (3) and Eq. (4)). Figure 5 (b) shows the development of flaw depth with temperature at steady-state strength, i.e. with temperature exposure longer than 15 mins. The flaw depth was evaluated based on Eq. (4). It can be seen that the flaw growth is accelerated when plotted as a function of temperature. It is interesting to note that this temperature-growth relationship does not seem to follow an Arrhenius-type relationship. For shorter time periods, the flaw size growth also needs to be characterised as a function of time and temperature.

A better understanding of the underlying fundamental mechanisms for crack growth is required to develop a robust kinetic model. Moisture is assumed to play a major role in the crack growth mechanism. Driving factors such as atmosphere (nitrogen and dry air) and pre-stressing of fibres during heating will therefore be investigated in future work.

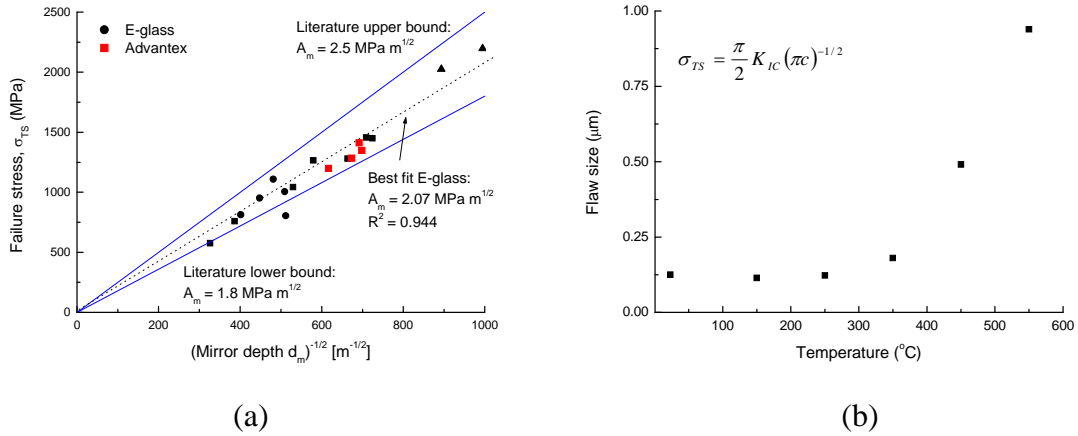(a)   (b)

Figure 5: (a) Plot of fracture mirror size against failure strength of the E-glass fibres. (b) Size of surface flaws at steady-state strength as function of temperature

RESULTS: CARBON FIBRES

Kinetic Model Approaches

PAN-based carbon fibres exhibit mass loss due to oxidation during high temperature exposure (temperature > 500°C). The driving force for mass loss is the oxidation of carbon fibres [8]:

$C + O_2 = CO_2$ and $C + 0.5O_2 = CO$.

In case of excessive oxygen being present (i.e. the oxidation rate is not limited by the amount of oxygen available), the mass loss may be described by:

$$\frac{dm}{dt} = -k\,ASA(t),$$ [5]

where m is the mass of the carbon fibres at time t, k is the reaction constant, D is the fibre diameter, and ASA is the active surface area of the fibres during oxidation. The reaction constant k is a function of carbon fibre properties, oxygen availability, carbon oxide partial pressures and temperature. If the active surface area is a function of the diameter alone, a linear loss of diameter with time is obtained during oxidation:

$$\frac{dD}{dt} = -K \ \text{ with } \ K = \frac{2k}{\rho}$$ [6]

The oxidation reaction is of Arrhenius-type:

$$K = K_0 \exp\left(-\frac{Q_{ox}}{RT}\right),$$ [7]

where T is the temperature in Kelvin and Q_{ox} is the activation energy for oxidation. R is the gas constant (8.314 J/mol K).

The mass-temperature dependence of the T700 carbon fibre is shown in Figure 6 (a). In this case, the diameter does not decrease linearly with time, which has previously been

found for T300 carbon fibers and been attributed to the fact that the active surface area does not remain constant as a result of micro-pore and porosity development [9]. Consequently, the activation energy was calculated for various percentages of diameter reduction according to Eq. (6). Figure 6 (b) shows that the resulting activation energy is constant with a value of $Q_{ox} = 105 \pm 5$ kJ / mol, which is in very good agreement with literature values reported for T300 (94 kJ/mol [9]).
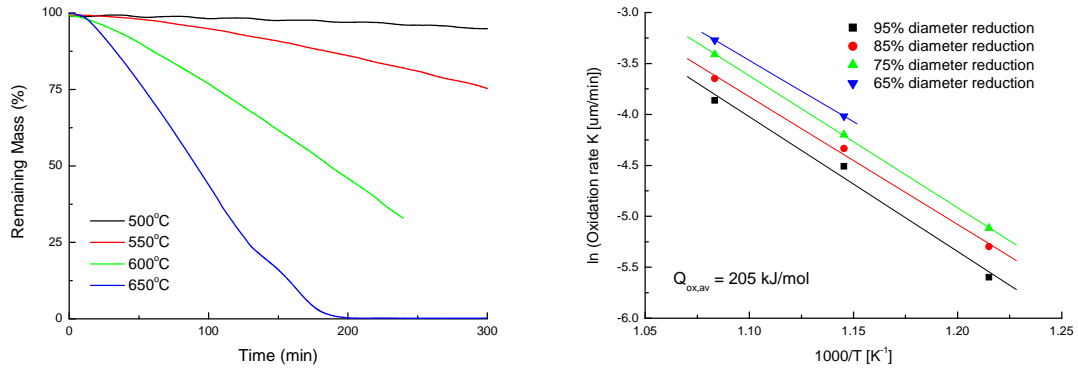

