**EFFECT OF HYDROTHERMAL AGEING ON THE MECHANICAL PROPERTIES OF FLAX FIBRE/ BIO-BASED RESIN COMPOSITES**

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**Abstract**

The aim of the present study is to evaluate the influence of hydrothermal ageing of flax fibre-reinforced bio-based epoxy resin laminates on the mechanical properties of the composites. Three different types of bio-based resins were used. Plates made of the different bio-based resins, reinforced with 8 layers plain weave flax fibers of 150 g/m2, manufactured using RTM technique. Three groups of specimens were cut out from the manufactured plates. The first one was used for the characterization of the as received materials under tensile, three-point bending and short beam test. Then the other 2 groups were immersed in distilled water at two different temperature 40oC and 60oC up to the saturation point. Following saturation, each group was divided in two. The first, wet subgroup, passed through the full characterization as the as received samples, while the second subgroup after drying at 50oC for 24 h, followed the same tests. The water absorption in all types of specimens follows a diffusion kinetic pattern which agrees to one dimensional Fickian behavior. The mechanical properties of the different composite plates after hydrothermal aging, shows a significant reduction and these properties do not return to their initial values even after drying of the specimens.

1. Introduction

The rising concern towards environmental issues and the need for more versatile polymer-based materials has led to increasing interest about polymer composites sourced from different synthesis route than petroleum. These composites originating from renewable sources are usually referred as “green” or biocomposites and may find several industrial applications. At first instance, biocomposites combine natural fibers such as flax or hemp as reinforcements and traditional thermopastic or thermoset resins as matrix materials and can be further environment-friendly when the polymer matrix comes from renewable sources as well. On the other hand some issues have to be properly addressed such as the impact of environmental factors on mechanical properties [1,2] and worse processability [3]. The current study concerns the effect of hygrothermal ageing on the basic mechanical properties of biocomposites prepared from commercially available epoxy resins reinforced with environmentally friendly synthesis routes.

2. Materials and Methods

As matrix material three bio-based epoxy resins (i) GreenPoxy 56 (supplied by Siconim, France), (ii) Super Sap INR (supplied by Entropy Resins, France) and (iii) RSF 816R-G (supplied by Axson Technologies, France) were used. As opposed to traditional epoxies that are composed primarily of petroleum-based materials, the selected material systems containing biobased renewable materials sourced as co-products or from waste streams of other industrial processes, such as wood pulp and bio-fuels production.

In all cases a 150 g/m2 flax fibre plain weave, supplied by Lineo company (France) has been used as textile reinforcement for the manufacturing of bio epoxy matrix composites utilizing the Resin Transfer Moulding (RTM) technique. Eight layers of the fabric were placed in a closed self heated mould with dimensions 300x300 mm and different composite laminates were produced using the flax fiber fabrics and the different bio based resin systems as mentioned above. Each resin was thoroughly mixed with the corresponding hardener and degassed for three minutes. outlines details about the laminates and materials utilized.

Table 1: Materials used in the present study.

|  |  |  |  |
| --- | --- | --- | --- |
| Epoxy | Hardener | Designation | Reinforcement  |
| GreenPoxy 56 | SD 8822 | GP | 150 g/m2 flax plain weave |
| GreenPoxy 56  | SZ 8525 | GZ |
| RSF 816R-G | RSF 816 | RSF |
| Super Sap INR | Super Sap INS | SP |

The hydrothermal behavior of the composite bio based materials was assessed and the impact of water absorption and corresponding effect on fundamental mechanical properties were investigated. The RTM molded composite laminates were cut to appropriate dimensions by diamond saw observing the standard requirements for the different experimental procedures. Three different groups of coupons were examined. The first group was used for the characterization of the pristine material. The pristine conditions correspond to drying the samples for 48 hours at 50oC to remove any initial moisture. The other two groups were used to assess the effect of immersion in distilled water until saturation at two different temperatures, 40oC and 60oC. All procedures followed were according to ASTM D5229/D5229 M-92 standard. Following saturation, each group was divided in two subgroups. The first subgroup, referred as “wet”, passed through the full mechanical characterization as the pristine samples. The second subgroup, was dried at 50oC for 24 h before being tested. This subgroup is referred as “dry”. The mechanical characterization tests included tensile, three-point bending and interlaminar shear stress tests.

