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Investigation on the surface free energy of a single flax fiber through adhesion measurement by atomic force microscopy

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Abstract

Surface free energy of a fiber is an important parameter for predicting the interfacial bond strength of fiber-matrix adhesion of composite materials. For mechanical characterization of bio-composite materials, the measurement of the surface energy of individual single microfibers is complicated due to their surface roughness, formation of chemical bonds, wicking characteristics, etc. This paper demonstrates a novel method for determining the dispersive component of surface free energy (γ_d) of single flax fiber by directly measuring the adhesion force between the probe tip of an atomic force microscope and the fiber surface. Johnson–Kendal–Roberts theory was employed to correlate the adhesion force with the surface energy and tip radius. Finally, the value of γ_d was determined, and its significance with respect to other methods was analyzed.

Keywords

Flax fiber, surface energy, micro-fibril angle, atomic force microscopy

Introduction

Flax fibers have been widely used as a reinforcement in bio-composite materials due to their higher strength and modulus, better sound absorption properties, lower specific density, non-toxicity, and lower cost.[1] Flax fibers are derived from the bast or stem of a flax plant, and they are typically a bundle of single fibers called technical fibers. An individual single fiber is an elongated sclerenchyma cell with a diameter of 10–15 μm, forming a complex hierarchical structure and a composite in itself,[2] as shown schematically in Figure 1. Unlike the glass or carbon fiber, the single flax fiber is not a uniform monofilament, but rather has several concentric layers naturally cemented together.

The key to acquire better mechanical performance of composite materials is higher interfacial bonding, which can be achieved by increasing physical adhesion between the fiber and the matrix, and/or by forming a strong chemical bonding, and by better mechanical interlocking. Although the higher roughness of flax fiber provides enhanced mechanical interlocking with the polymeric matrix, the hydrophilicity of the fiber surface may result in weaker interfacial bonding between fiber and matrix.[4–6]

Surface free energy (γ) of the fiber is an important parameter for quantifying the interfacial bond strength between the fiber and the matrix. One approach for measuring γ of a solid flat surface is to measure the contact angle formed by a liquid droplet on a solid surface. However, the contact angle approach for measuring the surface energy rests on a few assumptions. (1) The solid surface is not chemically affected by the liquid. (2) The contact angles to be measured are true equilibrium angles. (3) The difference between the interfacial surface energy at vacuum (γ_{sl}^0) and at saturation (γ_{sl}), known as the spreading pressure (π_e), is negligible. For most low energy surfaces, on which adsorption is relatively small, π_e, is negligible. (4) Errors due to orientational entropy effects are not important. (5) The solid is free from defects, dislocations, edges, and

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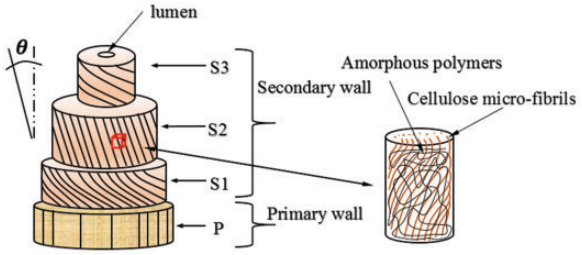

Figure 1. Schematic of a single flax fiber with primary and secondary layers. The secondary layer is composed of S1, S2, and S3 layer. A smaller portion of S2 layer is magnified and cellulose micro-fibrils are seen to be dispersed on an amorphous polymeric matrix. Concept adapted from Baley et al.[3]

corners.[7] Schellbach et al.[8] placed two similar diameter fibers in parallel with a spacing of 0.2–1 mm, so that a water droplet placed on them can form a bridge or column. The meniscus of the liquid bridge was then imaged and analyzed for measuring the contact angle which provided better estimates of contact angle than widely used tensiometry[9] and capable of measuring both advancing and receding contact angle.

