A note on the investigation of fibre–matrix adhesion in sisal fibre–polyester composites

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The nature of interfacial adhesion between chemically modified sisal fibre and polyester resin in composites was studied in relation to the emergence of fractographic features observed in SEM. Evidences of fibre fracture and residual deformed resin as river patterns attached to the pull-out fibre surface were supportive of improved fibre–matrix adhesion that was caused by copolymerization between methacryl functional attached fibre and polyester resin. Forming stable hydrophobic interphase region and desired compatibility of surface-modified fibre with resin matrix resulted in enhanced macro-mechanical properties of the composites. It was also observed that the improvement in the retention of composite strength was appreciable even under wet conditions.

THE concept of improving fibre–matrix adhesion has been used for meeting the property requirements in natural fibre composites[1–4]. One of the most effective methods is the application of coupling agents to a natural fibre aiming at improved wetting or providing fibre–matrix coupling[5–7]. The alkoxy groups of these coupling agents react with the surface functional groups of fibre to form covalent bond (fibre-O–M; M = central metal atom) while organofunctional portion interacts with the polymer matrices by a chemical reaction following the chemical bonding/interpenetrating networks theory[8]. The formation of a lock and key fit at the interface due to surface roughness can greatly increase the force required to separate the adhering materials besides a constructive effect[9] of pressure exerted by the matrix on the fibre due to thermal mismatch. This, in turn, affects interfacial shear strength significantly over untreated composites and also provides increased hygrothermal stability. Explanation of enhanced macro or micro-mechanical properties of composites by chemical/mechanical interference at the interface between surface-modified fibre and resin matrix merits further attention[10]. It is, thus, desirable to understand and correlate the interphase criteria with composite properties in developing natural fibre-based building materials.

In our previous publications[7,11,12], it was shown that improved physico-mechanical properties and shifting of failure mode from interphase controlled. to the next weakest parts (fibre and matrix) can be obtained by using chemically modified fibres. Providing an insight into this behaviour, a subsequent study on adsorptive interactions between coupling agents and sisal fibre has been made showing the role of secondary forces, in addition to covalent bonding[11]. In this study, we aimed at discussing the fibre–matrix adhesion in terms of chemical interactions between *N*-substituted methacrylamide modified fibre and polyester matrix in sisal composites. Since sisal fibre is weaker than the synthetic fibres, the fibre fracture rather than fibre pull-out occurred during single fibre pull-out measurement. For this reason, fractographic features such as fibre fracture and adhering of resin matrix onto fibre surfaces were used to evaluate fibre–matrix adhesion. The comparative evaluation of interfacial adhesion in untreated and treated composites was also made with respect to the variation in mechanical properties. This is the first report on this system to the best of our knowledge.

The sisal fibres of 320 ± 5 aspect ratio, obtained from local source were used in this study. Isophthalic-based polyester resin (gel time –25 min, acid value –16 mg KOH/g, volatile content ~30%) was purchased from M/s Bakelite Hylam Ltd., Hyderabad. *N*-substituted methacrylamide coupling agent (methacrylamide functional amine adduct of pyrophosphato titanate-QB-012) was received from M/s Kenrich Petrochemical Inc., USA and used as received.

Sisal fibres were treated with *N*-substituted methacrylamide coupling agent solution in water (1% by wt of fibre). The procedure of surface modification of fibres was described in our earlier publication[7]. The presence of treating compound onto fibre surfaces was confirmed by FTIR–ATR spectroscopy (C=O stretching at 1708 cm^{-1}, N–H bending at 1530 cm^{-1}, N–H stretching at 3413 cm^{-1}, >C=C< at 1597 cm^{-1})[11]. The chopped strand mats of weight 400 ± 20 g/m^2 have been prepared using these surface-modified fibres binding with poly(vinyl acetate) emulsion as mat former. The composite laminates have been prepared from chopped strand mats (4 plies) and isophthalic-based polyester resin on a hydraulic press at a pressure of ~1.5 MPa for 2 h. The laminates were cured at room temperature for 24 h and then post-cured at 80°C for 4 h at ~1 MPa moulding pressure. The tensile and flexural properties (Instron Model 1342) of composites were carried out according to ASTM D 638-82 and ASTM D 790-86 respectively. The span-to-depth ratio in flexural test was 16:1. The reported values were the average of five measurements. Fractography of the fractured surfaces was made on a scanning electron microscope (Phillips 501). The fractured surface of failed samples was vacuum coated with a thin film of Au/Pd coating to render them conductive.