For the tensile tests an Instron 8872 universal testing machine was utilised and the specimen’s dimensions were according to ASTM D 3039/D3039 M standard. The imposed crosshead speed was 2mm/min.

The three point bending tests were conducted according to EN ISO 14125 standard. The flexural modulus, flexural strength and strain to failure were assessed.

Finally, Interlaminar Shear Strength (ILSS) tests were carried out according to ASTM D 2344 / D 2344M standard. The span length is set to be four times the specimen thickness and the imposed deflection rate was 1.0mm/min.

3. Results and discussion

3.1 Hydrothemal ageing

In the present study, five samples per material system and temperature have been used. The average moisture content for each one of the material systems and temperatures is given in Figure 1. The symbols represent the experimental average values and the curves the respective Fickian curve.



**Figure 1:** Water absorption for flax based biocomposites at 40oC and 60oC.

From Figure 1 it is obvious that the hydrothermal behavior of the bicomposites is compatible with the Fickian model with small deviations more notable for GZ composite. The GZ composite exhibits the largest water uptake for both considered temperatures. The computed diffusion constant is 1.14 10-11 m2/sec for 40oC and 3.21 10-11 m2/sec for 60oC. GP composite showed lower water uptake reaching 9.49% at 40oC and 9.96% at 60oC. The respective diffusion constants were 2.16 10-12 m2/sec for 40oC and 9.75 10-12 m2/sec for 60oC. The composites with the least moisture uptake were the RSF and SP with very similar behavior.

**Table 2**: Moisture content at saturation $M\_{\infty }$ and diffusion constant D at 40oC and 60oC.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Bicomposite | $M\_{\infty }$, % (40oC) | D, m2/sec (40oC) | $M\_{\infty }$, % (60oC) | D, m2/sec (60oC) |
| GP | 9.49 | 2.16 10-12 | 9.96 | 9.75 10-12 |
| GZ | 12.52 | 1.14 10-11 | 13.6 | 3.21 10-11 |
| RSF | 7.23 | 2.99 10-12 | 7.68 | 3.22 10-12 |
| SP | 6.98 | 1.12 10-11 | 7.95 | 1.05 10-11 |

In general, the increase of temperature results in increasing rate of diffusion. This can be attributed in two reasons. Firstly, the temperature rise causes an increase of the diffusion of water molecules in the polymer and secondly, the saturation point is increased as well requiring more water quantities to reach equilibrium. At this point the partial pressure of the liquid environment is equal to the partial pressure of the polymer and therefore no exchange of moisture takes place. At equilibrium stage the moisture content reaches a constant value. This value is likely to be the result of two competing phenomena. On the one hand, the material reduces its weight due to chemical degradation (leaching of fiber constituents) and on the other it increases its weight from water absorption as the failures in the structure of the composite creates free spaces for its entrance [4]. The later degradation mechanism can be the reason for the deviation from the Fickian behaviour observed for GP and GZ biocomposites.

The water uptake and subsequent drying had a profound effect on sample dimensions, especially their thickness. As the samples absorb water they tend to swell increasing their thickness which reaches a maximum at saturation. Once samples are dried the absorbed water is discarded and their thickness is decreased towards the initial value. The average thickness change of the different biocomposite samples is shown in Table 3. The average change in thickness of the samples is given as percentage of the thickness in pristine condition for the considered temperatures.

**Table 3:** Thickness change (swelling) due to water absorption of biocomposite samples.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Biocomposite | Wet at 40oC (%) | Dry at 40oC (%) | Wet at 60oC (%) | Dry at 60oC (%) |
| GP | 10 | 7.39 | 12.2 | 7.88 |
| GZ | 11.39 | 4.15 | 12.66 | 6.29 |
| RSF | 6.34 | 2.56 | 9.64 | 7.22 |
| SP | 7.08 | 2.33 | 10.33 | 8.11 |

The increase in the thickness of the specimens is due to swelling of the fibers and the matrix. The increase is more pronounced as the temperature increases. This is probably the result of increased water content at 60oC compared to 40oC as evident from .

