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Effects of surface modification on physical properties of bio-composites

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Treated sisal fiber-based materials exhibit permeability, resin flow direction, and tensile strength changes compared with untreated samples.

Bio-based, naturally available materials have significant applications in modern society and scientific applications (e.g., in car door panels, natural foams, and engine insulation). These materials are manufactured with the use of established molding techniques, such as hand layup molding, press molding, pultrusion, resin transfer molding, and vacuum infusion molding.[1,2] Natural fibers, however, do not easily adhere to non-polar resins (because of polar groups). It is therefore necessary to overcome this problem if natural fibers are to be used efficiently.

It has previously been shown that the adhesion problem of natural fibers and non-polar resins can be solved through chemical modification of the fibers.[3] Such chemical modifications can increase the compatibility between the fibers and a matrix, which thus leads to enhanced stress transfer levels at the fiber–matrix interface. It is thus important to have a good conceptual understanding of the bio-fibers. For instance, it is essential to understand the impact of process parameters and structural properties.

In this work, we therefore aim to study processing phenomena (e.g., permeability, which is a key parameter for making flow predictions during vacuum infusion molding[4]) and to characterize the mechanical properties of sisal-based natural fiber mats. For our tests, we used a vacuum infusion process experimental setup (see Figure 1). In this approach, a vacuum bag was used to cover the entire top of the mold, including the sealant tape. The blended resin, which cures at room temperature, was then poured into the beaker. We used a diglycidyl ether of bisphenol A/epoxidized soybean oil (ESO), i.e., a bio-based, mixture for this purpose. Subsequently, we added triethylenetetramine—a curing agent—to the mold and stirred the mixture for a few minutes. We let the vacuum persist until the resin had completely gelled. In our study, we also use an improved Carman–Kozeny equation (for the prediction of permeability) to assess a new contact angle model we have proposed.[5] This model can be expressed as:

Figure 1. *Photograph illustrating the vacuum infusion process setup. A vacuum bag covers the entire mold, including the sealant tape.*

$$k = \frac{c\Phi}{a + b\left(\frac{1}{\phi} + \frac{\theta^2}{2} - \frac{\theta^2}{2\phi} - 1\right)} \tag{1}$$

where k is permeability, ϕ is porosity, θ is the contact angle, and a, b, and c are empirical constants.

In our experiments, we characterized the physical properties of untreated sisal fiber mats and mats made from sisal fibers treated with a variety of substances, i.e., sodium hydroxide (NaOH), silane, and isocyanate. Our results show that the untreated mat has lower permeability than the other composites. We attribute this to a weak interaction between the ESO-blended resin and the sisal fibers.[6] We also find that NaOH treatment causes an increase in surface roughness, which results in better mechanical interlocking and thus a greater amount of cellulose being exposed on the fiber surface. The surface free energy can thus increase, probably because of the decrease in the contact angle, and allow better fiber wetting and permeability of the mat. We observe a similar trend in the permeability measurements of the isocyanate-treated fibers. There is, however, a decrease in the permeability of the silane-treated

