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ORIGINAL CONTRIBUTION

Proposition of an Accelerated Ageing Method for Natural Fibre/Polylactic Acid Composite

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Abstract Natural fibre composite based on polylactic acid (PLA) composite is of special interest because it is entirely from renewable resources and biodegradable. Some samples of jute/PLA composite and PLA alone made 6 years ago and kept in tropical climate on a shelf shows too fast ageing degradation. In this work, an accelerated ageing method for natural fibres/PLA composite is proposed and tested. Experiment was carried out with jute and flax fibre/PLA composite. The method was compared with the standard ISO 1037-06a. The residual flexural strength after ageing test was compared with the one of common wood-based panels and of real aged samples prepared 6 years ago.

Keywords Natural fibre composite · Ageing · Polylactic acid

Introduction

Increase of crude oil prices and growing environmental awareness have aroused interests in green products in the past years. Natural fibres have proved to be an efficient reinforcement for natural fibre composites (NFC), having high specific strength and reduced weight, cost and carbon footprint [1]. Furthermore, NFC can be made fully biodegradable when used as a biodegradable bioplastic such as PLA. Yet this biodegradation must not occur too fast notably when the product is in service because it can lead to a loss in mechanical properties and aesthetic. Furthermore, a short lifespan of the product is not eco-friendly because the environmental superiority of NFC may vanish if its components have significantly lower operating life compared to non-eco-friendly competitor materials such as glass fibre/polyester composite [2]. Those parameters have to be understood and controlled.

Accelerated aging is an artificial procedure for establishing the lifespan or shelf life of a product in an expedited manner when actual lifespan data is unavailable. They are often made at elevated temperatures, in order to accelerate chemical breakdown [3].

From the past work, it has been observed that samples of PLA alone and PLA/jute composite made 6 years ago and kept in a room in a humid tropical region (Kolkata, daily mean room temperature 29 °C, 72 % relative humidity (Rh) [4]) presents some degradation such as brittleness, surface fibre peeling, delamination and decrease in bending strength (Fig. 1).

Most degradations have been observed during the 4 months monsoon season of West Bengal (June–July–August–September) when Rh is 100 % for 70 days, an average daily high temperature of 32.7 °C, with pick at 42 °C [4].

After new flexural measurements, this observation was confirmed as the untreated aged composite has lost 48 % of its strength in 6 years. Thus this too fast ageing is not acceptable for an interior use such as furniture and for quality products. Even if the material is used in temperate climate, such degradation could occur next to a heat source or in a damp environment and has to be controlled and improved.

This fast biodegradation did not occur equally on all the samples. It has been observed that a 6 years old sample

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Fig. 1 An old sample with degradation (lamination)

with jute fibre treated with sodium hydroxide (NaOH) shows lower degradation than the untreated ones.

During the flexural test, the fibre pull out is much more predominant in the untreated aged composites (Fig. 2a) than in the NaOH treated aged composites (Fig. 2b). The flexural measurements revealed that the NaOH treated aged composite has lost 22 % of its strength in 6 years compared to 52 % observed for the untreated aged composite. This indicates that a fibre treatment helps in reducing the degradation by a better adhesion of the fibre to the matrix and the mechanism has to be understood.

A previous study on water absorption of the jute/PLA composite [5] demonstrates that NaOH treated jute/PLA is also more water resistant than untreated one.

SEM observation of this 6 years old aged composite shows that a quite similar degradation has occurred in the sample put in water for 24 h (Fig. 3).

Thus it can be deduced that water absorption (high Rh of tropical climate [4]) is involved in the ageing of the fibre and the NaOH treatment enhances resistance to degradation mechanism. In the same study [5], it is demonstrated that the degradation of the fibre/matrix adhesion is provoked by water absorption of the fibre, resulting in a diameter expansion and then reduction after drying. It contribute to the loss of compatibilization between fibres and matrix, which results in debonding, weakening of the interfacial adhesion, generation of internal stresses and delamination [6].

