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Gareth Price, Marie-Laetitia Pastor, Arnold Towo, Martin Ansell, David Packham. Shear strength at Sisal fibre–polyester resin interfaces: use of inverse gas chromatography to study pretreatment effects. *Composite Interfaces*, 2007, 14 (1), pp.21-31. <10.1163/156855407779230335>. <hal-04075982>

HAL Id: hal-04075982

<https://insa-toulouse.hal.science/hal-04075982v1>

Submitted on 28 Dec 2025

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Shear strength at Sisal fibre–polyester resin interfaces: use of inverse gas chromatography to study pretreatment effects

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Abstract—Inverse gas chromatography, IGC, has been used to investigate changes to the surface of Sisal fibres on treatment with sodium hydroxide. By determining the retention of a series of alkane probes and of probes with acidic or basic character, it was shown that little change to the chemical nature of the surface occurs as measured by the enthalpy of adsorption of alkane probes or the dispersion component of the surface free energy. This IGC study supports the conclusion of previous work involving S.E.M. which suggested that the major effect of the treatment was the removal of weak or adventitious layers from the substrate surface, thus increasing the interfacial shear strength when incorporated into polyester resin.

Keywords: Sisal fibre; adhesion; surface energy; inverse gas chromatography.

1. INTRODUCTION

There are important environmental reasons for the considerable current interest in developing renewable materials for use in fibre composites. We have recently published a study of the use of Sisal fibres as a reinforcement for polyester resin [1]. In that paper we presented evidence that pretreatment of the fibres with aqueous sodium hydroxide before incorporation into the resin led to an increase in interfacial shear strength and to an improvement in the consistency of the fibres, shown by a significant reduction in scatter of both tensile strength and interfacial shear strength measurements. For example, treatment increased the shear strength from 6.7 MPa to 10.4 MPa and the Weibull modulus increased from 2.7 to 5.7 indicating increased consistency in the latter results.

We made some tentative suggestions as to why the sodium hydroxide treatment improved the performance of the fibres. These were based on scanning electron microscopic examination of resin drops on the fibres and of fibre fractures. We now complement these investigations by considering whether the treatment produced significant surface chemical changes to the fibre surface, enhancing bond formation at the interface. Inverse gas chromatography (IGC) enables the change in surface energy, for instance arising from the introduction of acidic or basic groups at the surface, to be estimated and provides a convenient method for investigating chemical changes which the treatment might have produced [2]. There are a number of examples where IGC results have been shown to correlate well with changes in material properties of filled polymers [3–5]. This paper presents the results of such an investigation, and enables firmer conclusions to be drawn about the efficacy of the sodium hydroxide treatment of Sisal fibres.

2. INVERSE GAS CHROMATOGRAPHY (IGC)

In IGC a stationary phase is immobilised in a gas chromatography column. The properties of the stationary phase are determined by injecting probe molecules with known characteristics, which are eluted via an inert gas such as nitrogen. The term ‘inverse’ indicates that the material of interest is the stationary phase in the column, rather than the volatiles injected into the column, which are the object of most gas chromatography work.

The column, packed with the solid of interest (in this case the Sisal fibres), is placed between the injector and the detector of the GC and the measurement consists of timing the flow of injected volatile probes with known properties through the column. The recorded retention time for each probe is related to the surface properties of the stationary phase.

The primary measurement in IGC is the net retention volume, V_n , given [6] by

$$V_n = Jf(t_r - t_0), \quad (1)$$

where t_r is the retention time taken for the probe to elute from the column and t_0 that for a non-interacting marker, f is the carrier gas flow rate corrected to S.T.P. and J is the correction factor for pressure drop across the column and carrier gas compressibility.

In adhesion and composite material studies, IGC is generally carried out at infinite dilution, so that the probe-probe interactions are negligible and the retention time is governed by solid-probe interactions only. Under these conditions, V_n will be proportional to the surface partition coefficient between mobile and stationary phase, K_S :

$$V_n = K_S A c, \quad (2)$$

where A is the total surface area of solid phase and c is a constant which depends on such factors as the mass of the stationary phase and the reference thermodynamic

Table 1.