3.2. Tensile testing

Figure 2 shows the tensile stress-strain representative curves for the different biocomposite materials GP, GZ, RSF and SP at pristine state as well as after saturation “wet” and subsequent drying “dry” at the two different temperatures.

|  |  |
| --- | --- |
| (a) | (b) |
| (c) | (d) |
| **Figure 2**: Representative tensile stress-strain curves for (a) GP, (b) GZ. (c) RSF and (d) SP biocomposites. The reference curve refers to the pristine samples while the others correspond to hydrothermal ageing at 40oC and 60oC. |

It is obvious that exposure to distilled water results in significant modifications of the tensile stress-stain curves with the tensile modulus being reduced significantly with the ultimate tensile strength, while the strain to failure is increased. Initially, it is noted that hydrothermal ageing leads to a significant degradation of the modulus of elasticity, especially at the 60°C (higher degradation rates). The maximum degradation was observed in the case of GZ material at both ageing temperatures. SP is the material which is less affected with a drop of 43.06% and 56.87% at 40oC and 60oC respectively. In all cases, the drying process results in an improvement in the modulus of elasticity, since the effect of the hydrothermal ageing is reduced. The greatest effect of drying on the modulus of elasticity occurs for GZ material, which increases its value in “dry” condition by 82% at 40oC and 120% at “wet” state. Table 4 summarises the average value of tensile elastic modulus.

**Table 4:** Effect of hydrothermal ageing on tensile elastic modulus (average values) of biocomposite materials at 40oC and 60oC.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Biocomposite | Eref (GPa) | E (GPa)40oC wet | E (GPa)40oC dry | E (GPa)60oC wet | E (GPa)60oC dry |
| GP | 8.23 (± 0.16) | 4.29 (± 0.1) | 5.40 (± 0.2) | 3.15 (± 0.07) | 5.18 (± 0.06) |
| GZ | 5.64 (± 0.23) | 2.62 (± 0.1) | 4.82 (± 0.3) | 2.02 (± 0.1) | 4.46 (± 0.1) |
| RSF | 7.82 (± 0.06) | 4.27 (± 0.2) | 5.42 (± 0.1) | 3.00 (± 0.2) | 4.17 (± 0.2) |
| SP | 7.35 (± 0.09) | 4.19 (± 0.2) | 5.27 (± 0.2) | 3.17 (± 0.1) | 4.08 (± 0.1) |

A significant reduction of the tensile strength of all materials is observed after immersion in the water baths with the higher temperature resulting in greater degradation. GZ is the most sensitive material and SP the best performing one. After the drying cycle, GP, RSF and SP materials are observed to have suffered a further tensile strength reduction. However, this is not the case for GZ material as drying seems to improve its strength. Hydrothermal cycling has a pronounced effect in strain to failure as water absorption results in increased ultimate values which become greater as the temperature increases. When the samples were dried the strain to failure tends to decrease. The effect of water absorption on the ultimate tensile strength and strain to failure is given in Table 5.

**Table 5:** Effect of hydrothermal ageing on tensile ultimate strength $F\_{tu}^{ref}$and strain $ε\_{tu}$ (average values) of biocomposite materials at 40oC and 60oC.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Biocomposite | $F\_{tu}^{ref}$(MPa) | $ε\_{tu}^{ref}$(%) | $F\_{tu}$ (MPa) | $ε\_{tu}$ (%) | $F\_{tu}$ (MPa) | $ε\_{tu}$ (%) | $F\_{tu}$ (MPa) | $ε\_{tu}$ (%) | $F\_{tu}$ (MPa) | $ε\_{tu}$ (%) |
|  |  |  | 40oC wet | 40oC dry | 60oC wet | 60oC dry |
| GP | 103.27 (± 1.7) | 2.01 (±0.02) | 90.92 (± 1.6) | 4.09 (±0.02) | 73.76 (±1.5) | 2.53 (±0.03) | 83.08 (± 1.5)  | 4.64 (±0.04) | 73.33 (± 1.3) | 2.79 (±0.02) |
| GZ | 77.66 (± 2.5) | 2.14 (±0.02) | 57.27 (± 1.5) | 3.63 (±0.01) | 65.74 (±1.4) | 2.50 (±0.04) | 51.26 (± 1.2) | 4.02(±0.02) | 62.05 (± 1.1) | 2.99 (±0.02) |
| RSF | 99.67 (± 1.4) | 2.09 (±0.07) | 86.89 (± 1.5) | 4.22 (±0.02) | 70.36 (±1.5) | 2.33(±0.02) | 77.23 (± 1.3) | 4.97 (±0.04) | 65.32 (± 1.3) | 2.42 (±0.02) |
| SP | 88.07 (± 2.1) | 2.80 (±0.12) | 82.00 (± 1.4) | 6.25 (±0.03) | 75.91 (±1.5) | 3.33(±0.03) | 75.61 (± 1.4) | 6.52 (±0.06) | 64.82 (± 1.2) | 4.39 (±0.05) |