Another method for measuring the surface energy is the inverse gas chromatography (IGC),[10] which requires the fibers to be grounded in powder form, causing high end values of the surface energy of the materials.[11,12] The zeta potential of a system is correlated to the surface energy of that system and important information could be achieved regarding the nature of the surface through this measurement. Usually, the zeta potential of fibers is measured by streaming potential method where an electrolyte solution is pumped through the fiber bundle. This solution generates a current or potential resulting from the shear of the electrochemical double layer.[13] However, the measurement of zeta potential provides reliable information about surface energy only when the results are corroborated by other physico-chemical methods and the factors influencing the double layers are sufficiently known. Often, the surface conductivity is neglected which causes error in zeta potential measurement, particularly when the fibers are hydrophilic.[14] Moreover, the measurement may be affected by the degree of fiber swelling. Bellmann et al.[15] performed streaming potential experiments by an Electro Kinetic Analyzer (AKA) to study the polarity of fiber surface and swelling behavior of the fiber in water. They found that the higher the cellulose content and crystallinity are, the lower the amount of water adsorbed is. A lower equilibrium value of zeta potential corresponds to a higher adsorption capacity of the fiber. The acid base properties of the fiber surface can also be investigated by the electro-kinetic measurements.[16,17] Recently, atomic force microscopy (AFM) has become a powerful technique for measuring the surface energy of various polymeric and pharmaceutical materials.[18,19] This method has also been proved successful for the characterization of cellulosic fibers.[20,21] Pietak et al. investigated the surface properties of hemp fibers through AFM. They treated the hemp fibers in four different ways: steam, alkaline, combination of steam-alkaline, and enzymatic treatments and determined the variation of surface free energies among these four types of fibers. They also measured the contact angle formed by different liquids with these fibers, and predicted a relationship among the water contact angle, adhesion force, and surface free energy. However, no attempt is taken in the literature, according to the knowledge of the authors, to measure the surface energy of a single flax fiber by AFM. In this study, the adhesion force between the AFM tip and the single flax fiber was measured by AFM and correlated to the contact mechanics models for determining the dispersive component of surface free energy of single flax fibers.

Materials and methods

Flax fiber used in this study were Prairie Grande Flax, a medium early maturing oilseed flax (*Linum usitatissimum* L.), grown in Melita, Manitoba, Canada. At harvest, the average height of the plants were 60 cm, and observed to be dry or fully mature.

Enzyme retting was performed for extracting the fiber from the cuticularized epidermis and the woody core cells. Bioprep 3000L was used as the enzyme which is an alkaline pectate lyase. Flax stems were fully immersed in a 5% Bioprep 3000L plus Sodium Tetraborate Decahydrate (buffer) for 30 min at $21 \pm 2^{\circ}$C. Next, the stems were taken out and allowed to dry in oven at 55°C for 2 h.

After that the stems were again immersed in ethylenediamine tetraacetic acid (EDTA) plus buffer for 30 min at $21 \pm 2^{\circ}$C. Then, the stems were taken out and dried in the oven for 22 h at 55°C. The stems were then rinsed with water for 5 min and dried overnight in the fume hood.

The single fibers were carefully hand separated from the bundle and laid down on a glass slide coated with a thin layer of partially cured epoxy. The coating was deposited on the glass slide on such a time that the viscosity of the resin system is high enough not to flow. Only the lower part of the single fiber was in contact with the resin and the upper part was free from any contaminants. The resin was then left to cure for 24 h and the lower part of the fiber was firmly fixed with glass slide through the epoxy resin. As a result, during the measurement of the force distance curve, the fibers were rigidly supported by the glass slide.

Figure 2 schematically shows the adhesion measurement by AFM. In an ideal case, a perfectly smooth surface would be preferred for measuring the surface energy. However, as a natural fiber, the flax fiber offers limited opportunity for the manual surface finish, therefore, measuring the surface energy of a single flax fiber in its natural state was desired. A smooth region of the fiber was selected for each indentation.

Adhesion force measurements were performed using an AFM (Veeco, D3100) tapping mode at 23°C and 40% relative humidity (RH). The AFM probe used was from MicroMasch with the model NSC15 and made from n-type silicon. The cantilever had a length and width of 125 µm and 30 µm, respectively, with a resonance frequency of 320 kHz and a quality factor of 657. To convert the AFM cantilever deflection into its corresponding force component, the spring constant of the cantilever needed to be measured. Several methods are available for calculating the spring constant of the AFM probe, such as the thermal fluctuation measurement method, the kinetostatic method, the heterodyne interferometry method, and the extended added micro-drop method.[22–24] The Sader method[25] was used here for determining the spring constant and calculated to be 37.5 N/m. The tip of the cantilever was characterized by Field Emission Scanning Electron Microscopy (FESEM) (JEOL JSM-7600F). The predetermined nanoindentation load on the fiber was 180 nN. The indentation was performed at 10 different locations of the flax fiber. The neighboring indentation distances were at least 500 nm apart to avoid the effect of adjacent deformations on the fiber. The corresponding reaction force vs. z-piezo displacement curve was recorded. The z-piezo displacement curve after the tip-sample contact was a combination of the sample deflection and the cantilever deflection.

