Durability under thermal loads of polyvinyl alcohol fibers

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ABSTRACT

In the present paper, the thermal durability of polyvinyl alcohol fibers (PVA) was studied after fiber samples had been subjected to temperatures ranging from 90°C to 250°C. Residual mechanical properties, such as tensile strength, elastic modulus and elongation at break, and physical properties, such as density were determined. Weibull statistics were used to quantify the degree of variability in fiber strength, at the different temperature. In addition, thermal analysis of PVA fibers were carried out employing thermogravimetry and differential scanning calorimetry up to the temperature of 800°C. SEM analysis of heated and unheated samples had been carried out in order to allow the identification of the changes in the microstructure of the fibers. The degradation process of PVA fibers manifests itself in a significant loss of mass, stiffness and strength of the fibers, which is progressive with increasing temperature. Thermal analysis has shown that the melting point of PVA fibers begins at approximately 200°C and thermal degradation initiates at about 239ºC. However, progressive loss in tensile strength and elastic modulus was observed starting at a temperature as low as 90°C, due to glass transition temperature of PVA fibers at approximately 66°C. At 220°C, the elastic modulus and strength were reduced at about 45% and 52%, respectively, when compared with respective values of unheated samples. With regards to Weibull modulus, the statistical parameter did not exhibit significant influence on temperature for samples heated up to 145°C, which ranged from 23.4 to 28.8. However, samples heated to 220°C showed a sudden reduction in Weibull modulus to 8.6, indicating that a significant change occurred in the populations of fracture inducing flaws at this temperature level, which clearly affect the tensile strength and Weibull modulus.

Keywords: PVA fiber, thermal durability, thermal analysis, residual properties, Weibull modulus.

1 INTRODUCTION

Polyvinyl alcohol fibers (PVA) are synthetic fibers obtained from polyviny1 acetate which is readily hydrolysed by treating an alcoholic solution with aqueous acid or alkali [1]. The fibers possess an ideal combination of properties and find applications on a large scale around the world in industry and agriculture. Items such as fishing and seaweed nets, ropes, hoses, belts, tire codes and paper making felts are made from those fibers, which serve as well as reinforcing material for cementitious composites [2, 3].

PVA fibers used for reinforcing material have the following advantages: high strength (800 – 1500MPa), elongation capacity of about 6% and high modulus of elasticity (23 - 41GPa) and furthermore do not present any health risk during usage [4, 5].

There are several types of PVA fibers, each fitting a separate application. The fibers used in this research are of type REC15, manufactured by Kuraray, Japan. REC15, one of the new types of PVA fiber, has been designed for strain hardening cementitious composites (SHCC) with the purpose to control the fiber-matrix bond, due to the hydrophilic nature of PVA fibers [6, 4, 7].

SHCC is a special type of high performance fiber reinforced cementitious composite, which exhibits a strain hardening behaviour under tension loads with multiple cracking and features a strain-stress curve with a shape similar to that of a ductile metal with yielding point [8]. The high ductility (strain capacity typically

exceeds 3%) associated with strain hardening behaviour has resulted in more durable structures [6, 9].

In order to obtain a better understanding of the thermal behaviour of SHCC, it is of great interest to study the behaviour of reinforcement fibers subjected to thermal conditions considering that, the mechanical properties of composites are highly depending on the properties of reinforcement fibers.

This study focused on the influence of high temperature exposure on PVA fibers behaviour. The fibers were investigated after being subjected to temperatures up to 250°C in terms of residual mechanical properties, such as tensile strength, elastic modulus and elongation at failure, and physical properties, such as density. To study the deterioration mechanism of PVA fibers under thermal loads, thermal analysis (TG/DTG/DSC) and microscopic analysis of heated and unheated samples had been carried out. Weibull statistics were used to quantify the degree of variability in yarn strength at different temperature levels.

2 EXPERIMENTAL PROGRAM

2.1 Material

Polyvinyl alcohol (PVA) fibers with trade-name REC15 and manufactured by Kuraray Co – Japan, with a diameter of 40 μm, density of 1.3 g/cm³, modulus of 40 GPa and tension strength of 1600 MPa (data provided by the manufacturer), was used in this experiment.

The surface of the PVA fibers is coated with a proprietary hydrophobic oiling agent of 1.2% by weight to control the interfacial bonding properties between the fiber and matrix for composite performance [6].

