THE EFFECT OF ALKALISATION ON THE MECHANICAL PROPERTIES OF NATURAL FIBRES

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ABSTRACT

A study on the effect of alkalisation using 3% NaOH solution was carried out on Flax, Kenaf, Abaca and Sisal to observe the impact that the common pre-treatment process has on fibre mechanical properties. The result of the investigation indicated that over-treatment of natural fibres using NaOH could have a negative effect on the base fibre properties. It is concluded that a treatment time of less than 10 minutes is sufficient to remove hemicelluloses and to give the optimum effect.

1. INTRODUCTION

Alkalisation is a common pre-processing technique used on base natural fibre to remove hemicelluloses, fats and waxes that may reduce the interfacial strength between the resin and matrix when processed into composite form. It is of great interest to understand the effect this has on the base fibre mechanical properties, as whilst it may ultimately increase the resultant composite strength through increasing fibre matrix adhesion, the strength of the fibre itself may reduce. Due to this, to allow fuller understanding of the process effects on mechanical properties tensile testing of alkalised fibre is extremely beneficial. It is additionally beneficial to investigate current literature to aid in understanding of other effects that alkalisation may have. These include transformation of cellulose type, and also improved ability for microfibrils to rearrange to accommodate loading of the fibre [1-5].

2. LITERATURE ON ALKALISATION

Alkalisation aims to remove hemicelluloses from natural fibre, which often results in a change in fibre surface energy in a polar or dispersive manner [2]. Hemicellulose, which is thought to consist principally of xylan, polyuronide and hexosan has been shown to be very sensitive to Caustic Soda. The Caustic Soda (*Sodium Hydroxide*) is said to exert only minimal influence on the lignin in the fibres and the high strength alpha-cellulose. Other effects reported from alkalisation of natural fibres are shown in Table 1.

Table 1: Alkalisation effects and observed behaviour of treatment from literature.

Observation	Comment
(1) Removal of hemicelluloses causes the interfibrillar regions of the fibre to become less dense and rigid.	Fibrils are now more capable of rearranging themselves along the direction of tensile deformation. This promotes even load distribution in the fibres and reduces stress concentration likelihood.
(2) Removal of hemicelluloses in the interfibrillar regions also softens the interfibril connections.	Adversely affects the stress transfer between the fibril in some loading directions, thereby affecting the overall stress development in the fibre under tensile deformation.

(3) Partial removal of Lignin during alkalisation of the fibres	The middle lamella joining the ultimate cells is observed to become more plastic as well as homogeneous due to the gradual elimination of micro voids, while the ultimate cells are only affected slightly.
(4) Change in crystallinity through alkaline treatment reported in Coir and Flax.	The increase in percentage crystallinity index through alkali treatment occurs because of the removal of cemented materials, which leads to a better packing of cellulose chains.
(5) Treatment with NaOH leads to a decrease in the spiral angle.	Reductions in microfibril angle / spiral angle improves load alignment by transferring load closer to the fibre axis and therefore increasing molecular orientation.
(6) Randomness introduced in the orientations of the crystallites due to the removal of non-cellulosic matter.	Again, this allows the crystallites to align more freely under load when not in the composite form. Other treatments with a dilute resin solution are sometimes applied to encompass the crystallites and the extra surface area of the fibre internals to improve interfacial strength.
(7) More imperfections and crevices noticed on fibre surface	These imperfections may have been in the fibres previously; however the removal of the surface matter makes them more apparent. Additional imperfections may be the result of handling during processing or over treatment. Can lead to improved 'interlocking' between fibre and the resin when in composite forms.
(8) Lower ability of treated fibre to absorb moisture	With the removal of hemi-cellulose, this makes fibres far more stable when exposed to moisture and has been reported by a number of authors.
(9) Change in proportion of alpha cellulose and cellulose-II.	Over alkalisation of cellulosic fibres alters the alpha cellulose to cellulose-II in the fibrils. This is not desired as the alpha cellulose displays greater alignment in crystalline structure, and exhibits more desirable mechanical properties.
(10) Swelling of the fibre during treatment	This swelling has been reported to be from a reaction in which the natural crystalline structure of the cellulose relaxes. The type of alkali (KOH, LiOH, NaOH) and its concentration will influence the degree of swelling and hence the degree of lattice transformation to cellulose-II.
(11) Breakage of the fibre during alkalisation.	It has been suggested that when swollen the fibres should not be put under tension as they are very vulnerable due to transformations occurring in the crystalline structure.
(12) Uncontrollable swelling of the resulting composite after alkalisation.	Swelling of the fibre in the composite can cause micro cracking in the matrix. This has been reported to be from poor washing of the fibres after alkalisation.