Gutmann donor (DN) and acceptor (AN*) numbers [2]

Probe	DN /kJ mol ⁻¹	AN*/kJ mol ⁻¹	Characteristic
Diethyl ether	80.3	5.9	Basic
Chloroform	0.0	22.6	Acidic
Tetrahydrofuran	83.7	2.1	Basic

adsorption state. Since K_S is essentially an equilibrium constant, it is related to the standard free energy of adsorption, ΔG_a° , by:

$$-\Delta G_a^\circ = RT \ln K_S = RT \ln V_n + c', \quad (3)$$

where R is the gas constant, T is the absolute temperature and c' is a constant related to c and A .

Assuming that probe adsorption occurs only on the fibre surface, the enthalpy of adsorption, ΔH_a° , can be found by plotting the results according to a van't Hoff treatment, which gives:

$$\Delta H_a^\circ = -R \frac{\partial \ln V_n}{\partial (1/T)} + c'. \quad (4)$$

In this work, straight chain alkanes (pentane to octane) were successively injected in order to characterise dispersion force properties of the untreated and treated Sisal fibres. Information about active acidic or basic sites on the fibre surfaces was sought by studying the IGC adsorption of acidic and basic probes. Chloroform, diethyl ether and tetrahydrofuran were used. The Gutmann donor (DN) and acceptor (AN*) numbers for these probes (Table 1) show the first to be acidic and the last two basic.

3. EXPERIMENTAL

3.1. Materials

The fibres used in this study were Sisal, *Agave sisalana*, from Tanzania. The chemical probes were all of analytical reagent grade and were purchased from Aldrich.

3.2. Preparation of fibres

The Sisal fibres were soaked in distilled water for approximately 3 h to clean them and remove any impurities from the surface. They were then placed between tissue paper overnight in order to remove excess moisture. Further drying in an air-circulating oven overnight at 80°C followed.

A portion of the washed fibres was immersed in a 0.5 mol dm⁻³ sodium hydroxide solution and stirred for an hour at room temperature [7]. The treated Sisal fibres were then washed with water until a neutral pH was reached, and finally dried at 60°C for four hours.

3.3. Inverse gas chromatography

It proved difficult to insert long lengths of Sisal into the GC column without introducing a large void volume that made measurement difficult and imprecise. A range of solutions was trialled, the most effective being to pack the column with short, 3–4 mm lengths of the Sisal fibres. These were then compacted to minimise the void volume. Inevitably, this procedure exposes significant amounts of the fibre interior in addition to the exterior surface. However, no other procedure gave columns suitable for measurements.

The filled columns contained ~20–25 g of fibre and were placed in the thermostat-controlled oven of a GC6000 Vega series 2 chromatograph. Prior to measurement, the columns were conditioned at 120°C under a flow of 5 cm³ min⁻¹ of nitrogen for 15 h to dry the fibres.

To record data, the nitrogen carrier gas (oxygen free and passed through a drying tube) was passed through the column at flow rates of 5–20 cm³ min⁻¹, measured by means of a soap-bubble flowmeter. The chromatograph oven was set to the desired operating temperature and ~0.2 μl of the probes injected using a Hamilton microliter syringe. Five separate injections were made of each probe at each temperature chosen, and the average retention times were calculated.

4. RESULTS

4.1. Alkane probes

Pentane, hexane, heptane and octane were employed as alkane probes. Their retention times increased with chain length, showing that the higher molecular weight probes were more strongly adsorbed, as expected due to the greater van der Waals interactions. Retention times fell with increasing temperature in a manner consistent with a thermally activated process. These points are illustrated in Fig. 1 where the logarithm of net retention volume for two alkane probes is plotted against reciprocal absolute temperature (*cf.* equation (4)).

