Recent innovative results on natural fibre composites

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Abstract: A novel fibre treatment recently proposed in the literature was optimised in the case of woven jute fabric/vinylester laminates to obtain the best tensile properties. It consists on an alkali treatment superimposed to biaxial tensile stress. Optimisation was performed by changing the treatment time. The novel fibre treatment was compared with traditional chemical methods. Tensile properties exhibited a maximum with the treatment time at 4 h due to the less efficient period of time and to the excessive fibre damage for times shorter and longer than 4 h, respectively. All composites with fibres treated with alkali under stress exhibited improved tensile strength in comparison with the composites with untreated fibres or with fibres treated with traditional methods due to the better interfacial properties and the structural changes of the fibres promoted by the novel treatment. Stiffness values were only higher for the composite with fibres treated with alkali under stress for 4 h, probably in correspondence with a maximum in the stiffness of the individual fibres.

Keywords: natural fibres; fibre treatment; mechanical properties.

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1 Introduction

The advantages of natural fibres such as low specific gravity, low cost, and renewability and biodegradability (Aziz and Ansel, 2004) make them very attractive as reinforcement of polymers in many applications. Nevertheless, natural fibre reinforced composites exhibit significantly poorer mechanical and water resistance properties than their synthetic counterparts. Therefore, several modifications of the fibres, the matrix or both have been reported (Mehta et al., 2005; Ray et al., 2002; George et al., 2001; Gassan and Bledzki, 1999a) to solve this problem or at least, to minimise it.

Reinforcing fibres can be modified by physical and chemical methods, being the latter the most frequently used methods. It has been established in the literature (Plackett and Vázquez, 2004; Cyras et al., 2004) that chemical treatment applied to natural fibres may not only modify the matrix/fibre interface, but also may induce different changes on the interphase between elementary fibres and, on the roughness and density of the technical fibres. Other factors such as the orientation of microfibrils of cellulose within each elementary fibre also play a significant role (Mukherjee et al., 1993). All these factors complicate the scenario in the evaluation of the effect of treatment methods on the mechanical properties of composite reinforced with natural fibres (Rong et al., 2001; Vázquez et al., 1999).

On the other hand, relatively good adhesion between natural fibres and thermosetting matrices is frequently achieved as a result of the existence of polar groups in these fibres. However, several fibre treatments conducted on natural fibres (i.e., alkali treatment, silane treatment, acetylation, acrylonitrile treatment, etc.) have been developed to obtain composites with better mechanical properties.

One of the most attractive methods from the economic point of view (Aziz and Ansel, 2004; Ray et al., 2001; Bisanda, 2000; Gassan and Bledzki, 1999a; Ray and Sarkar, 2001) seems to be the alkali treatment. This treatment promotes the removal of impurities such as waxes, pectin, mineral salts and some hemicellulose's and lignin. It also induces extensive structural changes strongly dependent on the treatment parameters (i.e., Na(OH) concentration, temperature and time of treatment). The analysis of the effect of alkali treatment on the composite properties is very complex due to differences in treatment conditions and in fibre and matrix combinations and, also due to the diversity of morphology and composition of natural fibres (Van de Weyenberg et al., 2006).

The treatment with alkali may modify the crystallographic cell from cellulose I to cellulose II and it may also greatly affect the surface morphology of natural fibres. Intra and interfibrillar swelling may significantly change fibres accessibility (Stana-Kleinscheck et al., 1999; Bledzki et al., 2004). As a function of the treatment condition, the alkali treatment produces a rough surface, and the number of anchorage points increases offering a good fibre-matrix mechanical interlocking (Mwaikambo and Ansell, 2002).

The present paper deals with the optimisation of a novel fibre treatment consisting on an alkali treatment superimposed to biaxial tensile stress in the case of woven jute fabric/vinylester laminates, by changing the treatment time to obtain the best composite tensile properties.