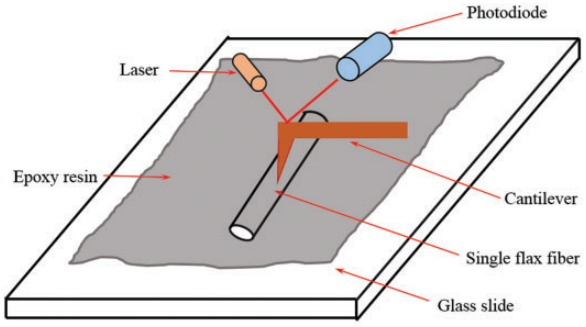

Figure 2. Schematic representation of the adhesion measurement process by AFM.
AFM: atomic force microscopy.

Results and discussion

Figure 3(a) reveals an FESEM image of the surface of a single flax fiber. The surface is nearly smooth except for a few localized inclusions. In Figure 3(b), AFM was used for numerical quantification of the surface roughness, and the root mean square value of the surface roughness of the single fiber was determined to be 25 nm within a 1.5 µm × 1.5 µm area.

Figure 3(b) reveals some of the intricate details such as the meso-fibrils of a single flax fiber. Although the mesofibrils in the S2 layer is covered by the primary layer and the S1 layer, it is possible to probe those meso-fibrils by AFM. The dimensions of these meso-fibrils of flax fibers vary from 0.5 to 1.5 µm. There exist tiny grooves in between the regions from one meso-fibril to another. These grooves may contribute to a higher surface roughness of a single flax fiber.

The meso-fibril angle of a single flax fiber determined by AFM was found to be approximately 11°. A lower meso-fibril angle is responsible for lower strain but higher strength and modulus.[2]

Figure 4(a) shows an FESEM image of the side view of the silicon AFM tip used in this experiment. A magnified view of the tip (Figure 4(b)) shows that the tip

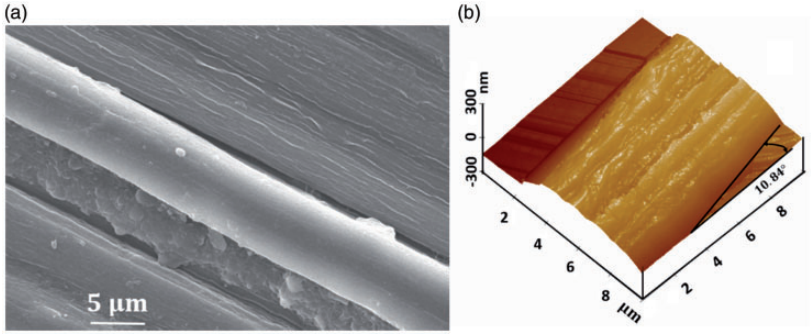

Figure 3. (a) FESEM image of a localized surface topography of a single flax fiber. (b) AFM 3D image of individual visible meso-fibrils.
FESEM: field emission scanning electron microscopy; AFM: atomic force microscopy.

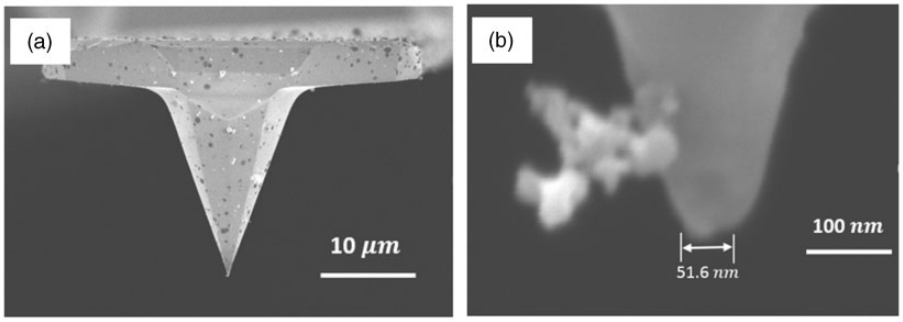

Figure 4. (a) FESEM image of the AFM tip, and (b) magnified view of the tip diameter.
FESEM: field emission scanning electron microscopy; AFM: atomic force microscopy.

