

DIFFUSION OF LATENT HARDENER IN EPOXY RESIN

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Keywords: Self-healing, Sisal fibres, Latent hardener, Boron trifluoride, Diffusion

ABSTRACT

Introduction

Most thermoset polymer-based self-healing systems have healing agents separated in two compartments, which means that damaging cracks need to rupture these different containers for healing to occur. However, if one of the constituents can be dispersed a priori in the matrix, the uncertainty of rupturing the right number of capsules or compartments is removed to a great extent. Based on this idea, a latent healing agent that uses boron trifluoride (BF₃) as a catalyst has been developed for epoxy resin [1]. Short chopped sisal fibres (2-3 mm long) are soaked in a solution of BF₃, coated with polystyrene (as BF₃ is highly reactive) and then washed with ethanol. These fibres are then embedded into epoxy allowing BF₃ to diffuse out of the polystyrene shell into the epoxy matrix to act as a latent hardener. Epoxy microcapsules are introduced separately and any crack has to rupture these microcapsules for the epoxy to be exposed the other healing agent (BF₃) on the crack surface.

Knowledge of the amount of BF₃ introduced into the fibres during the soaking (“loading”) process is useful for predicting the amount of BF₃ available to react with epoxy, as well as its rate of diffusion out into the surrounding epoxy. The length of sisal fibre used is also important in determining the mechanical properties of the composite. The present paper investigates the efficacy of using such short fibres by systematically studying the degree of BF₃ penetration into a fibre and its diffusion rate. For a better control and deeper understanding of the related phenomena the investigation has been aided by the use of long sisal fibres.

Current Work

To study the degree of BF₃ penetration, a process similar to that for soaking and coating of the short fibres was applied to longer fibres (~40 mm long). Fibres were individually coated (using 1.5% polystyrene in dichloromethane) and embedded carefully inside epoxy resin. After the resin was cured, these specimens were fractured perpendicular to the length of the sisal fibres to expose a cross-section.

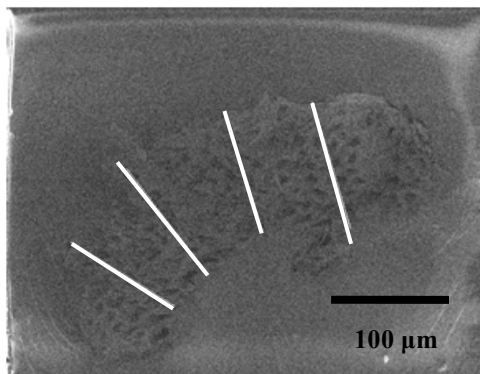


Figure 1: Line scans over a sisal fibre cross-section

These fractured specimens were placed in an environmental scanning electron microscope and analysed using energy-dispersive X-ray spectroscopy (EDS). Figure 1 shows typical line scans transverse to a single sisal fibre cross-section. It is to be noted that sisal fibres were fairly variable in terms of their geometry and size.

The line scans were used to determine the relative weight of carbon (C), boron (B), oxygen (O) and fluorine (F) transverse to the cross-section the fibre. To measure the presence of BF₃, F was chosen to represent BF₃ in the epoxy as B was too similar to C to compare. Control scans across regular sisal fibres or plain epoxy showed a relative weight of F close to zero, so even a low result like the one obtained in Figure 2 (0.6%) indicates that BF₃ is present.

To compare the distribution patterns, two different cross-sections were selected – one in the middle of the sisal fibre, and one at the end (approximately 0.5 mm from the edge). Characteristic line scans for both of these cross-sections can be seen in Figures 2(a) and 2(b) (smoothed using averaging).