2.2 Heating of samples

PVA fiber samples were heated in an electric furnace from room temperature (~20°C) to peak temperatures of 90°C, 110°C, 145°C, 190°C, 220°C and 250°C at a slow increasing rate of 1°C/min. When the target peak temperature was reached, the furnace temperature was maintained for 60 minutes and then the furnace was turned off and samples were allowed to cool down to room temperature. Tests were performed when the samples were cool enough to handle.

3 TEST PROCEDURE

3.1 Thermal analysis of PVA fiber

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed in simultaneous analyses equipment TG/DTA/DSC TA – Instruments, model SDT Q600, with a 10°C/min constant heating rate, from 35 to 800°C in nitrogen flow (100mL/min). Samples of about 4mg were used in open platinum pans.

3.2 Residual density tests

Helium pycnometer model AccuPyc 1340 acquired from Micrometrics Instrument Corporation (USA) was used to measure the absolute density of unheated and after heating fiber samples. The samples, of about 3g each, were previously dried at $40 \pm 1°C$ up to constant mass and then placed in desiccators. They remained in the desiccators until they were individually removed, had their weight recorded and transferred to the pycnometer chamber.

The helium gas was then admitted into the cell chamber filling the pores. This procedure was repeated according to the number of the pre-determined runs (five were used in this work). At the end of the last run a summary report was printed out giving the density for each run, the average sample absolute density and their standard deviations.

3.3 Tensile tests

Tensile tests were performed on heated and unheated samples following the procedures established by the ASTM D3822-2007 [10]. Thirty single yarn samples with the gage length of 30 mm were tested under tension load.

For this test cardboard rectangles of 60x70mm were prepared. An opening of 20x30mm was cut into the cardboard centre to which randomly selected samples, glued to slotted paper holders, were inserted (Figure 1b). The sample with the paper holder was mounted into a tensile test rig. Tests were started after the outer edges of the cardboards were carefully cut. Samples were stretched until failure at a rate of 0.5 mm/min. A

1000N load cell was used to measure load. The tensile test rig and the sample set up are shown in Figure 1a. Before the tensile test, the cross sectional area was evaluated from the diameter measured by the scanning electron microscope for each sample. Loads and corresponding displacements were continuously recorded during the tests.
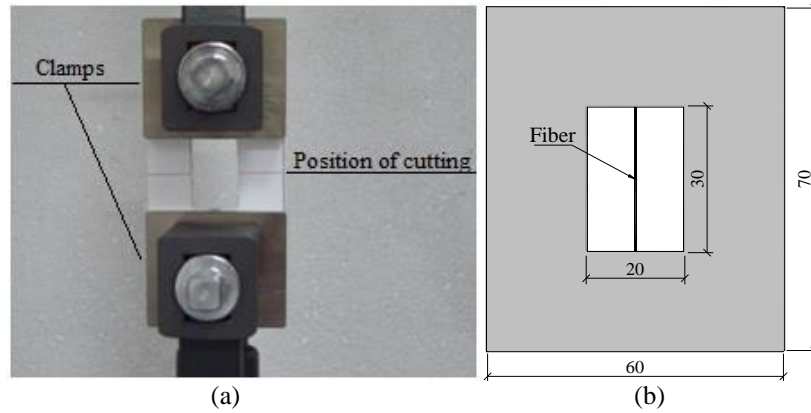

<div align="center">(a)   (b)</div>

Figure 1: Tensile test setup (a) and specimen setup (b) (all dimensions in millimeter).

To accurately measure of Young's modulus and elongation of fiber, the compliance of the loading and gripping system was determined by obtaining the force versus displacement behaviour of the fiber at various gage lengths following the methodology used by SILVA et al [11] and CHAWLA et al [12]. The total cross-head displacement during fiber testing, δt, is expressed by:

$$\frac{\delta_t}{F} = \left(\frac{1}{EA}\right) 1 + c \tag{1}$$

Where c is the machine compliance, F is the applied force, E is the Young's modulus of the fiber, and A is the cross-sectional area of the fiber. Thus, a plot of $\delta t/F$ versus l (gage length), will yield a straight line of slope $1/(EA)$ and intercept c, the compliance of the load train. As a result, the machine compliance (c) of 0.028 was obtained.