Over the last two decades, many researchers have focused on improving the interfacial adhesion by modifying the fibre surfaces via physical and chemical treatments to enhance the chemical compatibility with the matrix [7], which prevents water swelling of the fibre besides improving the mechanical strength. The main component of the natural fibre is cellulose, which is held by hemicellulose and several fibres are cemented together by lignin. The water is mostly absorbed by the lignin and the hemicellulose of the fibre [8]. Those two components contain hydroxyl and other oxygenated groups that attract moisture through hydrogen bonding. Thus it becomes important to remove the lignin and the hemicellulose to reduce the water absorption of the fibre. The chemicals to be used for chemical modification must be capable of it, as NaOH does [9].

It appears that pieces of PLA without fibres also got degraded by itself after 6 years and is also responsible for the too fast degradation of the composite. PLA, as a biodegradable material, is highly sensitive to moisture, as well as to temperature rise [10]. In active compost, PLA will degrade quickly and disintegrate within weeks to months. Georgette et al. [11] explain the mechanism of environmental degradation of the PLA. The primary mechanism of degradation is hydrolysis, followed by bacterial attack on the fragmented residues. During the initial phases of degradation, the high molecular weight polyester chains hydrolyze to lower molecular weight oligomers. The

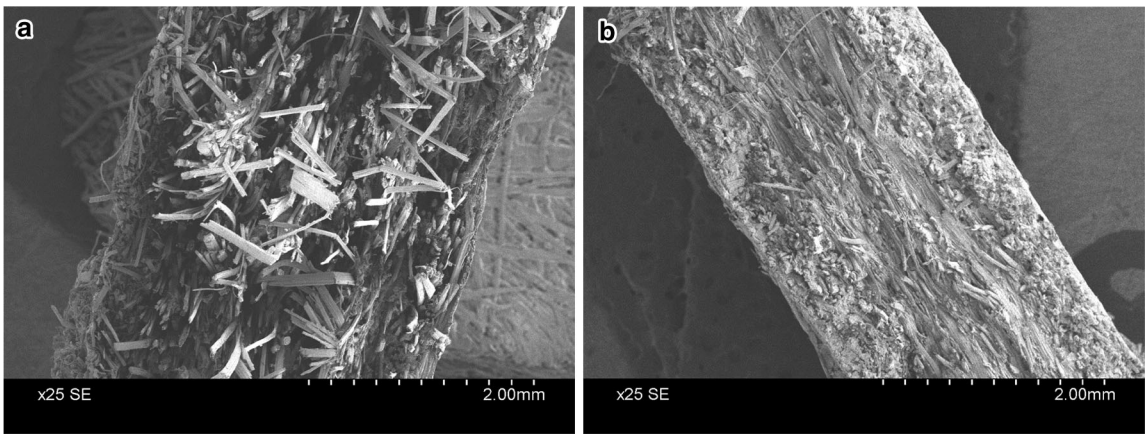

Fig. 2 Samples made 6 years back and after recent bending test. More fibres are pulled out of the untreated composite (**a**), than of NaOH treated one (**b**)

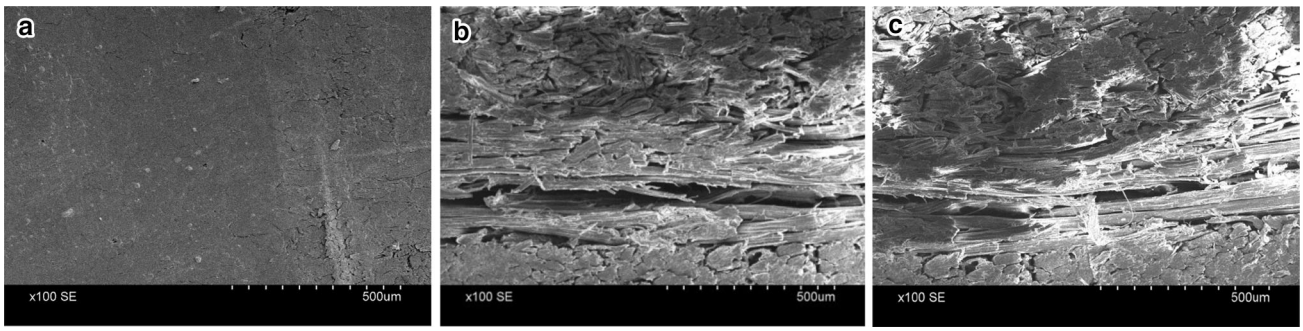

Fig. 3 SEM view of cut edges of **a** untreated samples, **b** of the same sample after 24 h into water and **c** of a real old aged untreated sample

rate of hydrolysis is accelerated by acids or bases and is dependent on the moisture content and temperature.