From the information in Table 1, an indication of the effect that alkalisation has on the fibres' properties can be obtained. However, it is also essential to know to what effect concentration and process time has on the resulting mechanical properties of the fibres. There are various alkali solutions that can be used including Hydrogen Peroxide (H_2O_2) and Sodium Hydroxide (NaOH). Hydrogen peroxide [2] is used much less frequently due to the dangers associated with its use. Sodium Hydroxide however is most commonly used for fibre pre-treatment and is freely obtainable in the form of Caustic Soda.

From Table 2, NaOH has substantial effects on improving mechanical properties, even with low treatment concentrations and process times. With the correct pre-treatment process, a 30% increase in interfacial strength in the composite can be generally achieved, with higher mechanical properties of the fibres also observed. The general concentration range of NaOH from the papers investigated seems to be 1-25% and processing time of 1-60 minutes. It can also be highlighted that minimal effects are reported towards higher process times above 60 minutes [8], and even above 30 minutes treatment time, little resultant effect has been noticed in Flax, even at low alkali concentrations. Figure 1 gives the constituent breakdown of the fibres and aids in understanding of the required alkalisation process conditions for each fibre as hemicellulose / cellulose content ratio varies between fibres.

Table 2: Alkalisation literature information to aid in compilation of testing conditions

Fibre	Alkali	Concentration	Treatment Times	Ref	Comments / Effect
Coir	Sodium Hydroxide (NaOH)	5% Aqueous solution	0-200 hours	[8]	Tensile strength increases from 200MPa – 225MPA @100 hrs then begins to decrease
Sisal	Sodium Hydroxide (NaOH)	5% Aqueous solution	0-120 hours	[8]	Steady increase in tensile strength from 500 – 1100 MPa @ 90 hours. Decreases after this.
Sisal	Sodium Hydroxide (NaOH)	2% w/v	1hour @ 25 ^{0}C, dried at 60^{0}C for 24 hours	[1]	Research into improving bond strength. 30 % increase in interfacial shear strength.
Flax (loose fibre)	Sodium Hydroxide (NaOH)	1,2,3%	20min	[3]	Washed in acified water (HC1 0.1 Moles in 1litre of water). Dried at 80^{0}C for 8hrs. Increase in both longitudinal and transverse strength in composite.
Flax	Sodium Hydroxide(NaOH)	1,2,3%	20min	[4]	Washed in cold water, then acified water, then washed again. 30% increase in longitudinal strength @ 3% solution.
Flax	Sodium Hydroxide (NaOH)	10-25%	1-30 minutes with intermediate intervals	[11]	Optimum result obtained @16% NaOH solution. High concentrations lead to degradation. Treatments longer than 10 min have only minor added effect
Flax	Sodium Hydroxide (NaOH)	'Boiled' in 2 – 10% solution	30 min	[10]	Washed in distilled water. Hurds removed. Fibres 'purified' with fibre separation increased.
Flax Hemp Jute Sisal	Sodium Hydroxide (NaOH)	Only states 'mild'	60 minutes	[11]	Rinsed with distilled water containing a small amount of acetic acid. Generally 10% increase in composite properties.