The measurements contained more scatter and hence greater uncertainty than is usual in IGC work. This was a result of the difficulty in making measurements on the relatively low surface area fibres used here. The resulting retention times were low, even at the lowest flow rates that could be used reliably. It is possible therefore that true equilibrium conditions might not have been established. However, the trends and differences in the results will be valid and so comparisons between the treated and untreated fibres can be made. The plots are reasonably linear, indicating that measurements were recorded well below any phase transition temperatures. The gradients of the lines in Fig. 1 are related to the enthalpies of adsorption, ΔH_a° . The values varied between 1.1 and 4.5 kJ mol⁻¹. These are rather lower than usually found for adsorption onto solids although it should be noted that since the c' term cannot be evaluated for the systems studied here, the values are not strictly comparable.

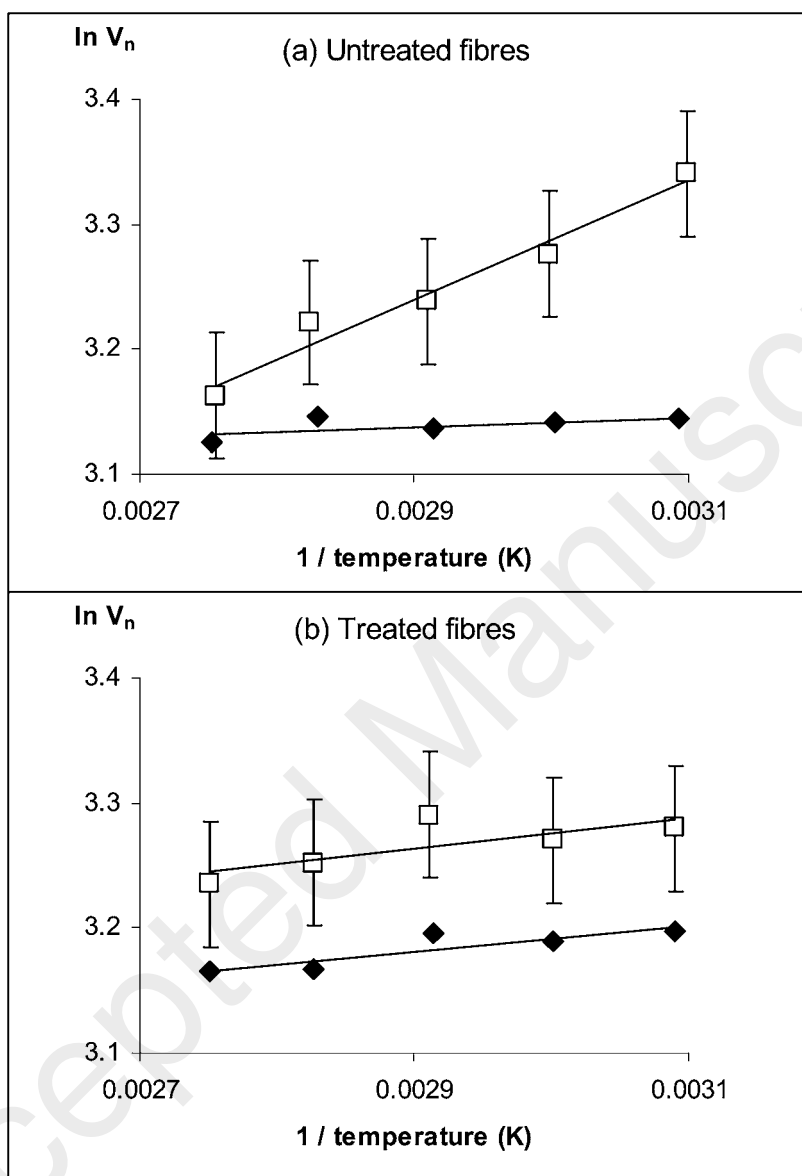


Figure 1. Adsorption of alkane probes on Sisal fibres (a) untreated, (b) treated with 0.5 M sodium hydroxide: variation of net retention volume (V_n) with temperature. \blacklozenge n -pentane; \square n -octane.