Ho et al. [12] showed that hydrolysis occurs for extruded PLA films after more or less 10 weeks at 50 and 100 % relative humidity at 25 °C (Fig. 4). When kept for 2 weeks at 22 °C (RH 33 or 53–54 or 97–98 %), no changes were observed for molecular weight distribution and for thermal properties (Tg, Tm, Td). And after 2 weeks at 50 °C (RH 33 or 51 or 96 %) the Mw was decreased with the increase of RH and with the time of experiment [12].

Blending the PLA with natural fibres which naturally contains or attracts moisture by capillarity can extend the hydrolisation and environmental attack possibilities of the PLA [6]. Thus temperature and humidity are both responsible for the too fast ageing of the NFC/PLA composite and accelerating the degradation process [13].

A common accelerated aging technique is based on Arrhenius equation, quoted for paper industry and for polymers aging measurement. Yet this equation has frequently been criticized in the last decade quoting on the fact that it takes into account only temperature rise and not humidity parameters and moisture content of the cellulose fibres [3]. It has been shown that an increase in relative humidity (RH) rate is also important in the degradation of biopolymer such as PLA and of natural fibres [14].

A test standard to evaluate the ageing behaviour of natural fibre composite for interior application doesn't exist. Furthermore, ageing tests for wood-based panels (WBP) for an interior application don't exist either (ASTM D1037 is for an exterior application). Ageing tests for plastics are not applicable to PLA and biocomposites as they do not take into account the humidity which is important regarding PLA hydrolysis and water absorption of natural fibres. Long-lasting PLA is not a priority in research as biodegradation is a marketing and eco-friendly advantage for this plastic used for packaging. Yet, ageing of biocomposite is a crucial consideration for longer-lasting applications and it has not been well developed.

The accelerated-aging test ASTM D 1037 [15] is intended for exterior use of WBP, but it has been chosen here because it takes into account the humidity and temperature variation which occurs in lesser extent in interior space and are responsible of the biocomposite degradation. Furthermore, the future use of this biocomposite (i.e. furniture) is closer to wood-based materials than synthetic composite or plastic applications. Finally, WBP are also made of cellulose fibre (wood fibre) similar to that of jute or flax fibres. All cellulose fibres absorb moisture in their cell and it is well-known that WBP must not be used in potentially damp applications because it would cause a certain amount

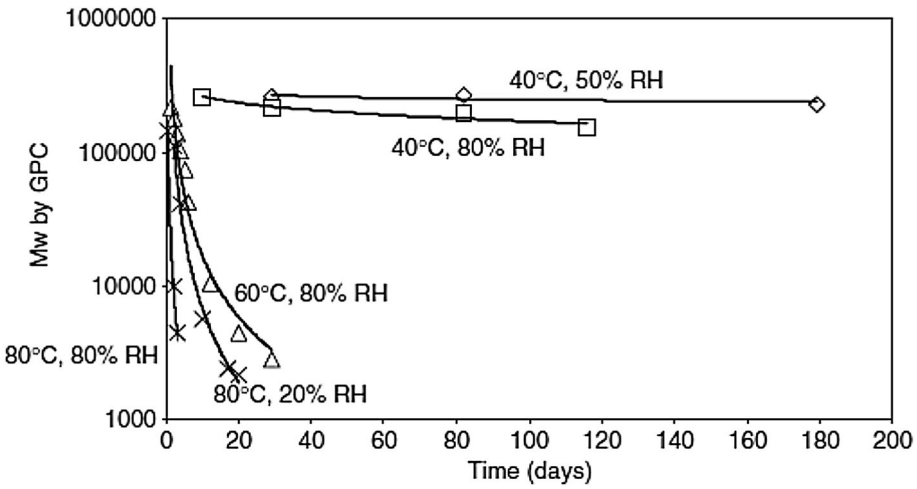

Fig. 4 The degradation of PLA (molecular weight loss) stored at various aggressive temperatures and humidity [12]

of surface disfigurement [16]. Due to similar chemical characteristics, WBP and NFC should react quite similarly to the ageing test.