Weibull statistics were used to quantify the degree of variability in fiber failure strength at different temperature levels. According to the Weibull analysis [13, 14], the failure probability under a uniform stress state is given by:

$$P(\sigma) = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_o}\right)^m\right] \tag{2}$$

Where σ is the fiber strength for a given probability of survival, σo is defined as the characteristic strength and m is the shape parameter (often referred as Weibull modulus). The higher the value of m the lower the variability in strength.

Probabilities of failure were determined using ranking statistics [13]. Ordering the failure data from smallest to largest and assigning a ranking number i, the probabilities of failure were then assigned by the following relationship:

$$P(\sigma)_i = \frac{i}{N+1} \tag{3}$$

Where $P(\sigma)i$ is the probability of survival corresponding to its strength value and N is the total number of fibers tested. Substituting Eq. (3) into Eq. (2) yields:

$$\ln\left[\ln\left[\frac{N+1}{N+1-i}\right]\right] = m.\ln\sigma - m.\ln\sigma_o \tag{4}$$

The Weibull parameter (m) is obtained by linear regression by plotting $\ln\left[\ln\left[\frac{N+1}{N+1-i}\right]\right]$ against $\ln\sigma$.

4 EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1 Thermal analysis of PVA fiber

TG and DTG curves of PVA fibers are shown in Figure 2. The TG results indicate that the onset degradation temperature of the PVA fiber is about 239°C. Three temperature regions of mass loss can be identified in the TG/DTG curves. In the first region (239°C – 300°C) the fiber samples experienced a mass loss of about 4% due to partial dehydration of PVA accompanied by polyene formation [15, 16]. In the second region (between 300°C - 410°C), with a maximum decomposition rate at 371°C, the PVA fiber suffered a more intense mass loss of 71% due to polyene decomposition yielding low-mass oxygen containing products (such as, acetaldehyde, benzaldehyde, acrolein) and the decomposition of polyene macroradicals to cis and trans derivatives [15, 17]; while in the third region (between 410°C - 480°C), the mass loss was 20% due to thermal decomposition of primary polyenes to cis and trans derivatives followed by their cyclization and the condensation of polyaromatic structures [17]. The residual percentage of the weight was equal to 1.5% at approximately 800°C.
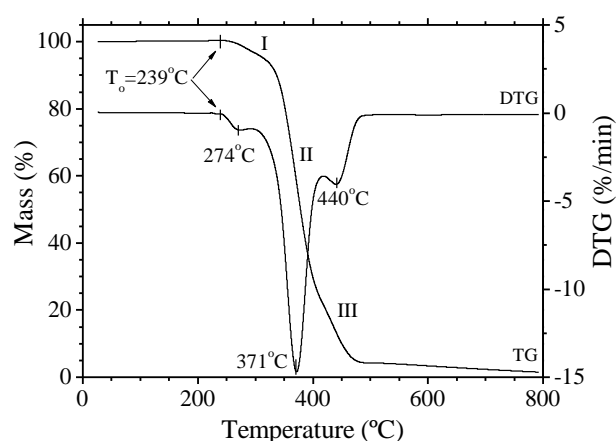

Figure 2: Thermogravimetry (TG) and differential thermogravimetry (DTG) curves

A differential scanning calorimetry (DSC) was applied for determining information of glass transition (Tg) and melting (Tm) temperatures. Figure 3a shows the DSC curve of PVA sample in the range of temperature from 20°C up to approximately 800°C. The plot shows the heat flow as a function of sample temperature and an endothermic response is oriented downwards. The onset melting temperature (To) was determined at the temperature at which a deflection from the established baseline is first observed. The value of Tg was determined by the point on the thermal curve corresponding to 1∕2 the heat flow difference between the extrapolated onset temperature (Tf) and temperature of return to baseline (Tr) in the DSC curve (Figure 3b), according to recommendation of ASTM E1356 [18].