Figure 2 shows how the logarithm of net retention volume increased with number of carbon atoms in the alkane chain, n . The linear relation is due to the additional interaction possible on adding a CH_2 methylene group to the probe. Since the term c' in equation (3) does not vary within a particular series of results, the increment in Gibbs free energy of adsorption for each additional methylene group

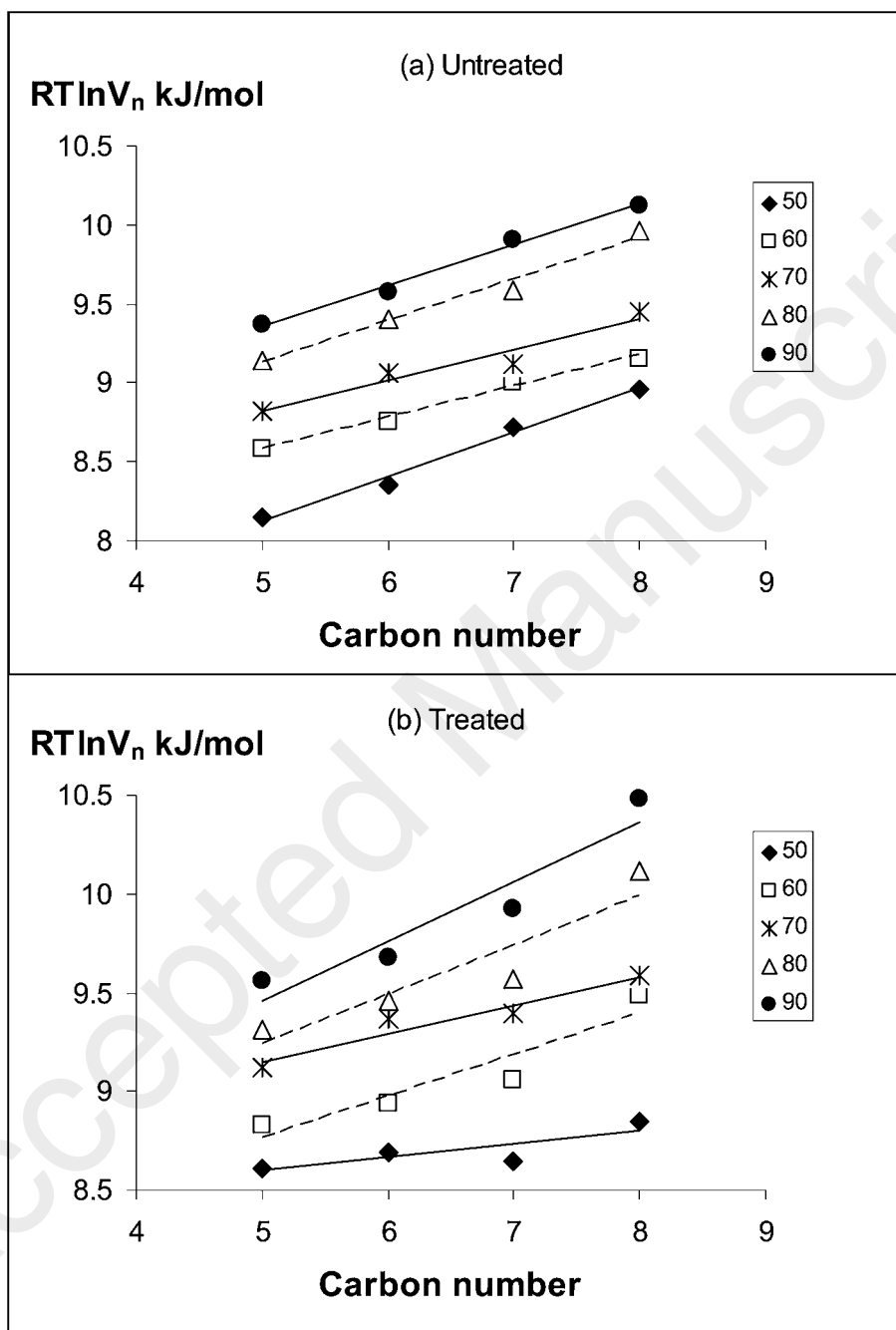


Figure 2. Adsorption of alkane probes on Sisal fibres (a) untreated, (b) treated with 0.5 M sodium hydroxide: effect of alkane chain length on adsorption energy ($-RT \ln V_n$). The key shows the measurement temperature in $^{\circ}\text{C}$.