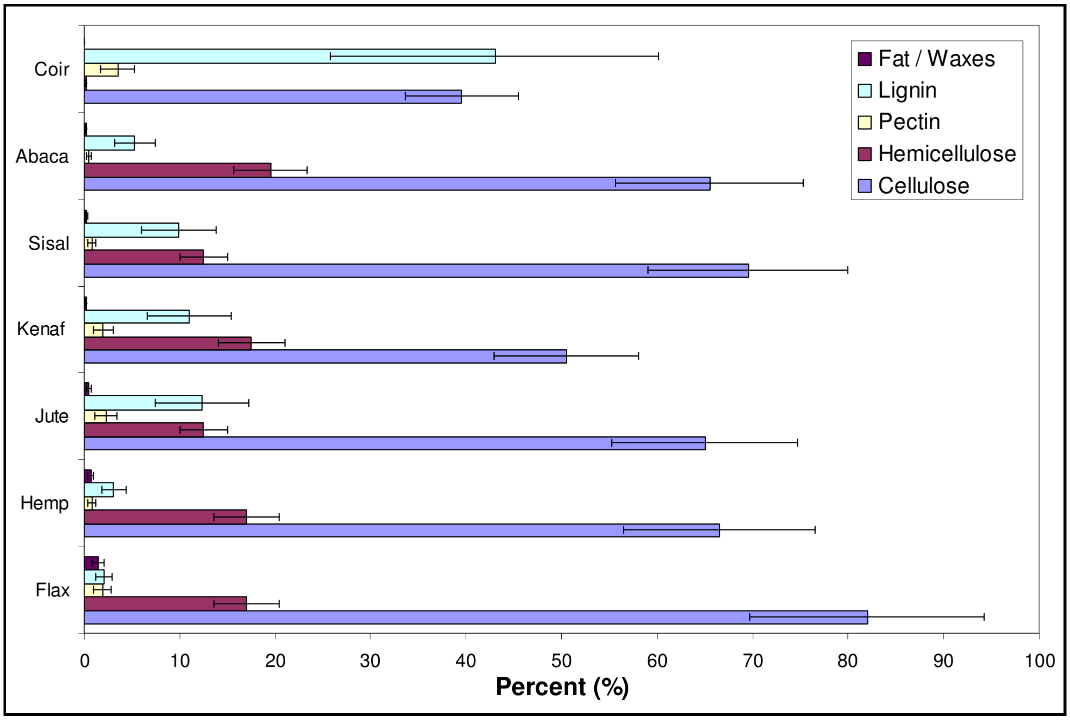

Figure 1: Percentage constituent make up of the target fibres. Error bars are given to show how properties vary for each of the constituent ratios.

3. THE ALKALISATION PROCESS & TESTING METHOD

For the tensile testing of natural fibre, the closest applicable standard used was ASTM D 3822-01 the *'Standard for Tensile Properties of Single Fibres'*. This ASTM standard is typically used to quantify the mechanical properties of textile fibres and threads, which are often from a natural source, such as flax or cotton. This provides a good guideline as it is on the correct testing scale with the fibres being fine in cross section. A Lloyd LRX tensile testing machine was used to carry out the tensile testing of the alkalised fibre, and is fitted with a load cell of 0 – 50 N.

From the information taken from the literature study, an alkalisation process time of 10, 20 and 30 minutes in 3 % NaOH (*Sodium Hydroxide* or *Caustic Soda*) solution was deemed to be reasonable to gain a feeling for the process. In reality, due to the differences in constituents between each natural fibre as shown in Figure 1, process conditions including treatment times and NaOH concentrations may be required to vary for each fibre to be optimal. In this investigation however, the parameters for the study remained consistent to allow for comparison of alkalisation effect between fibres. The experimental process of alkalisation, washing and tensile testing is given below in Table 3 and was carried out for Flax, Abaca, Kenaf and Sisal.

Table 3: The alkalisation process steps used.

Step	Action	Comment
1	Take fibres and dry to consistent moisture content	In oven at 60^0C for 1 hour
2	Take fibre samples and immerse in 3% NaOH solution	-
3	After 10min take out sample of each fibre type	Wash in slightly acidic solution and cleanse thoroughly with ionised water.
4	After 20 min take out sample of each fibre type	Wash in slightly acidic solution and cleanse thoroughly with ionised water.
5	After 30 min take out sample of each fibre type	Wash in slightly acidic solution and cleanse thoroughly with ionised water.
6	Leave fibres to dry naturally	-
7	Dry fibres to consistent moisture level	In oven at 60^0C for 1 hour
8	Organise and test fibres as before.	Using ASTM D 3822-01

After conducting the alkalisation of the natural fibres as in Table 3**,** tensile testing was carried out according to ASTM D 3822-01. The results of this testing can be found in the following section.