The DSC curve shows a glass transition (Tg) of approximately 66ºC. This value of Tg is in agreement with that reported previously in the literature [19, 20]. Melting peak is observed at 244°C with an onset melting temperature (To) at 200°C. Additional endothermic and exothermic peaks are observed at 354°C and 493°C, and these are thought to be due to the degradation process of the fibers constituents.
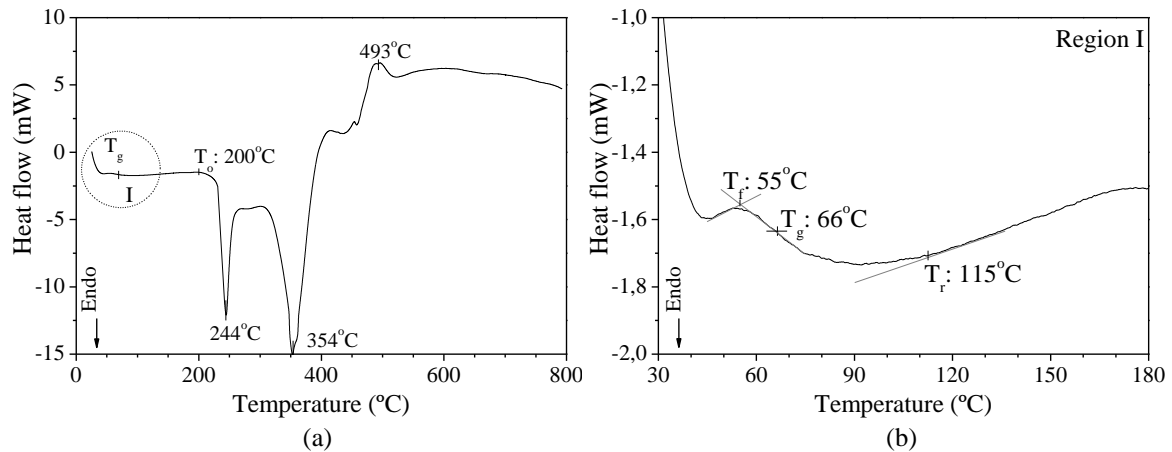
Figure 3: (a) Differential scanning calorimetry (DSC) curve and (b) DSC of the region I selected in (a)

4.2 Tensile properties of PVA fibers after exposure to elevated temperatures

The stress–strain behaviour of the PVA fiber, showing the ''as-measured'' data and that corrected for load strain compliance, is presented in Figure 4. Strain was calculated from cross-head displacement of the machine taking into account the machine compliance. Thus, the tensile strain (ε) of samples was determined by the following equation: $\varepsilon = (\Delta L\text{-}cF)/l$, where ΔL is the cross-head displacement, c the machine compliance, F the applied force and l the gage length. The initial elastic modulus was determined on the basis of corrected stress − strain curves as the tangent of the inclination angle of the straight line connecting the origin with the point corresponds to 0.4% of strain.

All samples tested (unheated and heated samples) failed in a brittle manner by exhibiting a sharp drop in strength after failure stress. The tensile strength and elastic modulus for unheated PVA were 1576.2 MPa and 39.9 GPa respectively. This finding is consistent with the work of other researchers [4, 21, 22].
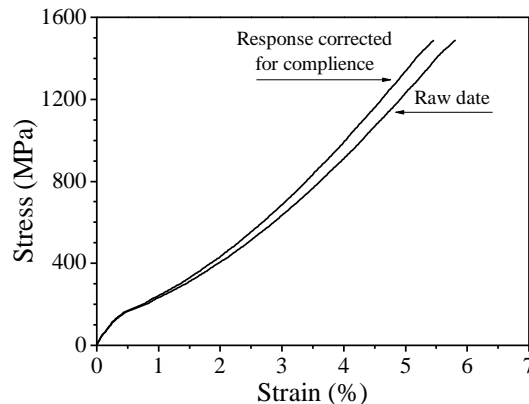

Figure 4: Stress–strain behaviour of a PVA fiber sample, showing the ''as-measured'' data and that corrected for load strain compliance.