2 Experimental

Commercially available woven jute fabrics (Casthanal, Textil CIA, Brazil) were used as reinforcement. The matrix material was prepared from general purpose vinylester resin (Derakane Momentum 411–350 from Dow, kindly provided by Poliresinas San Luis, Buenos Aires, Argentina) and accelerator in a weight ratio of 1 : 0.05, respectively. Jute fabrics were treated with Na(OH) aqueous solution (5% w/v) for different periods of time (1, 2, 4, 6, 12 and 24 h) with continuous shaking at 25°C under biaxial tension. The elongation was kept at 1.2% during treatment in an especially designed device as described elsewhere (Stocchi et al., 2007). Then, the fabrics were washed with distilled water until all the sodium hydroxide was eliminated, that is the pH was neutral. Finally, they were dried at 80°C until constant weight was attained.

To prepare the composites, each layer of jute fabric was pre-impregnated with matrix material and placed one over the other in the mould by a hand lay-up technique, taking care to keep practically achievable tolerances on fabric alignment. Four layers were compression moulded in a hydraulic press for 1 h at 80°C. Then, the plaques were postcured 2 h at 80°C followed by 2 h at 140°C in an oven. Different composites with treated and untreated fabrics whose fineness are shown in Table 1, were prepared. For all composites, jute content was close to 40 wt%.

Table 1 Fineness of jute yarns

Fabric treatment	*Fineness* (*tex*)	*Std. deviation*
Untreated	351.8	76.63
Alkali-tension 1 h	328.4	89.73
Alkali-tension 2 h	303.2	40.56
Alkali-tension 4 h	279.4	33.12
Alkali-tension 6 h	258.0	55.54
Alkali-tension 12 h	299.6	59.62
Alkali-tension 24 h	253.2	61.18

Tensile specimens of $3 \times 10 \times 70\ mm^3$ were machined from compression-moulded plaques. Uniaxial tensile tests were performed by following ASTM D3039M – 95 Standard (2005) recommendations in an Instron dynamometer 4467 at 2 mm/min by using an incremental mechanical extensometer to measure actual elongation during the tests. Stress-strain curves were obtained from these tests and Young's modulus and tensile strength values were determined from these curves. Five measurements were done for each composite.

Fracture surfaces of specimens broken in tensile tests were also analysed by Scanning Electron Microscopy (SEM) after they had been coated with a thin layer of gold.

3 Results and discussion

Table 2 presents Young's modulus and tensile strength values for the composites with fabrics treated with alkali under stress at different treatment time. The results for the composites with fibres untreated and with fibres treated with traditional methods (i.e., alkali treatment without stress and acetylation) reported in a previous paper (Stocchi et al., xxxx) were also included in this table for comparison. The results for the composites with fibres treated with alkali under stress for 4 and 24 h have been originally published by Stocchi et al. (2007).

Table 2 Young's modulus and tensile strength values for the composites with fabrics treated with alkali under stress at different treatment time

Treatment	*Young`s modulus* [GPa]	*Std. deviation*	*Coef. of variation*	*Tensile strength* [MPa]	*Std. deviation*	*Coef. of variation*
No treatment	5.97	0.42	0.070	40.83	8.47	0.2074
Alkali-tension 1 h	4.72	0.37	0.078	47.83	5.81	0.1215
Alkali-tension 2 h	4.73	0.18	0.038	53.7	3.27	0.0609
Alkali-tension 4 h	7.68	0.38	0.049	59.21	1.54	0.0260
Alkali-tension 6 h	5.42	0.16	0.030	57.69	6.04	0.1047
Alkali-tension 12 h	4.12	0.20	0.049	45.27	2.61	0.0577
Alkali-tension 24 h	5.96	0.67	0.112	46.60	2.50	0.0536
Alkali without tension 24 h	5.24	0.33	0.063	37.04	5.17	0.1396

It is clearly observed in Table 2, that a significant improvement in stiffness was only achieved for the composite treated with alkali under stress during 4 h.

On the other side, tensile strength values for the different composites investigated (Table 2) showed that irrespective of the time of treatment used, the composites with fabrics treated with alkali under stress were always stronger than the composites with untreated fibres or with fibres treated with traditional methods (including the alkali treatment without stress). A maximum in tensile strength with treatment time for the composite with fibres treated with alkali under stress for 4 h was also observed.