4. ALKALISATION TEST RESULTS - MAXIMUM STRAIN AT FAILURE

The results of alkalisation on the tensile failure strain of the natural fibres Flax, Abaca, Kenaf and Sisal can be viewed in Table 4. These results are additionally shown graphically in Figure 2. From initial observation, it is apparent that as treatment time is increased, the fibre strain at maximum load decreases and in the case of Abaca, reduced by nearly 50% in comparison to the untreated fibre. In the case of Sisal and Flax, there seems to be a steadier decrease in strain at max load according to treatment time with NaOH solution. The decrease in ability for the natural fibres to deform and strain may be attributed to the removal of the hemicelluloses during processing which would normally bind between the microfibrils and provide a supportive matrix to allow the fibres to deform to a greater extent during loading. In Figure 3 it is interesting to observe the changes in standard deviation between the treatment times. In general it is observed that after alkalisation treatment the standard deviation for the fibres strains at failure all reduce to a reasonable extent. This indicates that through the removal of hemicelluloses, fats and waxes through alkalisation, the predictability margin of failure for the base fibres are narrowing. In the case of Sisal it has reduced remarkably with the standard deviation falling in the region of 70% after 30 minutes of treatment.

Table 4: Tensile strain to failure results for NaOH treated fibre including standard deviation

Fibre	Untreated	10 min	20 min	30 min
Flax	2.54 +/- 1.112	1.95 +/- 0.632	1.92 +/- 0.587	1.61 +/- 0.489
Abaca	4.95 +/- 1.65	3.14 +/- 0.794	3.17 +/- 0.578	2.39 +/- 0.768
Kenaf	1.98 +/- 0.427	1.06 +/- 0.423	1.37 +/- 0.216	1.37 +/- 0.33
Sisal	2.82 +/- 1.182	2.13 +/- 0.502	1.86 +/- 0.32	1.6 +/- 0.366

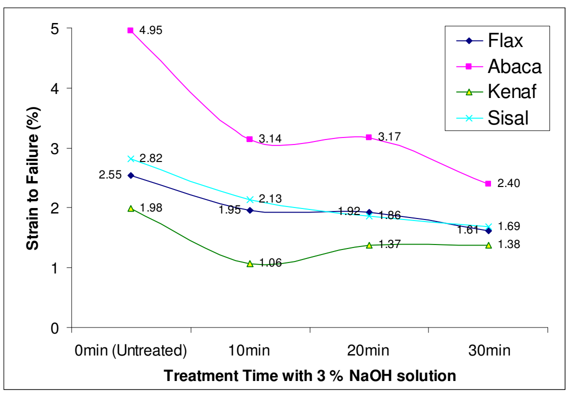

Figure 2**:** The effect of 3 % NaOH treatment on tensile strain to failure of chosen natural fibres

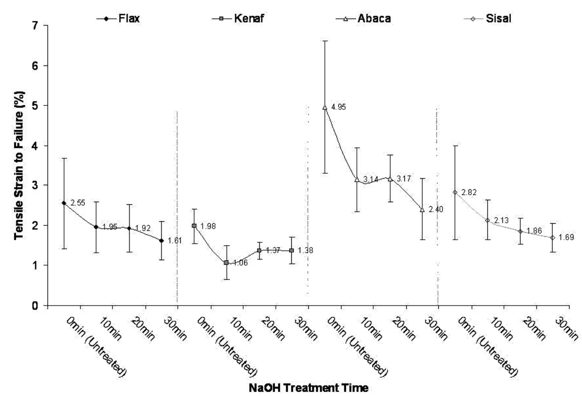

Figure 3: The effect of 3 % NaOH treatment on the tensile strain to failure showing the standard deviation

5. ALKALISATION TEST RESULTS – TENSILE STRENGTH

The results of alkalisation on the fibre tensile strength of the natural fibres Flax, Abaca, Kenaf and Sisal can be viewed in Table 5. These results are additionally shown graphically in Figure 4. From analysing the results, it can be seen that the Flax and Abaca generally seem to lose fibre strength as the alkalisation time increases. In the case of Kenaf, maximum stress seems to remain similar for all treatment times. However it is interesting to see that Sisal increases in failure strength after 10 minutes, however dips back to similar values to the untreated base fibre for 20 and 30 minutes alkalisation duration.