in the probe molecule, $\Delta G_a^{\circ, \text{CH}_2}$, is given by

$$\Delta G_a^{\circ, \text{CH}_2} = -RT \ln \left(\frac{V_g^{\circ}(n+1)}{V_g^{\circ}(n)} \right). \quad (5)$$

The application of equation (5) to the results yields values of $\Delta G_a^{\circ, \text{CH}_2}$ of $239 \pm 40 \text{ J mol}^{-1}$ and $192 \pm 94 \text{ J mol}^{-1}$ for the untreated and treated Sisal, respectively. These values correspond to dispersion components of the adsorption Gibbs free energy of $24.2 \pm 3.8 \text{ mJ m}^{-2}$ and $19.4 \pm 5.1 \text{ mJ m}^{-2}$. These values can be compared with the $\sim 40 \text{ mJ m}^{-2}$ measured for cellulose by Dorris and Gray [8].

The value of γ_s^d represents the interaction of the surface with an alkane and hence is a measure of how easily the surface can polarise the probe. At infinite dilution, the probes will interact most strongly with the high surface energy sites so, for a heterogeneous surface, the γ_s^d results will predominantly reflect these, rather than being an average across the whole surface.

Although the values are unexpectedly low, the difference between them is also relatively small but may be significant. It suggests that the NaOH treatment may remove some polar groups or sites from the surface, reducing the surface energy but that any effect is small.

4.2. Polar probes

If there are acidic or basic sites on the fibre, stronger adsorption of respectively basic and acidic probe molecules would be expected. In this work, chloroform (acidic), diethyl ether (basic) and tetrahydrofuran (basic) probes were used.

Several different ways of analysing IGC results from such probes are given in the literature [2, 6, 9]. Nardin and Papirer [10] suggested an empirical method using vapour pressure to estimate the specific interactions of polar molecules. A plot of $RT \ln V_N$ against logarithm of the saturated vapour pressure (P_v) of the probe liquid gave a straight line for alkane probes. Data for probes which could interact with the surface by specific interactions lay away from the line; the deviations from this line giving an indication of the strength of the interactions.

This form of analysis has been used in the present work. Values of P_v for the probes at the experimental temperatures were calculated using Literature data [11] and the Antoine equation:

$$\log_{10} P_v = A - B/(t + C). \quad (6)$$

Here t is the temperature in degrees centigrade and A , B , C are constants characteristic of the probe over the given temperature range.

The results analysed in this way are given in Fig. 3. The best fit lines for the alkane probes are drawn. Small, but not negligible, scatter of points is seen. The points for acid and basic probes do not generally deviate very much from the alkane line. This implies that neither the untreated nor the treated Sisal fibres have strongly acidic or basic sites. The differences between the adsorption properties of the treated and