It has been previously reported by Cyras et al. (2004), that the treatment with alkali leads to an increase in stiffness and strength of individual natural fibres due to the change of cellulose I into cellulose II which leads to a tighter packaging of the chains and an increase in the degree of molecular orientation. This effect was expected to be favoured by the biaxial tensile stress superimposed to the treatment with alkali used in this investigation.

Gassan and Bledzki (1999b) have also reported similar results for jute/epoxy quasi-unidirectional composites treated with alkali under different shrinkage conditions. They have explained their results in terms of the rupture of the alkali-sensitive bonds between different fibre components, the formation of new hydrogen bonds between some cellulose chains, changes in parts of the crystalline cellulose and in the orientation of the molecular chains and a highly reduced fibre diameter**.**

In the case of the stiffness, it should not be expected to be affected by the interface quality as it is determined at low loads where the interface is still intact (Lauke and Bunzel, 1998). Therefore, the higher stiffness value for the composite with fibres treated with alkali under stress for 4 h could be attributed to the improved stiffness of the individual fibres as a result of the structural changes promoted by the novel mechanical-chemical treatment. The stiffness of individual fibres might be near a maximum for that treatment time. A maximum in the stiffness of the individual natural fibres with the time of treatment has been previously reported by Alvarez et al. (2003) for sisal fibres treated with alkali and also proposed by Stocchi et al. (2007) based on their experimental results of compliance for jute yarns treated with alkali under stress.

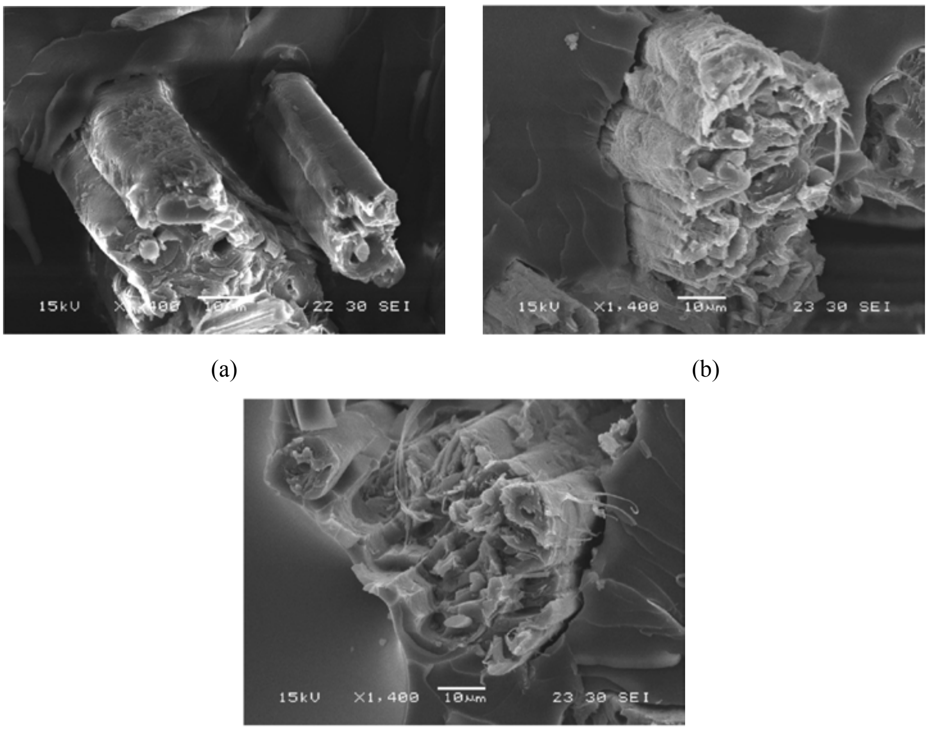
In addition, Stocchi et al. (2007) attributed the improved tensile strength values exhibited by the composites with fabrics treated with alkali under stress, to structural changes of the fibres as well as to a change in the fibre/matrix interfacial properties. The same assumptions are still valid for the results of this investigation.