Table 5: Tensile strength results table for NaOH treated fibre including standard deviation

Fibre	Untreated	10 min	20 min	30 min
Flax	1632.24 +/- 937	1188.95 +/- 461	1112.77 +/- 702	722.74 +/- 455
Abaca	945.70 +/- 299.7	778.48 +/- 242	513.50 +/- 241	549.5 +/- 331
Kenaf	473.27 +/- 241	481.6 +/- 133	417.4 +/- 152	419.72 +/- 240
Sisal	546.31 +/- 318.55	776.13 +/- 303	500.72 +/- 147	502.72 +/- 331

As the fibres are tested at similar moisture contents due to oven drying before testing, this effect is therefore unlikely to be caused by swelling of the fibre from moisture differences. In Figure 5 below, the upturn in the Sisal fibre can also be observed to have the narrowest strength deviation band of the four points. It is also interesting to note a general pattern from the standard deviations for the four fibres. It seems, in general, that alkalisation reduces the deviation of failure stress from the untreated base fibres through all the treatment durations. However, it is also noticed for Kenaf, Abaca and Sisal that the deviation increases after 30 minutes treatment with NaOH, which may imply damage to the structure of the fibres in some way.

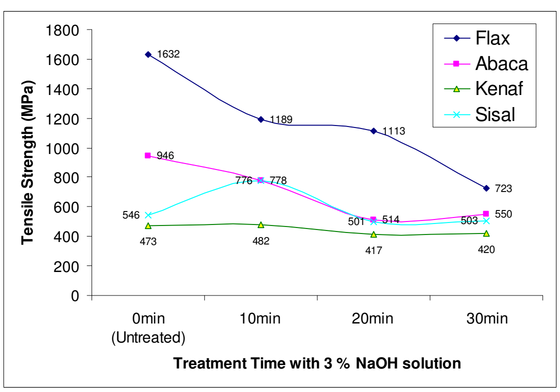

Figure 4: The effect of 3 % NaOH treatment on tensile strength of chosen natural fibres

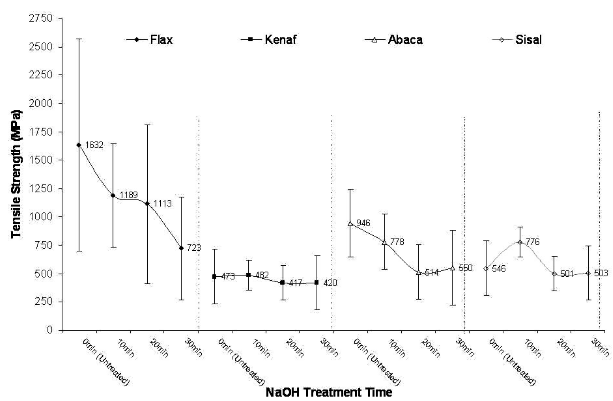

Figure 5: The effect of 3 % NaOH treatment on the tensile strength showing standard deviation

6. ALKALISATION TEST RESULTS – YOUNG'S MODULUS

The results of alkalisation on the Young's Modulus of the natural fibres Flax, Abaca, Kenaf and Sisal can be viewed in Table 6. These results are additionally shown graphically in Figure 6. After 10 minutes of treatment time both Kenaf and Sisal increase significantly in modulus. For the natural fibres Flax and Abaca, Young's Modulus remains similar to the untreated fibres for 10 minutes treatment time, with the modulus dipping for the 20 minutes alkalisation period. After 30 minutes, the modulus of Flax continues to drop, where conversely that of Kenaf seems to rise to approximately a similar modulus of the untreated fibre.

Table 6: Young's modulus results for tensile testing of NaOH treated fibre including standard deviation

Fibre	Untreated	10 min	20 min	30 min
Flax	66.19 +/- 22.23	68.15 +/- 17.47	64.32 +/- 44.2	51.51 +/- 24.9
Abaca	23.43 +/- 6.466	25.63 +/- 11.32	18.14 +/- 8.3	25.48 +/- 12.2
Kenaf	34.21 +/- 17.17	49.49 +/- 17.75	37.27 +/- 15.79	35.04 +/- 14.25
Sisal	17.37 +/- 8.415	38.14 +/- 14	28 +/- 6.8	33.17 +/- 12.19

Interestingly, when considering Table 1 and the observed effects from alkalisation in literature, some speculations of cause of modulus increase can be made. Observations (1), (2) and (5) all indicate that the removal of the binding hemicelluloses in the interfibrillar regions allow fibre microfibrils to re-arrange themselves and transfer loads more effectively. Consequently this means less collective fibre deformation during loading, allowing microfibrils to perform more efficiently.