However, the 6 cycle tests recommended in the ASTM are probably damaging this material too much and hence, should be limited to 1–3 cycles. The loss in mechanical properties will be compared to the loss in properties of the samples made some years ago.

The ASTM method consists of 6 cycles consisting of of six steps of immersion, steaming, freezing and drying in oven and requires 12 full days. After cyclic tests, strength reduction is acceptable if less than 50 % and deflection (deformation) increase is less than 100 % than that of un-cycled controls [16] for an exterior application. There is no specification for interior use.

A simplification of the test has been tried in order to shorten the 12 days test duration as required for the ASTM 1037-06a test method and to verify more easily if some improvements have been brought to the material. Relating to the article [17], it has been observed that the step of steaming the samples for 3 h has the most degrading action on the WBP, whereas, eliminating the 20-h freezing step from the exposure cycle did not significantly affect test results. In [18], the aging test on WBP has been shortened to repeated boiling/dry test, and one cycle (1 h boiling then drying) has been stated to be nearly equivalent to the WBP lost strength of 1 year outside. 20 cycles of boiled/dried reduce WBP strength by more than 90 %. 40 cycles were found to be equivalent to the degradation of standards for exterior plywood during 5 years outside. Yet, it is also mentioned that even if the ASTM D-1037 accelerated-aging test (or WCAMA test 6.1) is useful for quality control, this type of test should not be assumed to predict the number of years of exterior-type board products because the problem is not knowing each board's current degradation rate [17]. However, a correlation between indoor and outdoor resistance, which also depends on the degradation rate of each material doesn't exist in literature. Consequently, the ageing tests done here are mostly comparative and cannot predict an exact lifespan. ASTM 1037 and boil/dry ageing test are chosen to be tested on jute and flax/PLA biocomposite and WBP and results are compared.

Material and Method

Jute fibres were provided by Gloster Jute Mills Ltd, Kolkata. The PLA was bought from Sidaplast Ltd, Belgium. The trimethoxymethylsilane and maleated polypropylene were purchased from Sigma-Aldrich, India. The sodium hydroxide was purchased from Industrial and Chemical Concern, Kolkata. Plywood, MDF and particle board and HPL (High Pressure Laminate) from Green-Ply Ltd Company, Kolkata were used for comparison.

The samples were made of 50 % of fibre and prepared exactly like the 6 years old samples. NaOH treatment is carried out by immersing the fibre in 2 % NaOH solution for 2 h, and then dried for 48 h in air. The fibres are aligned in parallel in each layer and the layers of fibres (12 layers) are stacked with sheets of matrix material and oriented in 0/90 direction to form a cross-ply composite. Then they were compression moulded to form the laminate at 180 °C and 19.61 MPa pressure, and cooled with an external cooling system. Only well impregnated samples were taken into consideration in this study. They were cut into the same size as the real aged composites: 120 × 13 × 5 mm sized samples for boil/dry test, 6 pieces of same composition, and 170 × 52 × 5 mm sized samples for ASTM D1037, 3 pieces of same composition. The samples for ageing test were taken from the same board than the non-aged ones for flexural test.

The sample codes are:

- Old Unt. are 6 years old real aged samples with untreated jute and PLA.
- Old NaOH are 6 years old aged samples of NaOH treated jute. The fibres have been immersed in a 2 % NaOH solution for 2 h.
- Unt. Jute and NaOH jute are untreated jute/PLA or NaOH jute/PLA composite, samples made recently with the same parameters as that of the real aged samples.
- Unt. Flax and NaOH flax are untreated flax/PLA and NaOH treated flax/PLA composite, made recently with the same parameters as the other one.
- Plywood, MDF and particle board and HPL samples are cut in the same dimension, have the same thickness and the same number of pieces.

They undergo the boil/dry test for different hours (xh, b/d) for the 120 × 13 × 5 mm sized samples, and the first cycle of ASTM D1037 for 170 × 52 × 5 mm sized samples.