Figure 6: Fibre mass loss for T700S carbon fibres at high temperature

Mass loss may also be accelerated by the presence of trace amounts of platinum or sodium [10]. These elements at the surface cause a local acceleration in the oxidation rate, which results in surface pitting. Pitting is generally observed on the fibre surface along with uniform diameter reduction (see Figure 7).
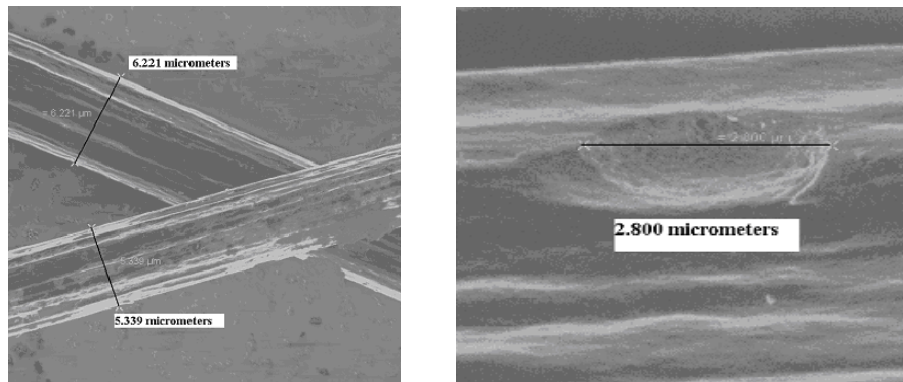

Figure 7: Diameter reduction and pitting on carbon fibre surface after exposure to 600°C for two hours

Figure 8 shows selected strength loss results of T700 carbon fibres after exposure to moderate temperatures for two hours (T< 500°C). For exposure at 450°C, the carbon fibres already show considerable strength loss in the order of 20%, which occurs prior to mass loss being recorded by TGA. Any modelling effort focussing on strength

reduction can thus not be based on mass loss alone. It is postulated that pitting as observed in Figure 7 may already have an influence at lower temperatures.

Table **1** shows that a minimal surface flaw increase from 26 to 43 nm is required to reduce the strength by 20% (calculations are based on Eq. (4) and strength values from Figure 8). On the other hand, a flaw depth of 0.5 μm (as estimated from Figure 7 (b)) will reduce the strength by 75%.
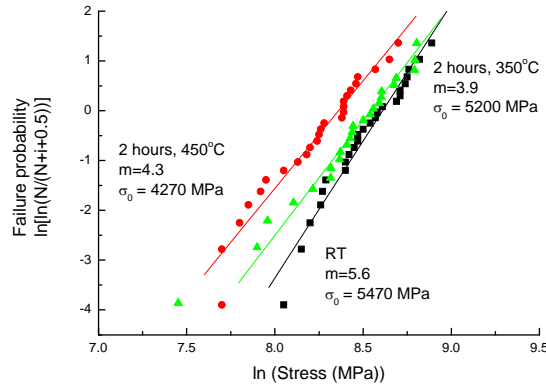

Figure 8: Fibre strength loss for T700S carbon fibres at elevated temperature prior to mass loss

Table 1: Estimation of flaw size on carbon fibre surface

2 hours	RT	350°C	450°C	600°C
Flaw size [nm]	26	29	43	500
Strength [MPa]	5470	5200	4270	1253

While the amount of strength loss is shown to be severely affected at moderate temperatures, the modulus of a homogeneous carbon fibre should be independent of temperature exposure if the reduction in cross-sectional area is considered. However, skin-core heterogeneity exists for fully stabilised PAN-based carbon fibres as shown schematically in Figure 9 [10]. The skin has higher orientation of carbon and therefore higher modulus. Removal of the outer skin layer might therefore reduce the overall modulus more than expected from diameter loss alone. This will give an indication of the thickness of the outer skin layer for the fibres investigated.
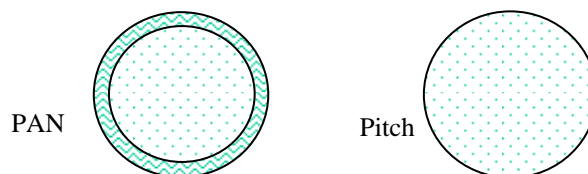

Figure 9: Cross-sectional orientation of carbon sheeting for carbon fibres

As no major mass loss was found to occur for temperatures less than 450°C, the modulus is expected to remain constant up to this temperature. This was confirmed by experimental observations (see Table 2). The modulus was found to be around 10% less than the manufacturer's value of E=235 GPa, which might be due to apparent nonlinearities in the stress-strain curve, which complicate the consistent evaluation of the modulus.

The underlying fundamental mechanisms and driving factors for pitting and mass loss are currently investigated to develop a robust modelling approach for property degradation. Fibres will also be exposed to inert atmosphere (no mass loss) to test the effect on strength and modulus degradation.

Table 2: Carbon fibre modulus as function of temperature

	RT	350°C	450°C
Modulus [GPa]	203 ± 11	210 ± 14	213 ± 14

ACKNOWLEDGEMENTS

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