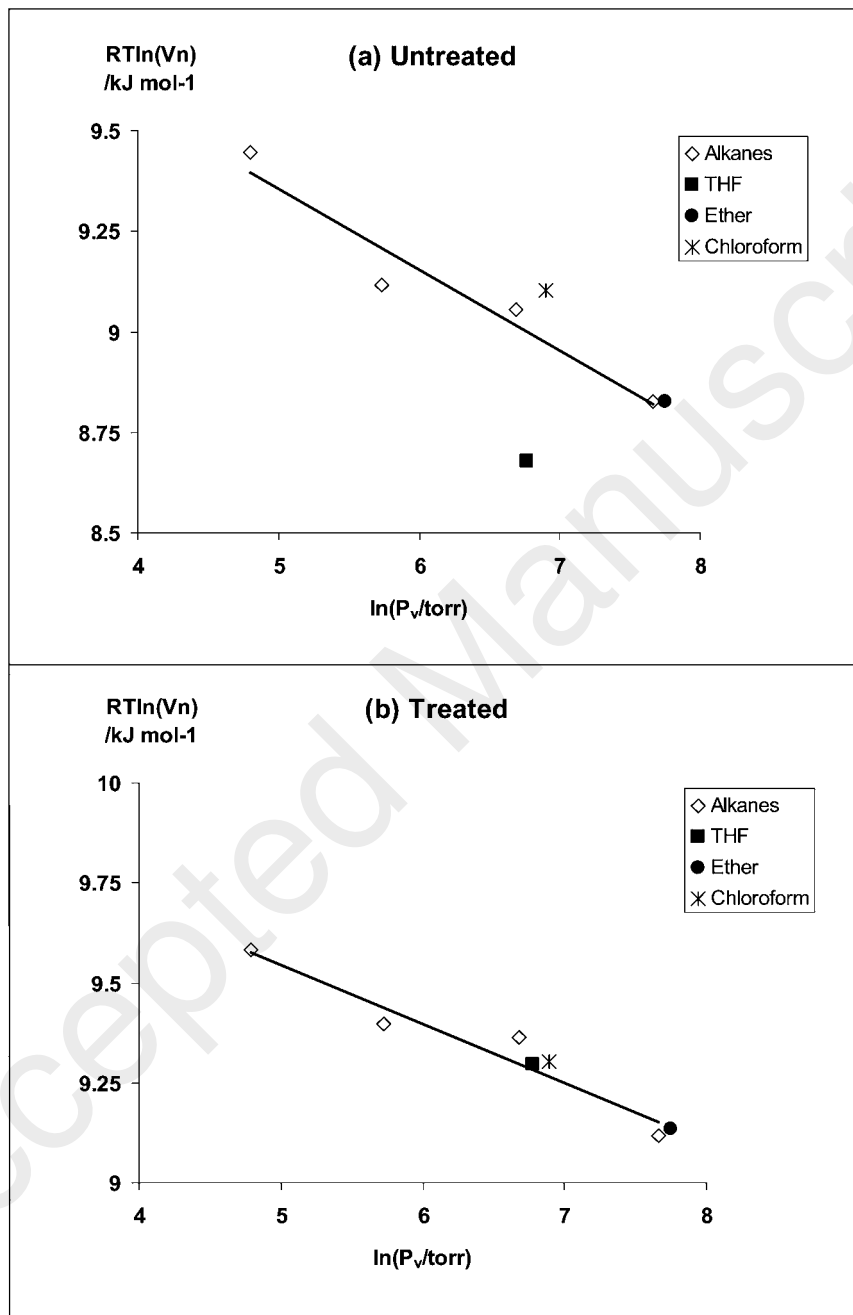


Figure 3. Adsorption at 70°C of probe molecules on Sisal fibres (a) untreated, (b) treated with 0.5 M sodium hydroxide: variation of adsorption energy ($-RT \ln V_n$) with vapour pressure (P_v).

untreated fibres are also not great, although the deviations from alkane behaviour are somewhat reduced after treatment with NaOH suggesting that any strongly polar sites on the fibre surface have been removed. This is consistent with the conclusion from other results [1], that the principal effect of the surface treatment was to clean up the surface removing spurious material. Some chemical effect such as the removal or masking of polar groups may also have occurred.

5. DISCUSSION AND CONCLUSIONS

5.1. Fundamental and practical adhesion

We can now return to the question as to why the polyester–Sisal adhesion is increased by sodium hydroxide treatment of the fibres. The practical adhesion between fibres and matrix was measured by the interfacial shear strength (IFSS), τ_f . We must first discuss how such practical adhesion may be related to the fundamental adhesion which is associated with forces on a molecular scale at the interface.