The boil/dry test follows the simplification of the ASTM method proposed previously. It consists of boiling the 120 × 13 × 5 mm samples for 15, 30 or 60 min, followed by drying at room temperature for 24 h.

The ASTM D1037 test consists of 6 cycling test of six treatment steps comprising:

– Immersion in water at 49 °C for 1 h,
– Steaming at 93 °C for 3 h
– Freezing at −12 °C for 20 h
– Drying at 99 °C for 3 h,
– Steaming at 93 °C for 3 h,

– Drying at 99 °C for 18 h.

Only one cycle with the 6 treatment is done. The samples are of 170 × 52 × 5 mm dimensions. After the accelerated aging test the specimens are conditioned at 65 % RH at 20 °C room temperature for 48 h.

Thickness and weights are measured before and 5 min after ageing test. An average of the thickness swell and weight gain (I_{tw}) is calculated as follows:

- % increase in thickness (I_t)

$$I_t = [(t - T)/T] \times 100 \quad (1)$$

where t is the initial thickness and T is the thickness after boiling in mm.

- % increase in weight (I_w)

$$I_w = [(w - W)/W] \times 100 \quad (2)$$

where w is the initial weight and W is the weight after boiling.

- Average increase in thickness and weight (I_{tw})

$$I_{tw} = (I_t + I_w)/2 \quad (3)$$

Flexural strength is measured using a universal Instrom machine model 4400 and following ASTM D1037 and ASTM D638, depending on the size of the samples. The aged samples strength has been calculated based on the initial thickness and width.

The residual flexural strength (RS) is the percentage of remaining strength after ageing. It is calculated doing an average on 5 or 3 similar samples of each type. It is based on the yield strength and is calculated using Eq. 4.

$$RS\ (\%) = [(S_i - S_a)/S_i] \times 100 \quad (4)$$

where S_i is the initial flexural strength and S_a is the flexural strength after aging test.

At the contrary, the loss in flexural strength (LS) is calculated as follows:

$$LS = 100 - RS \quad (5)$$

Discussion

Visual Observation

It can be observed that a light discolouration occurs on the surface of the real 6 years old aged sample in Fig. 5a. The NaOH samples after 2 h boil/dry (Fig. 5b) appears a lot more discoloured than the real aged sample (Fig. 5a). The sample submitted to 1/2 h of boil/dry test (Fig. 5c). exhibits quite same visual degradation than the 6 year old NaOH sample (Fig. 5a)

Visually, real aged or accelerated aged samples both show some discolorations, delaminations or surface fibre pull-out, depending on the sample composition and time of boil/dry test (Fig. 6). We can see in Fig. 6a an improperly impregnated sample from bad pressing condition and this sample is not taken into consideration for further work. Figure 6b is a NaOH treated and well impregnated sample which exhibits visually less physical degradation than (Fig. 6a). Figure 6c is an untreated well impregnated sample which exhibits discolouration, thickness swelling and delamination.

It can be seen in Fig. 7 that the only visual difference between flax and jute samples after ageing is that the flax sample is a little more discoloured.

From visual observations, 30 min boil/dry shows quite the same damage as that of the 6 years real aged samples and 1 cycle ASTM D1307 seems to cause more damages.

Flexural Measurement of Real and Artificially Aged Samples

As said before, the real aged untreated samples retained 54 % of strength compared to its original strength, which is not a proof of high quality. The old 2 % NaOH 2 h treated samples conserve 78 % of their strength which proves that they are more durable and damaged to a lower extent.