The occurrence of the fibre breakage and broken end sites on the fracture surfaces implies that the fibre–matrix interface is intact, leading to cohesive failure (Figure 1). An explanation of this behaviour is that the bonding between fibres and matrix is improved by the surface modification. This results in a higher amount of fibre fracture/tearing, a hindrance of matrix deformation between the fibres and a pronounced deviation of the

Figure 1. SEM of fracture surface of sisal–polyester composites showing fibre fracture/broken end sites .

Figure 2. SEM of fracture surface of sisal–polyester composites showing (a) interfacial failure, (b) matrix cracking, (c) resin river patterns deformation on the fracture surface.

major crack path around fibres. On the contrary, the fracture surface shown in Figure 2 indicates sign of interface failure with darkened regions extending down the side of the fibre. This effect could be caused by non-uniformity in surface treatment and lack of good wetting with resin prior to lamination. However, residual resin attached to pull-out surface is still seen at the debonded interface supportive of fibre bonding to the polyester networks. The fracture surfaces also reveal some interesting features such as river patterns initiated from fibre–matrix boundary, suggestive of superior adhesion and multiple resin cracking along with demarkated granular zone. Thus, it seems that resin matrix itself appears to have undergone at least some plastic shear deformation as well as brittle fracture. In the case of untreated composites, poly(vinyl acetate) emulsion provides hydrophobicity and a good resin wet-out to the fibres by an interaction between ligno-cellulosic groups and proton accepting groups of polymers. During resin impregnation of mats, poly(vinyl acetate) is dissolved in unsaturated polyester resin leaving sisal fibre with clean surface, indicating poor bonding between fibre and resin. The thick deposition of poly(vinyl acetate) on the fibre surface during mat preparation resulted in deterioration of mechanical properties. This is attributed mainly to the formation of distinct matrix interphase consisting of poly(vinyl acetate) and polyester resin near the fibre surface. The effect of poly(vinyl acetate) emulsion (used in the mat preparation) on the properties of palm/polyester composites has been reported earlier by Belmares *et al.*[13].

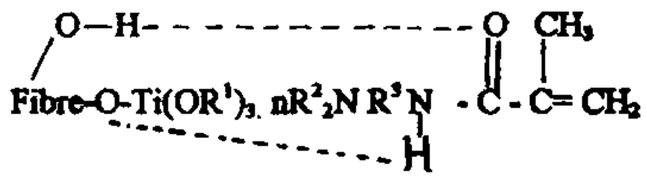
The enhanced fibre–matrix adhesion is attributed mainly to attachment of methacrylamide organofunctionality onto fibre surface (Figure 3). The stability of the attached group can be considered by the involvement of chemical interactions between functional groups of coupling agent and surface active protons of fibres (I). This seems to provide good wetting to the resin during application followed by chemical bonding at the interface. The presence of bulky organic groups on the nitrogen atom further contributes solution compatibility with polyester resin. It is expected that vinyl group of methacrylamide functional attached to the fibre surface can co-react with styrene in the polyester to form styrenated methacrylamide-modified fibre as reported similarly by Ishida and Koenig[14] for reaction between styrene and vinyl groups of methacryloxy propyl trimethoxy silane. This fibre, in turn, reacts with polyester resin via styrene attachment following conventional route (II). Thus, a stable bond is formed enabling enhanced fibre–matrix adhesion. Additionally, the possibility of bonding between methacryl functional attached to the fibre and unsaturation of polyester resin via addition reaction also exists (III).

The tensile and flexural strength of sisal–polyester composites are given in Table 1. The results indicate that the strength properties of composites were altered by the attachment of methacryl functional onto fibre surface that involves forming hydrophobic interphases with polyester resin. The extent of improvement in tension was significantly higher than that in flexure. Under wet conditions, the retention of wet strength was considerable that explains the dominating role of interphase in preventing wicking action of water. About 38% increase in area under stress–strain curve for treated composites was also observed over untreated ones, resulting from the absorption of energy through fibre breakage and matrix cracking. The difference in the increase in these properties is mainly due to the improved fibre–matrix adhesion as observed in fracture morphology discussed earlier. It can be seen that property modifications were

Table 1. Mechanical properties of untreated and *N*-substituted methacrylamide treated sisal fibre–polyester composites (exposure in wet condition ~60 days)