The relationship between fundamental and practical adhesion is rarely straightforward [12]. However it can be expressed in simple mathematical form by applying the Griffith-Irwin theory of fracture to a joint comprising a bond between two phases. In this approach, developed by Good [13], the fracture stress, τ_f , is given by

$$\tau_f = k(EG/l)^{1/2}, \quad (7)$$

where k is a constant, l is the length of the critical crack which leads to fracture, E is the modulus and G the fracture energy (per unit area). Within the adhesive joint, E and G are semi-local properties. Fracture will occur where the term EG/l is lowest, whether at or near the interface or within one of the bulk phases. Factors which alter E or G or l locally within the joint may alter its strength and other properties.

The fracture energy G will involve a term associated with the energy required for bond breaking at the interface when the joint fails. These may be primary or secondary bonds. This surface energy term will be the thermodynamic work of adhesion W_a or of cohesion W_c , depending on whether fracture occurs at the interface or cohesively within one phase [14]. To this surface energy term (represented by G_0) must be added a term ψ representing other energy absorbing processes — for example plastic deformation — which occur during fracture:

$$G = G_0 + \psi. \quad (8)$$

Factors which enhance either G_0 or ψ will increase the fracture energy of the bond and via equation (7) increase the IFSS.

Usually ψ is very much larger than G_0 , so the ‘other’ energy losses, ψ , make a major contribution to the adhesion fracture energy. However, a modest increase in G_0 may result in a large increase in adhesion because ψ and G_0 are often coupled. Stronger bonds (increased G_0) may lead to much larger increases in fracture

energy because they allow much more bulk energy dissipation (increased ψ) during fracture.

5.2. *The mode of action of the Sisal pretreatment*

Equations (7) and (8) enable the effects of surface treatment on practical adhesion to be rationalised. For the Sisal–polyester adhesion, poor wetting of fibres by the resin would lower adhesion by essentially lowering G_0 due to lowering the actual area of contact. Moreover poor wetting could lead to voids at the interface, effectively increasing the length, l , of the critical crack. There is S.E.M. evidence that wetting of both untreated and treated Sisal was good, although spreading on the untreated fibre may be somewhat less [1].

Where there is wetting, dispersion force interactions, at the very least, will occur across the interface. There is much evidence that these are generally sufficient for a strong adhesive bond. Some surface treatments introduce reactive chemical groups into a substrate surface, enabling acid-base interactions or ‘specific’ primary bond formation between fibre and resin. Such treatments enhance adhesion by increasing G_0 . They may also give improved durability to the bond, when under stress or in a humid environment. The evidence of this paper is that the aqueous sodium hydroxide treatment of Sisal does not lead to significant specific interaction of this type.

Surface treatment often alters the topography of a surface, often increasing roughness. This can enhance adhesion by means of several mechanisms, for example by altering the stress distribution at the interface and increasing energy dissipation terms (ψ in equation (8)) [15]. The S.E.M. evidence presented earlier [1], gave no suggestion of such an effect with the Sisal fibre pretreatment.

Finally, the result of pretreatment may be to remove weak or adventitious layers from the substrate surface. Such material may be undesirable because it is cohesively weak (low work of cohesion, so low G) or because it leads to voids at the interface (increase critical crack length, l). There was abundant S.E.M. evidence presented in our earlier paper [1] that the aqueous sodium hydroxide treatment produces a removal of surface debris, cleaning up the surface. The IGC results presented above (*cf.* Fig. 3a and Fig. 3b) confirm that the treatment leads to a more uniform, consistent surface which leads to enhanced interfacial shear strength. The evidence is that this is the major way in which the Sisal pretreatment used in this work gives improved properties.

Acknowledgements

Arnold Towo is funded by the Association of Commonwealth Universities, student ref. TZCA-2003-136. Marie-Laetitia Pastor is a visiting researcher from the Institut Français de Mécanique Avancée in Clermont-Ferrand.

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