On analysis of Fig. 8, it was found that untreated and NaOH treated jute and flax samples, boiled for only half an hour, have represented approximately the same remaining strength as that of the 6 years real aged ones (54 and 84 % respectively for jute, 41 and 84 % for flax). It means that 6 years ageing in a tropical climate is represented approximately through 30 min of boil/dry test in residual strength, in the condition of this experimentation. 15 min of boil/dry was not enough, 45 min of boil/dry was too high (where steaming was done for 6 h) on bigger samples shows higher degradation (41 % residual strength) and is equivalent to 45 min boil/dry test. Yet no change has been observed visually and physically (thickness and weight measurement) after freezing at −12 °C for 20 h and drying at 99 °C for 21 h, confirming that the attempt of shortening the ASTM D1034 ageing test for WBP as reported in earlier work [17], is practicable for NFC. A significant change occurred after 1 h in 49 °C water and after steaming for 6 h, but not as fast as with a boil/dry test. It means that 6 h steaming plus 1 h immersion at 49 °C gives 11 % less residual strength than half an hour boil/dry, which is a lot more time consuming in experimentation although shows quite the same result. The boil/dry test also saves material sample compared to the ASTM D1037 and with more accurate results because of the possibility of stopping the test at a specific moment. Bigger size samples are also more resistant to the test than smaller samples.

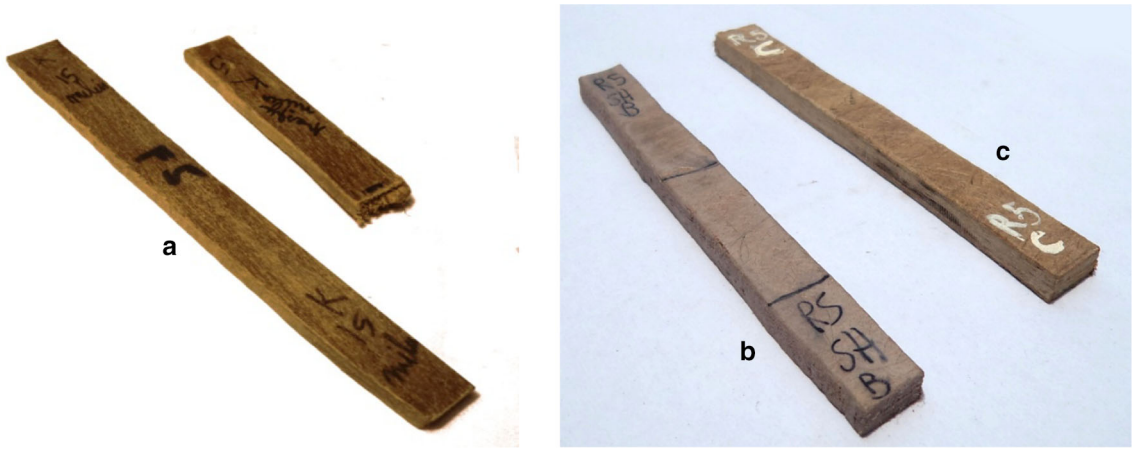

Fig. 5 A real aged NaOH sample (**a**), an NaOH samples after 2 h boil/dry test (**b**) and after 1/2 h boil/dry test (**c**)

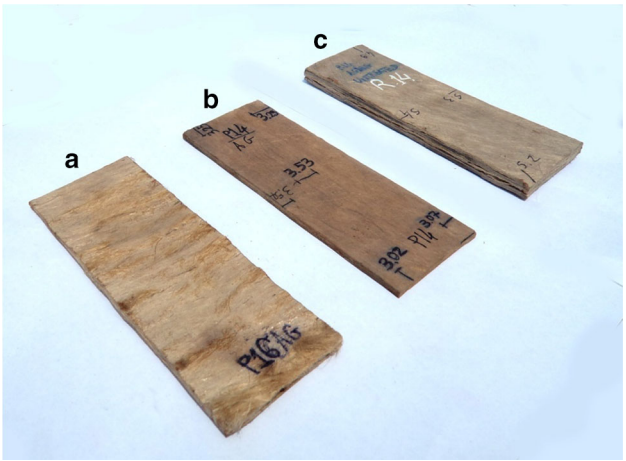

Fig. 6 Different samples after 1 cycle of ASTM D1037

As expected from real aged samples, NaOH treatment (2 %, 2 h) also shows some improvement with the boil/dry test (+29 % than untreated samples, 30 min boil/dry). NaOH treated jute or flax shows quite the same resistance at 30 min boil/dry, so it seems that they are equally resistant with real ageing. However, real 6 years old aged flax samples haven't been made for establishing an ageing test correlation with flax. Untreated flax is less resistant to the test than untreated jute (13 % less) which may be explained by a lesser adhesion of the flax fibre to the matrix when flax is untreated. Increasing the boil/dry timing (15, 30 or 45 min) is logically decreasing the strength of the treated or untreated jute composite.