Figure 5, Figure 6 and Figure 7 show the elastic modulus, tensile strength and elongation at break as a function of exposure temperature. The results presented show that, with an increase in temperature, the fiber degradation process identified in the TG/DTG and DSC tests resulted in reduction of fiber strength and initial elastic modulus. For example, after initial heating up to 90°C, both the elastic modulus and tensile strength of the PVA are reduced by approximately 4% and 8%. The curves also show that as peak temperature increases from 90°C to 145°C, both the elastic modulus and tensile strength continue to drop to approximately 86% and 83% of those of unheated reference samples, respectively. It's important to observe that although the PVA fibers did not show any mass loss at these temperatures (see TG/DTG curves in Figure 2) they were exposed to temperatures that are higher than the PVA glass transition temperature (~66°C), as seen in Figure 3b. The scanning electron microscopy images of the surface of unheated PVA and of the fiber samples heated to 90°C, 110°C and 145°C did not show significant sign of damage (see Figure 8).
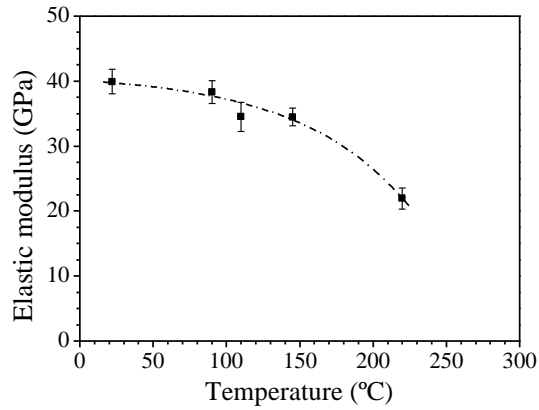
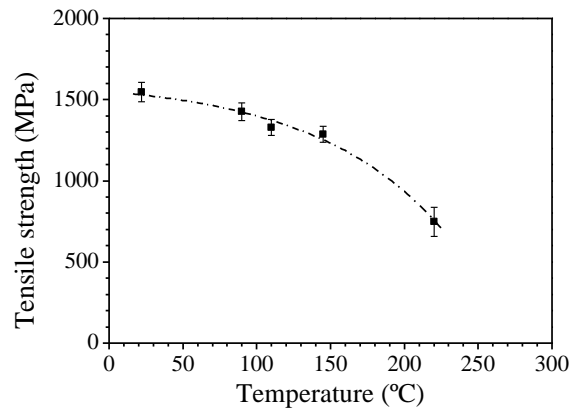**Figure 5:** Evolution of elastic modulus of PVA fiber as a function of temperature

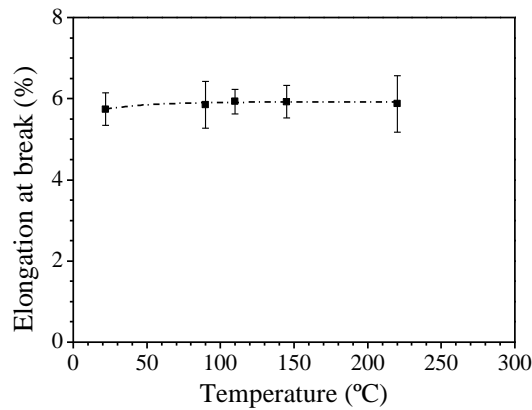**Figure 6:** Evolution of strength of PVA fiber as a function of temperature

Figure 7: Evolution of elongation at break of PVA fibers as a function of temperature

When the samples were subjected to temperatures in the range of 220-250°C the deterioration was quite significant. For example, the residual elastic modulus and strength of the fibers heated up to 220°C were approximately 50-55% of those of unheated reference samples. The fibers subjected to 250°C melted (see Figure 8f) and, therefore, tensile tests could not be performed. These results are in accordance with the TG/DTG and DSC test results (see Figure 2 and Figure 3) that indicate that the melting point of PVA fibers begins at approximately 200°C and thermal degradation initiates at about 239ºC. The microscopic analysis carried out on the surface of PVA fibers heated to temperatures of 220°C and 250°C (see Figure 8a-f) show changes on the fiber surface, especially for the fiber submitted to 250°C.