Furthermore, the presence of a maximum of tensile properties for the composite with fibres treated for 4 h, could be due to the less efficient treatment time and the damage induced onto the fibres by the treatment with alkali under stress for times shorter and longer than 4 h, respectively. Treatment times shorter than 4 h, appeared to be not enough to achieve the structural changes in the fibres required for maximum composite tensile properties. On the other hand, the severe alkali treatment promoted by the long treatment times, produced extensive damage in the cell walls and excessive extraction of lignin and hemicellulose, which play a cementing role in the structure of the fibres.

Figures 1 and 2 show SEM micrographs of the fracture surfaces of composites with different fibre treatments broken in uniaxial tensile tests.

It is clearly observed in Figure 1, that all jute fibres appeared clean of the matrix material and some free space between fibre and matrix existed, suggesting a relatively poor fibre-matrix interaction. Worse interfacial adhesion was found for the composites with alkali-treated and acetylated fibres (Figure 1(b) and (c), respectively) in comparison with the composite with untreated fibres Figure 1(a). Fibre pull out was also observed for the three composites promoted by the lack of interfacial adhesion mentioned before.

Figure 1 SEM micrographs of composites samples tested in tension: (a) composite with untreated fibres; (b) composite with fibres treated with alkali for 24 h and (c) composite with acetylated fibres



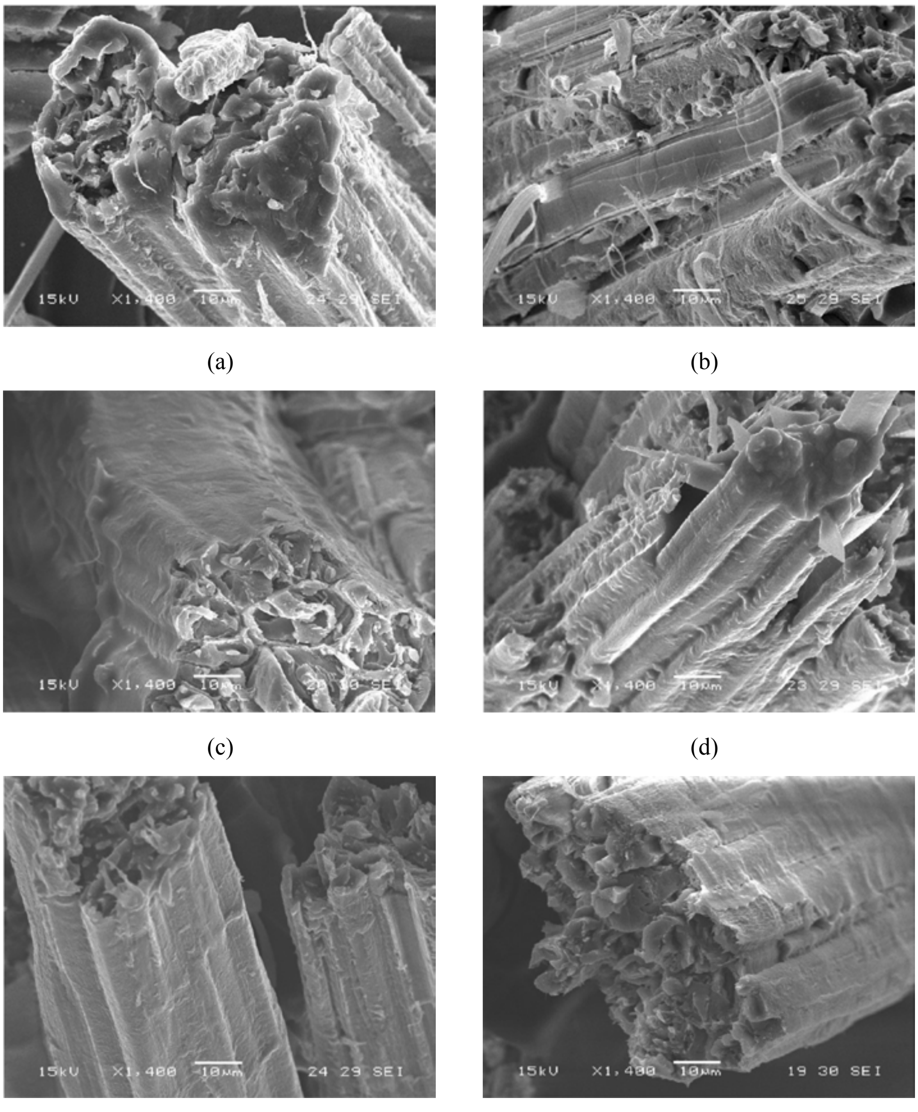
(a) (b)