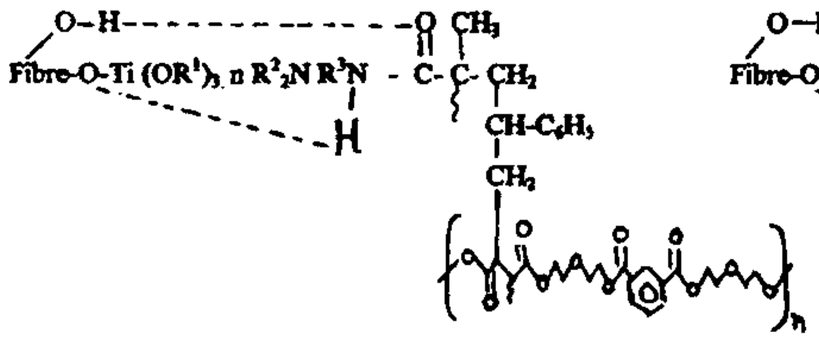
Property	Untreated composites	Treated composites	% Improvement
Tensile strength (MPa)			
(a) Fresh	29.66	39.48	33.10
(b) Exposed			
*95% RH	17.32	28.00	61.66
*95% RH/50°C	22.63	31.10	37.43
*Immersed in water	14.99	23.91	59.51
Tensile modulus (GPa)	1.15	2.06	79.13
Energy to break (MJ/m^2) × 10^5	7.96	11.06	38.94
Flexural strength (MPa)			
(a) Fresh	59.57	76.75	28.84
(b) Exposed			
*95% RH	29.42	33.97	15.46
*95% RH/50°C	26.15	32.00	22.37
*Immersed in water	20.52	29.62	44.34
Flexural modulus (GPa)	11.94	15.35	28.55

RH, Relative humidity.



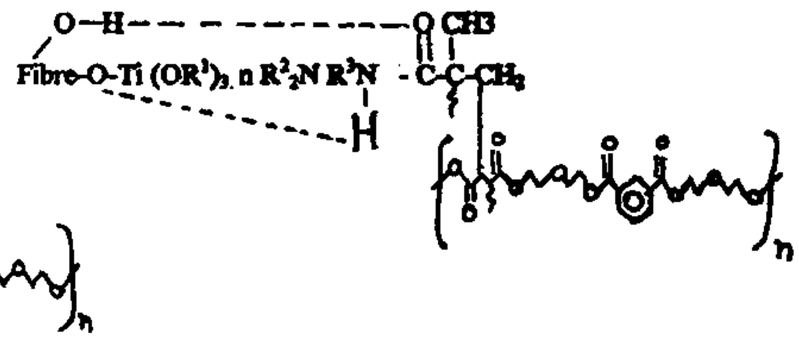
N-substituted methacrylamide modified sisal fibre

(I)



Interaction of methacryl functional attached fibre with polyester resin through styrene

(II)



Interaction of methacryl functional attached fibre with polyester resin

(III)

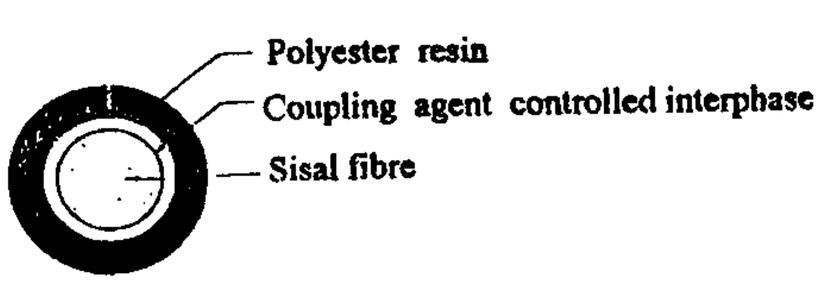


Figure 3. Schematic representation of sisal fibre–polyester resin interaction.

also accompanied by interphase-controlled failure, providing a basis for establishing structure–property relationships. Masking terminal hydroxyl groups of polyester resin, effort is continued for the resin matrix modification by the introduction of isocyanate moiety to obtain a tough, water-resistant interphase in composite materials.