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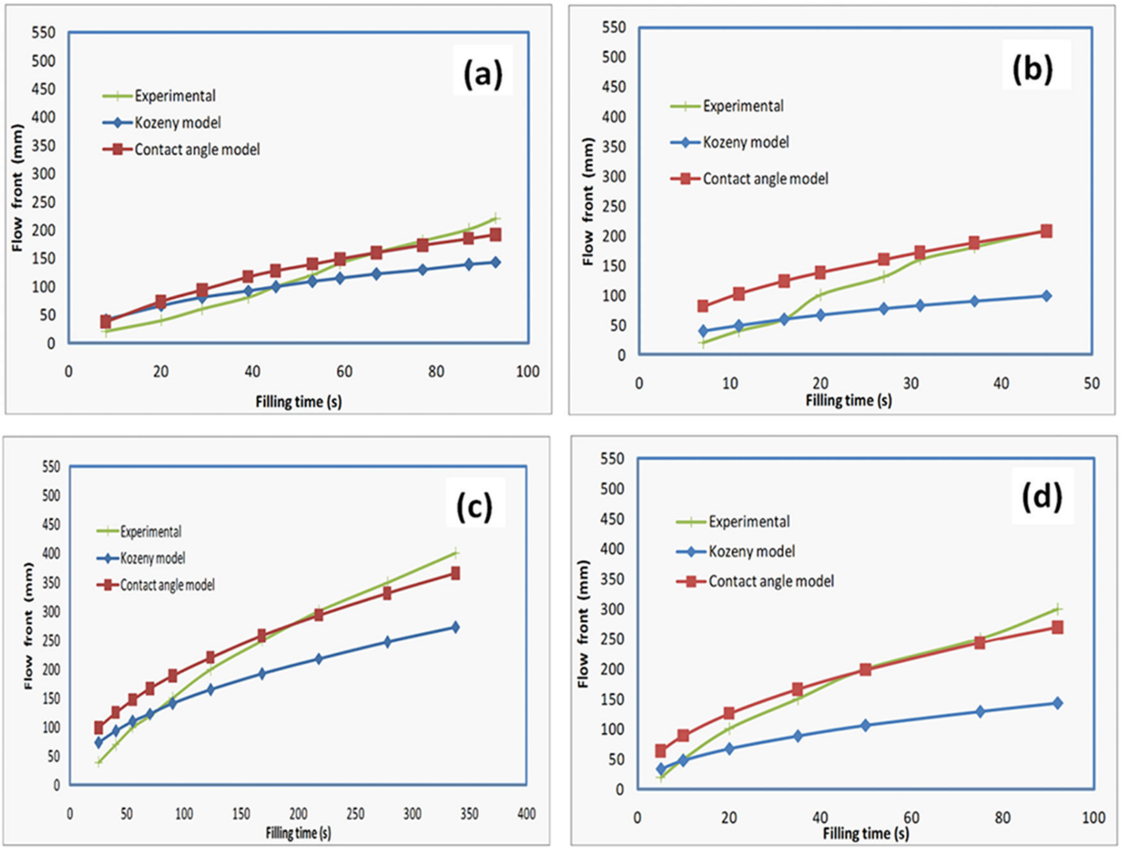

Figure 2. *Comparison of experimental permeability measurements and model predictions for composites made from (a) untreated, (b) sodium hydroxide-treated, (c) silane-treated, and (d) isocyanate-treated sisal fibers. Predictions from the Carman–Kozeny (Kozeny) model and the proposed contact angle model are shown.*

fiber mat. This indicates that a high repelling action was attained and that there is a polarity difference in the interaction between the fiber and the matrix. These experimental permeability results are shown in Figure 2, along with predictions from the Carman–Kozeny model and our proposed contact angle model. Our contact angle model generally matches the experimental data better than the Carman–Kozeny model. This is because it considers the capillary pressure and thus provides a better insight into the magnitude of the natural fibers compared with the synthetic fibers.

Our tensile property measurements (see Figure 3) clearly show that the chemical treatments improve the characteristics of the mat in all cases. We find that the NaOH treatment removes a proportion of the hemicellulose, lignin, wax, and other impurities that are present on the surfaces of the fibers. It also reduces the fiber diameter and therefore increases the aspect ratio. This leads to the development of a rough surface, which causes enhanced interfacial bonding between the fibers and the matrix, and thus the increased tensile strength. Our results also show that the silane treatment creates a bridge between the natural fibers and the resin. This causes an improvement in the interfacial adhesion between the fibers and the matrix. The formation of strong covalent bonds between the isocyanate and hydroxyl groups of cellulose leads to a significant improvement in the tensile strength of the isocyanate-treated fiber composites.[7]

We have also investigated how fiber loading, flow direction, and molding process affect the tensile strength of our composite samples (see Figure 4). Our results indicate that the tensile strength is lower in the transverse (Y) direction than in the longitudinal (X) direction. We believe this is caused by bundles of fibers (tows) that are aligned perpendicular to the load direction and which are weak in the transverse direction. According to unsaturated flow theory, if unidirectional fiber mats such as these are placed so that the tows are aligned in the X-direction (the same direction as the flow), the resin will flow easily

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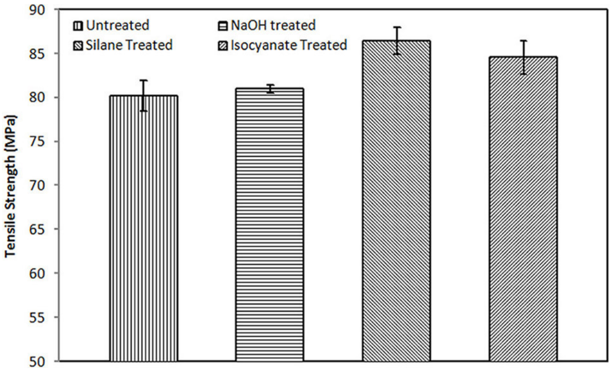