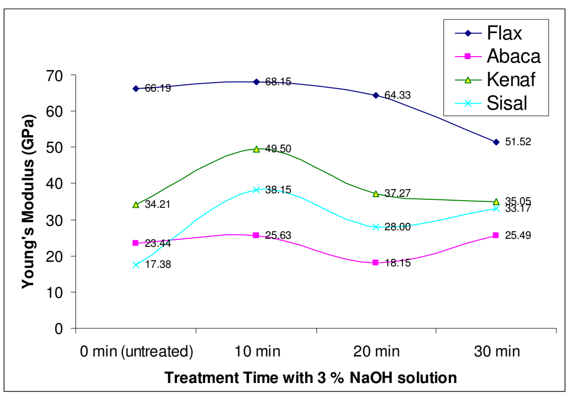

Figure 6: The effect of 3 % NaOH treatment on Young's Modulus of chosen natural fibres

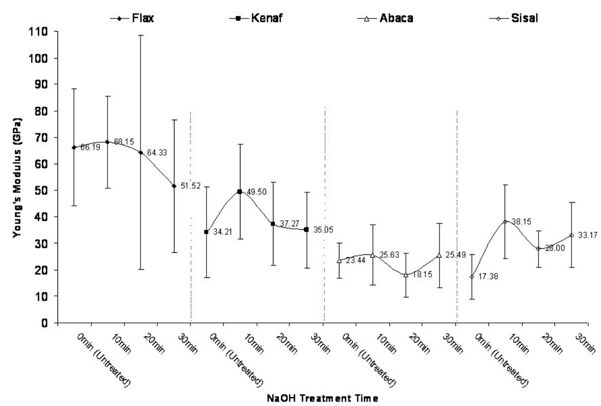

Figure 7: The effect of 3 % NaOH treatment on the Young's Modulus showing standard deviation

From Figure 7 it is apparent that a trend in the standard deviation of the tested fibres is not so obvious. In general, the standard deviations appear reasonably varied for each fibre during treatment time, However there is not a massive difference between each point. In the case of Flax however, at 20-minute treatment time, the standard deviation increases dramatically, whilst there is a downturn in average modulus value. This indicates something is changing in the fibre at this point, and it is interesting to note from Table 1 in point (9) that alkalisation of natural fibres can alter the alpha cellulose to cellulose-II in the fibrils. Alpha cellulose in general has more desirable mechanical properties than cellulose-II, and the large increase in standard deviation at this point may mark a transition point of the cellulose type at this treatment time, and hence a variability in failure stress and Young's modulus.

7. CONCLUSIONS

From the results of the tensile testing it is found that alkalisation can have a significant effect on the mechanical properties of natural fibres, primarily due to a significant reduction in the failure strains of the fibres after the hemicellulose, fats and waxes are removed. After 10 minutes of treatment time both Kenaf and Sisal increase significantly in modulus. Interestingly, when considering the observed effects from alkalisation in literature, some other speculations of cause of modulus increase can be made. Observations from literature indicate that the removal of the binding hemicelluloses in the interfibrillar regions allows fibre microfibrils to re-arrange themselves and transfer loads more effectively. This suggests the uptake of the load is reduced in the fibre during testing as the microfibrils are less restricted by the hemicelluloses in the radial direction of the fibre. As a result, this may suggest less collective fibre deformation through reduced uptake during loading which allows microfibrils to perform more efficiently. These observations cohere with a reduction in strain at failure, as observed in the results. For the treatment times of 20 minutes and 30 minutes for all the fibres, modulus dips may indicate further changes in the fibre structures from alkalisation, which can be attributed to the balances between tensile strength reductions and increases in strain for each fibre as treatment time increases. It is also apparent that there may also be an optimum treatment time between 0 and 10 minutes for which the base fibres can be alkalised satisfactorily whilst potentially optimising the mechanical properties for use in composite form.

Overall, the result of the investigation indicates that over treatment of natural fibres using NaOH could have a negative effect on the base fibre properties. Consequently, it is suggested that a treatment time of 10 minutes or less with 3% NaOH may be sufficient to remove hemicelluloses without significantly impacting mechanical properties of base fibres.

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