1. Woodhams, R. T., Thomas, G. and Rogers, D. K., *Polym. Eng. Sci.*, 1984, **24**, 1160.

2. Winfield, A. G., Project for UNIDO/Govt. of India, *Plast. Rub. Int.*, 1979, **14**, 23.
3. Singh, B., Gupta, M. and Verma, A., *Const. Build. Mater.*, 1995, **9**, 39.
4. Singh, B., Gupta, M. and Verma, A., *Res. Ind.*, 1994, **39**, 38.
5. Bisanda, E. T. N. and Ansell, M. P., *Comp. Sci. Technol.*, 1991, **41**, 165.
6. Varma, I. K., Ananthakrishnan, S. R. and Krishnamoorthy, S., *Composites*, 1989, **20**, 383.
7. Singh, B., Gupta, M. and Verma, A., *Polym. Compos.*, 1996, **17**, 910.
8. Plueddmann, E. P., *Silane Coupling Agents*, Plenum Press, New York,1982.
9. Miles, H. and Dickinson, J. T., *Appl. Phys. Lett.*, 1982, **41**, 924.
10. Mader, E., Jacobasch, H. J., Grundke, K. and Geitzelt, T., *Composites*, 1996, **27**, 907.
11. Singh, B., Verma, A. and Gupta, M., *J. Appl. Polym. Sci.* in press.
12. Singh, B. and Gupta, M., Proccedings of the International Conference on Composite Materials Energy, Montreal, Canada, May 1995, p. 19.
13. Belmares, H., Barrera, A., Castillo, E., Verheugen, E., Margarita, M., Pattoort, G. A. and Bucquoye, M. E. N., *Ind. Eng. Chem. Prod. Res. Dev.*, 1981, **20**, 555.
14. Ishida, H. and Koenig, J. L., *J. Polym. Sci. Polym. Phys. Ed*, 1979, **17**, 615.

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Ecobiological assessment of a freshwater lake at Schirmacher Oasis, East Antarctica, with reference to human activities

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The scale and magnitude of probable impact of human activities over a decade (1983–1994) on the freshwater lake Priyadarshini, at Schirmacher Oasis, East Antarctica, was assessed through an ecological study conducted over an annual cycle during January 1993 to January 1994. Air temperature ranged from –34.5°C to +8.2°C, water temperature (below frozen layer) from –1.5° to +4.7°C, and pH from 8.10 to 8.77. Dissolved oxygen varied from 8.4 to 12.1 mg l^{-1} with higher values during winter months (June–July). The biological parameters – phytoplankton, chlorophyll-*a* and microbenthos – showed a bi-modal pattern of fluctuations with one maxima in austral summer and another in spring (late winter). Fluctuations in the hydrobiological parameters were closely related to meteorological conditions over the area. Biological productivity of the lake was dependent on the availability of ice-free water and increase in atmospheric temperature. An in-depth analysis and comparison of certain lake environmental aspects over a decadal period indicate that the lake environment is in a healthy condition. However, intensive human activities in the catchment area may deteriorate the ecosystem and hence regular monitoring and stringent regulations are needed to maintain its quality.

THE Priyadarshini lake earlier refered as 'ZUB' lake on the geographical maps, is the second largest water body of Schirmacher Oasis, Queen Maud Land, East Antarctica (Figure 1). Limnological investigations of the water bodies at Schirmacher Oasis go back to 1964 (ref. 1). Since then, the lake environment has been the subject of scientific investigations by the Russian, German and Indian researchers[2–9]. However, except for the study of Loopmann[4] and Kaup[5] all others were based on seasonal observations restricted only to austral summer.

Aquatic environment in and around Priyadarshini has been studied extensively earlier during the austral summer of 1984–1985 (ref. 3), when the lake environment was not exposed to human activities. The Indian summer research station Maitri was established in the vicinity of this freshwater lake during February, 1985 (ref. 10); it was developed into a full-fledged permanent research station in 1988–1989. However, ever since the inception of the Indian Antarctic programme, this fragile and sensitive lake environment is under continuous ecological monitoring.

Due to the proximity of the Indian research station to Priyadarshini, it was possible to study the lake environment very closely around the year. The movement of vehicles and human beings has increased 5-fold in the last 15 years (i.e. since the landing of the first Indian expedition at Schirmacher Oasis in January 1982). The area was visited by both the authors during austral summer of 1984–1985, 1986–1987 and again in 1993–1994 and one of us (VKD) had an opportunity to spend 18 months at Maitri, when the present ecological data were recorded.

It has been recognized that dry-valley lakes are useful indicators of climate change in Antarctica[11]. Hence, it is necessary to gather biological data that documents the present condition of the Oasis lakes. This investigation was planned in this context, and was aimed at comparing the present ecological conditions with the earlier available data. Variations in biological parameters which occurred over a decade are discussed in relation to anthropogenic perturbations. The information and the arguments presented here may help in improved handling of the environmental effects.