Figure 3. *Tensile strength properties of treated and untreated sisal fiber and bio-based composites. Results are given (from left to right) for the untreated, sodium hydroxide-treated (NaOH), silane-treated, and isocyanate-treated samples.*

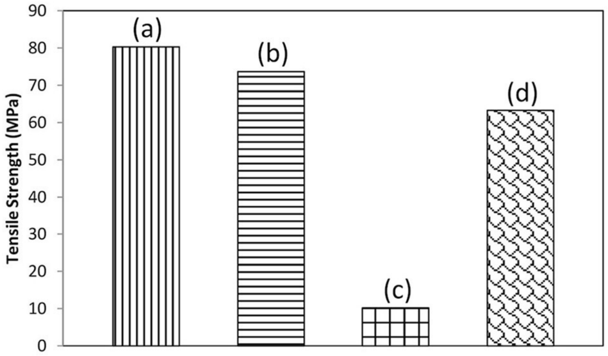

Figure 4. *The effect of fiber loading, flow direction, and process parameters on the tensile strength of the composites. Tensile strength measurements are shown for the vacuum infusion process, where (a) the flow and load are along the X-direction, (b) the flow is along the Y-direction and the load is in the X-direction, and (c) the flow is along the X-direction and the load is in the Y-direction, as well as for (d) the hand layup process, where the load is along the X-direction.*

through the inter-tow channels that are aligned with the fibers. This causes good wettability and a high permeability in the system. Furthermore, good wetting can enhance the adhesive bond strength between the fibers and the matrix, and thus lead to greater tensile strength. We find that our vacuum infusion sample has better mechanical properties than the composite produced using the hand layup molding technique. We attribute this difference to the minimization of voids, which is caused by the compression force (vacuum pressure) that is applied, and which is maintained until the resin completely cures, during the infusion process.[7]

In summary, we have conducted experiments to study the physical properties of sisal fiber-based composites. We find that our bio-based resin exhibits good permeability (i.e., flow ability), especially for composites that have been treated with NaOH and isocyanate. We also observe a significant enhancement in the tensile properties of our composites after various surface treatments. The tensile strength of the materials appears to be greater in the longitudinal direction than in the transverse direction. We can also conclude that vacuum infusion is a promising technique for the fabrication of bio-based composites with good mechanical properties. The next step in our work will be to correlate the surface energy and mechanical properties of bio-based composites.

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References

1. M.-P. Ho, H. Wang, J.-H. Lee, C.-K. Ho, K.-T. Lau, J. Leng, and D. Hui, *Critical factors on manufacturing processes of natural fibre composites*, **Compos. Part B: Eng. 43**, pp. 3549–3562, 2012.
2. G. Francucci, E. S. Rodríguez, and A. Vázquez, *Study of saturated and unsaturated permeability in natural fiber fabrics*, **Compos. Part A: Appl. Sci. Manufact. 41**, pp. 16–21, 2010.
3. D. Rouison, M. Couturier, and M. Sain, *The effect of surface modification on the mechanical properties of hemp fiber/polyester composites*, **Adv. Plastic Compon. Process. Technol. SP-1850**, 2004. doi:10.4271/2004-01-0728
4. A. Hammami and B. R. Gebart, *Analysis of the vacuum infusion molding process*, **Polym. Compos. 21**, pp. 28–40, 2000.
5. R. Subbiah, J. Tjong, S. K. Nayak, and M. Sain, *Studies on permeability of sisal fibre mat during thermoset resin filling in vacuum infusion process*, **Can. J. Chem. Eng. 93**, pp. 1364–1370, 2015.
6. S. Rajkumar, J. Tjong, S. K. Nayak, and M. Sain, *Wetting behavior of soy-based resin and unsaturated polyester on surface-modified sisal fiber mat*, **J. Reinforced Plast. Compos. 34**, pp. 807–818, 2015. doi:10.1177/0731684415580630
7. S. Rajkumar, J. Tjong, S. K. Nayak, and M. Sain, *Permeability and mechanical property correlation of bio based epoxy reinforced with unidirectional sisal fiber mat through vacuum infusion molding technique*, **Polym. Compos.**, 2015. First published online: 22 September 2015. doi:10.1002/pc.23797