The results of elongation at break (see Figure 7) and density of PVA fiber were not affected when fibers were heated to temperatures up to 220°C.
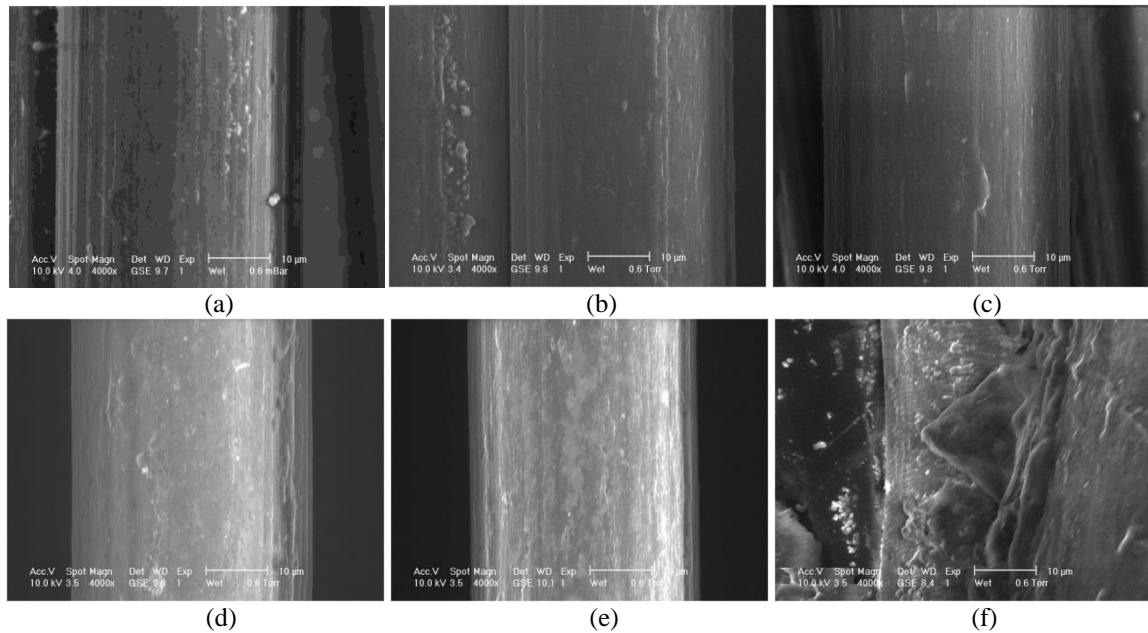
Figure 8: Scanning electron microscopy images of PVA fiber samples. Unheated (a) and after heating to 90°C (b), 110°C (c), 145°C (d), 220°C (e) and 250°C (f)

Figure 9 shows the influence of temperature on the Weibull modulus. As the Weibull modulus (m) is a measure of the amount of scatter in the sample strength, the high value of the Weibull modulus observed for PVA fiber indicates a relatively high uniformity of this fiber for temperatures up to 145°C. However, samples heated to 220°C showed a sudden drop in Weibull modulus, indicating that significant change occurred in the populations of fracture inducing flaws in this temperature level. The differences in Weibull modulus can be attributed to the nature and distribution of the flaws that may be present in the fibers after heating to a temperature that is very closed to its melting point. The appearance of these defects in the fiber, may affect not only their tensile strength but also the Weibull modulus.
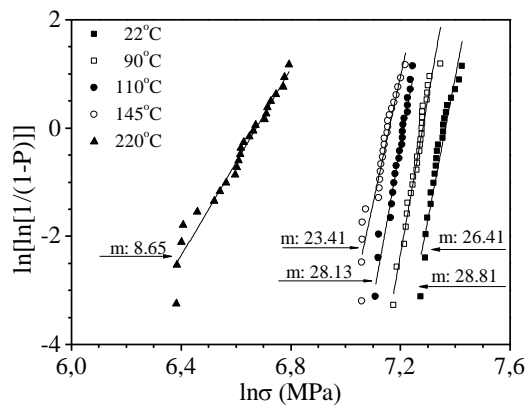

Figure 9: Weibull plots of PVA fiber at different temperatures

5 CONCLUSIONS

The experiments developed and conducted in this study delivered results on the PVA fibers behaviour, which are commonly used in manufacturing of strain hardening cementitious composites, after exposure to different temperatures levels. On the basis of the experimental results, the following conclusions can be drawn:

The presented results showed that up to 145ºC the loss in stiffness and strength of the fibers is in the range of 14-17%. At 220ºC, however, the elastic modulus and strength were reduced to approximately 55% and 48% respectively of those of unheated reference samples.

According to thermal analysis, a PVA fiber presents the glass transition temperature at approximately 66ºC and an onset melting temperature of about 200°C. In addition, the fiber begins to decompose at temperatures of approximately 239ºC.

Regarding to Weibull statistic analysis, the Weibull modulus, "m", was calculated to be 26.41 for unheated PVA sample and 28.81, 28.13, 23.41 and 8.65 for PVA samples heated up to 90ºC, 110ºC, 145ºC and 220ºC, respectively. The results clearly show that the heated PVA sample up to 220ºC has the lowest Weibull modulus and tensile strength, while there were not significant changes in the Weibull modulus for other heating temperatures.

6 ACKNOWLEDGEMENTS

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