Those WBP are the ones commonly used for interior use and furnishing. It can be seen that the jute and flax PLA

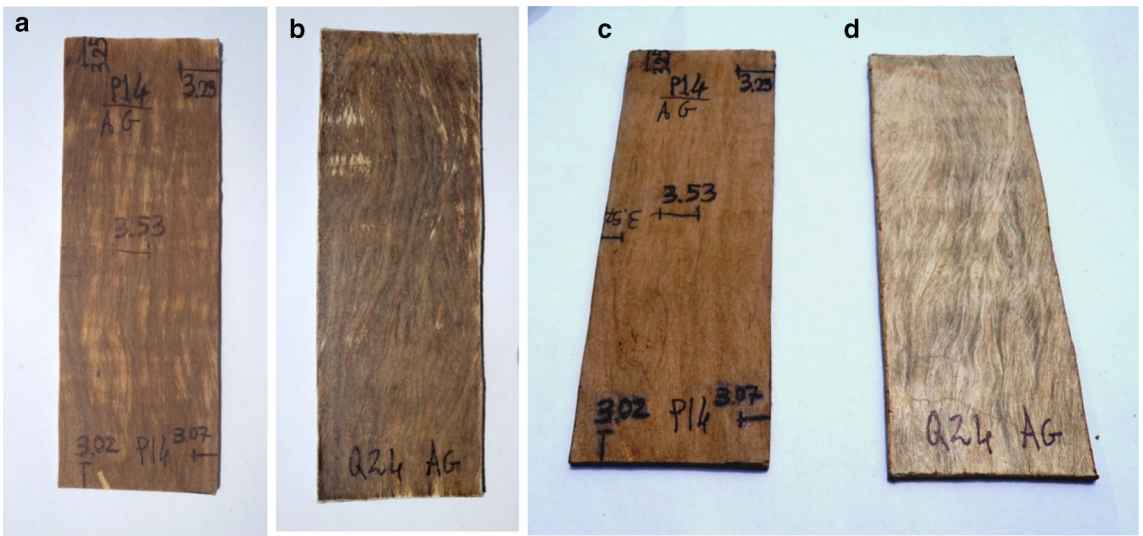

Fig. 7 Samples before ageing: **a**, **b** are NaOH treated jute and flax sample respectively; **c**, **d** are same samples after 1 cycle of ASTM D1037

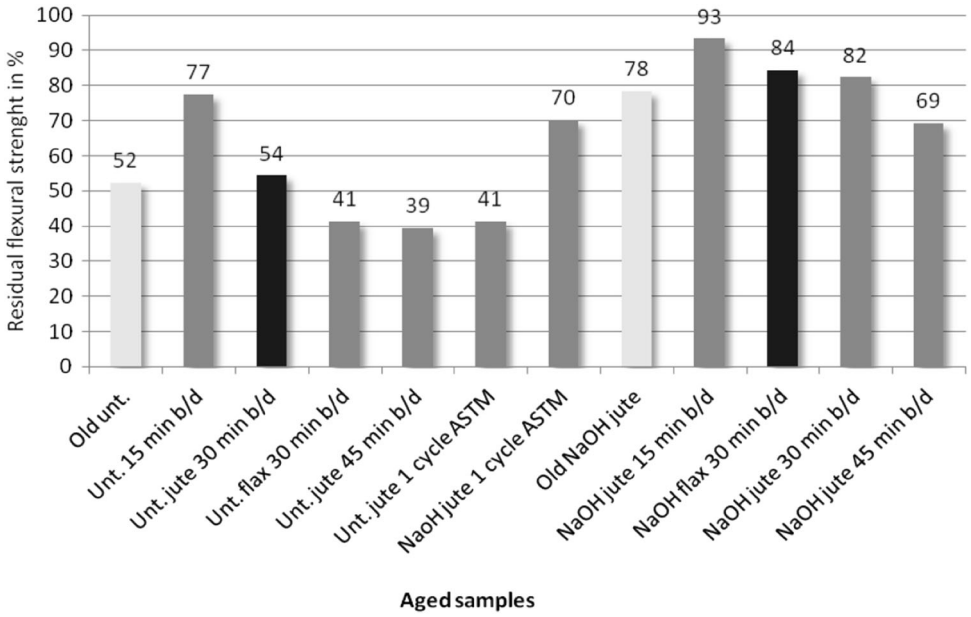

Fig. 8 The residual flexural yield of various jute composite in percentage and correlation with real aged samples