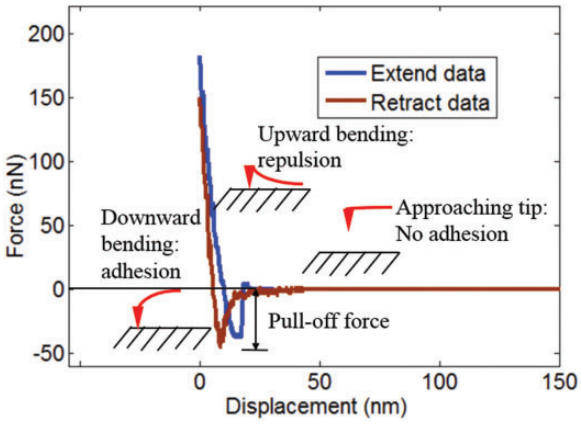

Figure 5. Force vs. displacement curve of the single flax fiber showing the pull-off force arising from the adhesion between the fiber surface and the probe tip.

radius is 25 nm, which correlates the adhesion force and the surface energy.

Figure 5 depicts the tip-surface interaction during the measurement of the adhesion force. When the two surfaces are close enough on the order of several nanometers, the short range van der Waals forces, both electrostatic and attractive in nature, become activated between the surface molecules, and they attract each other. This attraction phenomenon is generally referred to as the adhesion between the surfaces. When two surfaces are in contact due to this adhesion force, a certain amount of force is required to separate them. This separation force is known as the pull-off force, an indirect measure of the adhesion force present between the surfaces. When the tip was far from the surface, there was no interaction between the fiber and the tip. As the tip further approached to the fiber surface, due to the short-range van der Waals force, the tip had a sudden snap-in towards the surface. As the cantilever continued to be pushed down, the adhesion force decreased to zero, and the compressive force became activated. The blue curve represents the extend data, which were recorded when the AFM cantilever tip was approaching and indenting the sample, and the magenta curve represents the retract data, which were recorded when the AFM cantilever tip was retracting from the sample surface after the interaction. The region of the extension curve below the zero line represents the magnitude of the pull-off force or adhesion force, which was found to be 47.8 ± 12.5 nN. The measurement procedure is described in the Materials and Method section in detail.

Again from Figure 5, it can be observed that the value of the pull-off force in retract curve is slightly higher than that of the extend curve. Ideally, the value of the pull-off force from these two curves should be equal for linear elastic materials. However, most polymers are viscoelastic in nature and their load–deformation curve is sensitive to strain rate. Moreover, they show adhesion hysteresis, that is, more work is required to separate the contacting surfaces than the adhesion force required to bring them in contact. This may explain a bigger pull off force required for the retract data. A detailed analysis of the viscoelastic nature of polymeric materials was presented in Wahl et al.[26] They showed that the discrepancy between the experimental stiffness and theoretical stiffness predicted by the Johnson–Kendall–Roberts (JKR) model can be accounted for by employing a model that incorporates this viscoelastic effect at the periphery of the contact zone.

Contact mechanics models were employed for calculating the surface energy from the pull-off force. There are several models correlating the adhesion force to that of the surface free energy of the contacting materials. Among them JKR model[27] and Derjaguin–Muller–Toporov (DMT) model[28] are the most prominent. JKR model was derived by considering two elastic spheres in contact under zero external force. It was assumed that attractive force due to adhesion was present between the two spheres, and this establishes a finite contact radius. By performing numerical simulations of Lennard–Jones potential, Muller et al.[29,30] showed that JKR and DMT are two limiting models of the adhesion force. JKR model is more appropriate

when the radius of the AFM tip is larger and the material being probed is more compliant. This model takes into account only the strong adhesion force under the tip in contact with the object. On the other hand, DMT model is appropriate when the probe tip radius is small and the material being probed is stiff. This model also takes into account the long range weak adhesion force present between the periphery of the probe near the surface in addition to the strong adhesion force present under the tip in contact with the surface of the object.