The reduction in elastic modulus and tensile strength following hydrothermal ageing can be mainly attributed to the degradation of the flax fiber structure and to the compromise of the fibre and matrix interface [5]. More specifically, the multilayer structure of flax fibres leads to various interfaces between its components. Thus, water can directly affect the hydrophilic components and then weaken the interface between the layers [6]. In addition, flax fibers are not completely separated during the manufacturing process as they are in bundles in which the resin encounters difficulties to penetrate. Therefore, the absorbed water can weaken the interface between the elementary fibers and cause microcracks, which affect the mechanical properties of the composite material [7]. Another factor degrading the tensile strength and modulus in “wet” state is that flax fibers undergo a change in their bulk (swelling) which leads to stress concentrations at the matrix-fibre interface [3,8].

The increase in strain to failure can be attributed to the plasticization caused by the infusion of water molecules within the composite [9]. Furthermore, fibres can slide over each other during loading which leads to larger distortion and elongation.

After the drying process, as shown in the above diagrams, the strain to failure is greatly reduced, the modulus of elasticity increases and the strength decreases. These results are in line with different studies reported in literature [9, 10]. The increase in the tensile modulus is probably due to the reversible nature of the effect of the mechanisms occurring during water absorption such as plasticization and swelling of the fibres. With water removal, drying procedure, the fibre and the matrix are dried and become more brittle resulting in reduced strain to failure of the composite.

The tensile strength reduction is due to further matrix cracking, which leads to reduced load transfer capacity to the fibres. The removal of the water after drying, possibly created discontinuities due to the formation of voids which were covered in water at the wet state. Another possible mechanism for weakening of the fibre-matrix interface is the different degree of shrinkage of the materials after drying, which leads to further disruption of the interfacial bonds.

3.3. Three point bending test

The flexural modulus and strength are reduced considerably after water immersion. This is probably due to degrading effect of water to the fidre-matrix adhesion. As discussed in the previous section, possible mechanisms include fiber and matrix swelling, excessive matrix cracking, material plasticisation, degradation of the cellulose structure and fiber sliding. Similar effects have been reported for cotton [11] and sisal/coconut coir [12] natural fiber composites. The respective data are given in . Drying the samples results in a small recovery of flexural modulus.

Table 6: Effect of hydrothermal ageing on flexural modulus (Ef) and strength $σ\_{f}^{fu}\_{ref}$ of biocomposite materials at 40oC and 60oC (average values).

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Biocomposite | Ef ref(GPa) | $$σ\_{f}^{fu}\_{ref}$$(MPa) | Ef (GPa) | $$σ\_{f}^{fu}\_{ref}$$(MPa) | Ef (GPa) | $$σ\_{f}^{fu}\_{ref}$$(MPa) | Ef (GPa) | $$σ\_{f}^{fu}\_{ref}$$(MPa) | Ef (GPa) | $$σ\_{f}^{fu}\_{ref}$$(MPa) |
|  | ref | 40oC wet | 40oC dry | 60oC wet | 60oC dry |
| GP | 7.18 (±0.05) | 167.03 (±0.38) | 3.85 (±0.04) | 96.03 (±3.5) | 3.94 (±0.02) | 113.43 (±3.3) | 2.56 (±0.02) | 83.50 (±2.9) | 3.54 (±0.03) | 110.92 (±3.2) |
| GZ | 5.71 (±0.03) | 111.88 (±6.5) | 2.57 (±0.02) | 65.80 (±2.8) | 2.88 (±0.03) | 69.44 (±2.1) | 2.47 (±0.01) | 53.36 (±2.2) | 2.68 (±0.01) | 59.96 (±3.4) |
| RSF | 6.90 (±0.12) | 165.97 (±3.8) | 3.73 (±0.03) | 105.76 (±2.3) | 5.15 (±0.04) | 113.86 (±3.4) | 2.88 (±0.03) | 89.32 (±3.2) | 3.40 (±0.02) | 89.32 (±2.2) |
| SP | 7.38 (±0.09) | 167.82 (±2.4) | 5.47 (±0.05) | 106.93 (±2.1) | 5.65 (±0.04) | 118.77 (±3.5) | 3.71 (±0.02) | 91.77 (±3.1) | 4.05 (±0.04) | 89.45 (±2.1) |