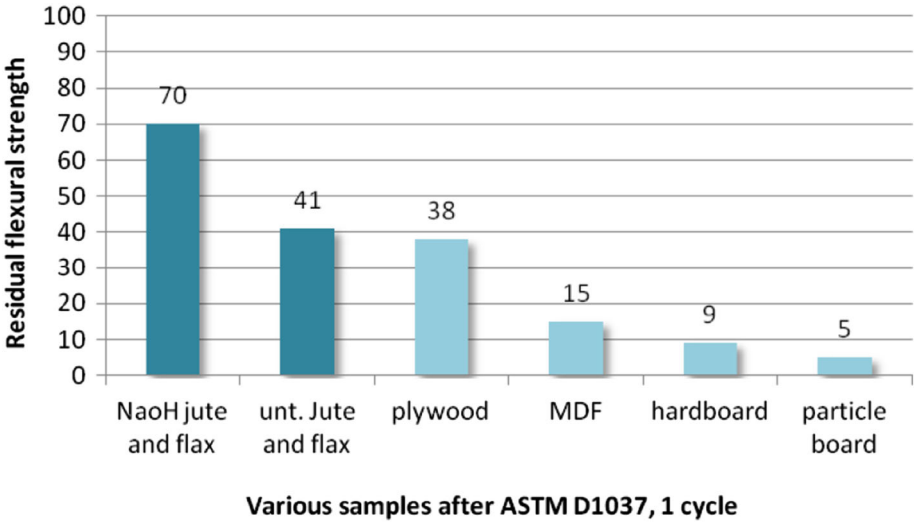

Fig. 9 Comparing the residual flexural strength in percentage of untreated and NaOH treated composite with some WBP

composites are more resistant than all of them after the boil/dry test (Fig. 9). NaOH treated jute or flax composite are 12 times more resistant than particle board to the test. It suggests that the NaOH treated composites would be longer lasting in tropical climate than those common WBP. Yet it cannot be fully asserted without real WBP aged in the same conditions as that of NFC and also due to PLA degradation behaviour.

Conclusion

It should be kept in mind that the aging of a material depends on various other parameters other than humidity and heat degradation, such as an incomplete impregnation, UV degradation, wear off, etc. Thus, those results have to be handled with care and this article does not state accurately the ageing rate and lifespan of this composite material but it is an attempt and provides tools to measure and compare it.

Lightening or discoloration of the surface, delamination of the material or fibre pull-out are visual signs of ageing and loss in mechanical properties.

45 min boil/dry test was found to give equivalent results in this test as that of one cycle of ASTM D1037 and it is much faster and easier to do, with more accurate results because of the possibility of stopping the test at a specific timing. Freezing and drying step of the ASTM D1037 don't appear necessary for jute and flax/PLA composite.

The treated and untreated composites have nearly proportional strength loss for real ageing and accelerated ageing, which shows that the boil/dry and ASTM tests are

performing similarly and quite similar to reality. The NaOH treatment brought effective improvement to the aging of the composite, both for real ageing and accelerated aging tests.

Six years ageing in the described environment condition of the jute/PLA composites have been represented in this experimentation half an hour boiling followed by drying of sample of size 120 × 12 × 3 mm.

Comparison with WBP shows that the NaOH treated jute or flax composites are much more resistant to the test than those materials commonly used in our interior. It means that the material could be used for the same use; yet it cannot be fully asserted without real WBP aged samples in the same conditions as that of the jute composite and for the degradation behaviour of PLA.

Further improvements of the composite would be necessary for a higher quality material and more years of real aging would give more accurate results.

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