(c)

In addition, the roughness of the fibres increased with chemical treatment especially with the treatment with alkali. In untreated fibres Figure 1(a), the cementicious material between the fibres cells which holds the structure together was clearly seen. On the other hand, some fibrillation of treated fibres was observed in the micrographs of Figure 1(b) and (c), evidencing the collapse of the cellular structure of natural fibres after chemical treatment (George et al., 2001; Stocchi et al., xxxx). The phenomenon of fibrillation has been reported to increase the effective surface area available for contact with the matrix, to reduce the fibre diameter and to produce a rougher surface. As a result of these, fibrillation may promote better mechanical interlocking (Li et al., 2005).

However, the results obtained by Stocchi et al. (xxxx) suggested that traditional treatments such as acetylation and alkali without stress, at least for the treatment conditions they used, appeared to be inefficient to improve interfacial adhesion. In Figure 2(a)–(f), on the other hand, no significant differences among the fibres treated with alkali under stress at different treatment times and the fibres treated with traditional methods were found. However, a decrease in the amount of cementicious material between the fibres cells which holds the structure together was observed in comparison with untreated fibres Figure 1(a). In addition, the roughness of the fibres was found to increase as a result of the mechanical-chemical treatment.

Figure 2 Composite with fibres treated with alkali under stress for different treatment time: (a) 1 h; (b) 2 h; (c) 4 h; (d) 6 h; (e) 12 h and (f) 24 h



Furthermore, in a previous paper (Stocchi et al., 2007) have been observed that as the time of treatment increased individual ultimate fibres became more visible and appeared more fibrillated. Better adhesion has also been reported by these authors for alkali-tension treated fibre composites in comparison to the untreated one. Nevertheless, no significant differences in the interfacial properties between composites treated during 4 h and 24 h have been found. The detrimental effect of the alkali treatment time under tensile stress on tensile properties has been attributed by Stocchi et al. (2007) to the damage induced onto the fibres by that treatment that would have counteracted an improvement of interfacial properties and an increase in fibre crystallinity.

From the tensile results of this investigation and other previous results, it can be concluded that irrespectively of the time of treatment, the treatment with alkali under biaxial tensile stress led to fibres with higher roughness and less amount of cementicious material. These effects contributed to an increase in fibre/matrix adhesion which was reflected by the tensile strength results: all composites with fibres treated with alkali under stress exhibited higher tensile strength values than the composite with untreated fibres or with fibres treated with traditional methods. In addition, the structural changes induced by the novel treatment also contributed to the better strength exhibited by composites with fibres treated with alkali under stress as well as to the improved stiffness for the composite with fibres treated for 4 h.

4 Conclusions

In this work, a novel fibre treatment consisting on an alkali treatment superimposed to biaxial tensile stress was optimised in the case of woven jute fabric/vinylester laminates to obtain the best composites tensile properties.

Irrespectively of the time of treatment, the composites with fibres treated with alkali under stress were always stronger than the composites with untreated fibres or with fibres treated with traditional methods. This was attributed to the combined effect of an increase in interfacial adhesion and structural changes of the fibres induced by the mechanical-chemical method.

For treatment times shorter than 4 h, the treatment appeared to be less effective to induce the structural changes on the fibres partially responsible of the improvement of the composites tensile properties.

On the other hand, the increase in the time of treatment further than 4 h had a deleterious effect on the composites tensile properties for the treatment conditions used in this investigation (i.e., Na(OH) concentration and temperature). This was attributed to the extensive damage in the cell walls and the excessive extraction of lignin and hemicellulose, which play a cementing role in the structure of the fibres holding the structure together.

In addition, composite stiffness could only be improved when the treatment time was 4 h, probably in correspondence with a maximum of stiffness of individual fibres promoted by the structural changes induced by the novel treatment.

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