3.4. Short beam test

Similarly to the aforementioned mechanical properties, interlaminar shear strength is affected by water absorption and subsequent drying as shown in . The maximum degradation is observed in GP material (-23.03%) at 60°C. Degradation of shear strength may be associated with weakening of the fiber and matrix bond due to moisture absorption.

**Table 7:** Effect of hydrothermal ageing on interlaminar shear strength ($F\_{sbs ref} $) of biocomposite materials at 40oC and 60oC (average values).

|  |  |
| --- | --- |
| Biocomposite | Fsbs (MPa) |
|  | ref | 40oC wet | 40oC dry | 60oC wet | 60oC dry |
| GP | 22.1 (±0.46) | 17.97 (±1.3) | 18.76 (±1.1) | 17.01 (±1.2) | 18.76 (±1.3) |
| GZ | 17.25 (±0.7) | 14.02 (±1.1) | 14.84 (±1.2) | 13.69 (±1.1) | 13.17 (±1.2) |
| RSF | 24.40 (±1.5) | 23.05 (±1.5) | 20.30 (±1.1) | 21.42 (±1.3) | 18.84 (±1.3) |
| SP | 24.13 (±1.2) | 20.67 (±1.4) | 18.87 (±1.3) | 20.68 (±1.3) | 19.80 (±1.4) |

After drying, some materials improve their interlaminar strength, while others lead to further downgrading of the shear strength. It should be noted that even for in the case of strength improvement, the eventual value is significantly less than that of reference samples. As in the previous cases, drying can have a beneficial effect. On the other hand, fiber “peeling” and degradation of fibre-matrix interface bonds are mechanisms associated with irreversible changes.

4. Conclusions

The effect of hydrothermal ageing on the mechanical properties of flax biocomposites materials has been investigated. The coupons were prepared by RTM method. The type of resin and water temperature was the key parameters that have affected water absorption of biocomposite materials. The results show that for the same ageing temperature, GZ material absorbs the highest water content, while the SP material the smallest among the four material systems that were investigated. In all cases the water uptake at 60oC was higher than that of 40oC and the absorption behavior can be adequately approximated by the one-dimensional Fickian model. Hydrothermal ageing is found to degrade all mechanical properties to a significant extend with the degradation being more pronounced for the ageing temperature of 60oC. GZ material shows the greatest degradation in strength and modulus of elasticity in tension while SP is the least affected.

A drying cycle following the water saturation affects the mechanical properties in different ways with a general trend to partial recovery of the initially properties. The tensile modulus is increased but the tensile strength and strain to failure decreased. The flexural properties are only marginally affected and the shear strength is further reduced for all materials except GP for which a slight increase was recorded. It should be noted that hydrothermal ageing had a pronounced effect on coupon dimensions, especially their thickness which can increase up to 12.6% for GZ material at 60oC. The material that is less affected is the SP with 10.33% thickness increase at 60oC and with no significant swelling after drying at 40oC of 2.33%.

In summary, the hydrothermal ageing of composite materials with flax fibers is a complex phenomenon as it includes a set of mechanisms that degrade the materials and thus their mechanical properties. The basic active mechanisms are the plasticization of the matrix due to moisture, the fiber and matrix swelling, the microstructure damage and the degradation of the fiber-matrix interface. Other mechanism includes the differential fiber and matrix shrinkage and formation of matrix cracks.

Upon water removal, due to drying, some of the properties are recovered as the mechanisms that cause the degradation like plasticization, swelling and sliding of the fibers are reversible. This recovery however is only partial since outer fiber layer decomposition and interface bond disruption leads to irreversible changes and have a permanent impact on mechanical properties.

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