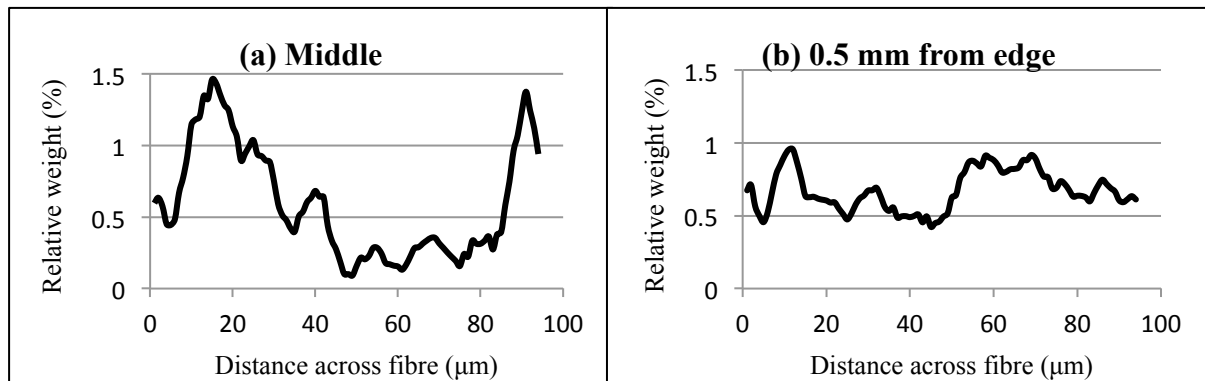


Figure 2: Distribution of BF_3 over a cross-section in (a) the middle of a coated long sisal fibre, and (b) near the edge of a coated long sisal fibre

Both cross-sections show a slightly different average amount of BF_3 ; however, this is expected due to inherent variability in the loading and coating processes. The distribution of BF_3 across the middle cross-section, Fig. 2(a), shows the maximum amount of BF_3 at the periphery of the sisal fibre. The distribution of BF_3 across the end cross-section, Fig. 2(b), shows a more consistent pattern. It can be ascertained that this difference is due to sisal fibres not being symmetrical; the uptake of BF_3 through the ends occurs via capillary action and the uptake through the walls occurs via diffusion. The absorption of BF_3 into the middle section of the sisal fibre is dominated by radial diffusion. There is very little presence of BF_3 in the middle of the fibre as BF_3 has to migrate through the large length of the fibre via capillary action, thus leading to big dip in BF_3 presence in the middle of the fibre.

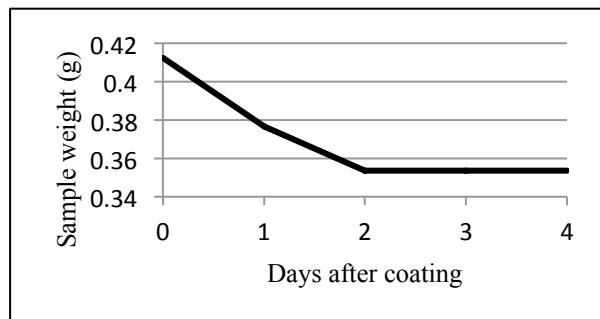


Figure 3: Weight loss of BF_3 -loaded sisal fibres over time

To study the uptake of BF_3 in short fibres, the soaking and coating process described at the beginning was carried out on short sisal fibres (chopped to 2-3 mm). Figure 3 shows the weight loss of sisal fibres due to BF_3 diffusing out of them as they are exposed to ambient air over several days. Around 14% of the total weight of short loaded sisal fibres consists of BF_3 . This value can be compared to the weight loss figures obtained for long-fibre specimens to quantify the difference in uptakes for long and short fibres.

Conclusions and Future Work

The uptake of BF_3 in long sisal fibres is highly dependent on the length and geometry of the fibre. Long fibres need to be further examined near the ends to determine a “critical length” beyond which increasing the length of the sisal fibre would not result in increased BF_3 uptake. A cylindrical model is being developed, which is used to predict the time taken for BF_3 to diffuse out of sisal fibres into the surrounding epoxy resin. This will aid in predicting the amount of time taken to reach a minimum concentration of BF_3 required for self-healing to be effective.

REFERENCES

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