Usually, two non-dimensional physical parameters, Tabor's parameter μ,[31] and Maugis parameter λ,[32,33] are used to quantify the transition between JKR and DMT models. They are related by the equation $\lambda = 1.1570\mu$, where

$$\mu = \left(\frac{16Rw^2}{9K^2{z_0}^3}\right)^{1/3} \quad (1)$$

$$\lambda = 2\sigma_0\left(\frac{R}{\pi K^2 w}\right)^{1/3} \quad (2)$$

where z_0 is the equilibrium separation of surfaces, R is the tip radius, w is the interfacial energy per unit area or work of adhesion, K is the combined elastic modulus of the tip and the sample, given by $K = \frac{4}{3}((1-{\upsilon_1}^2)/E_1 + (1-{\upsilon_2}^2)/E_2)^{-1}$, where E_1 and E_2 are the tip and the sample Young's modulus, respectively, and υ_1 and υ_2 are the Poisson ratio of the tip and the sample, respectively. σ_0 is the constant adhesive stress acting over a range δ_0 in Dugdale square well potential model. If $\lambda > 5$, then JKR model is more appropriate and if $\lambda < 0.1$, DMT model applies.

In the present experiment, the elastic modulus of the probe tip $E_1 = 165.1\,\text{GPa}$, $E_2 = 50\,\text{GPa}$, $\upsilon_1 = 0.223$, $\upsilon_2 = 0.1$,[34] $z_0 = 0.6$ nm, and $w = 178\,\text{nJ/nm}^2$.[35] Thus $\mu = 16.06$, and $\lambda = 18.577 > 5$, as $\lambda = 1.1570\mu$. As a result, JKR model is more appropriate here for calculation of surface energy.

For the calculation of surface free energy, the pull-off force from the extend data and the equations from JKR model were used.

$$F_{(pull-off)} = -\frac{3}{2}\pi RS \quad (3)$$

$$S = 2\sqrt{\gamma_1^{\text{d}}\gamma_2^d} \quad (4)$$

where γ_1^d and γ_2^d are the dispersive component of the surface energy of the tip and the sample, respectively. The surface energy of the silicon was used as $1250\,\text{mJ/m}^2$.[36] Thus, the dispersive component of the surface energy of a single flax fiber was found to be $32.9 \pm 2.1\,\text{mJ/m}^2$.

Table 1. Comparison of the dispersive component of surface energy values with different methods.

Method	γ_2^d (mJ/m^2)	Materials	Sample preparation
IGC[37]	43.1	Flax fiber	Sample needs grounded in powder form. High energy sites are probed.
IGC[38]	41	Untreated jute	
IGC[38]	37	Silane treated jute	
Capillary rise[38]	23	Jute fibers	Grounded sample is tightly packed into a holder. Gravity may influence the results
Capillary rise[39]	29.2	Flax fiber	
[40]	27.5–50	Flax fiber	
Capillary rise[41]	24	Flax fiber	

IGC: inverse gas chromatography.

The obtained value of the dispersive component of the surface free energy of a single flax fiber agrees well with other published literature values that are listed in Table 1. It should be noted that the underlying principles used to determine the surface free energy among different methods can be different. In general, the measurement of surface energy of single flax fiber is subjected to the method of separation of fibers, surface treatment applied on the fibers, degree of retting, and the method of measurement used.

During the measurement of adhesion force by AFM, with the presence of humidity, the adhesion force between the probe tip and the sample surface is mainly governed by the short range van der Waals force and the capillary force.[42] The situation may be more complicated due to the presence of electrostatic force and the formation of chemical bonding.[43] Due to the presence of high humidity, the sample surface is generally covered by a thin water film. This thin film may form a capillary bridge between the probe tip and the sample surface; therefore, the capillary force would be superimposed with other interactions such as van der Waals force.[44,45] However, the effect of this capillary force is subjected to the wettability of water to the sample surface and the probe tip. A hydrophobic sample surface would result in a very small capillary force. Binggeli et al.[46] studied the condensation of water around an AFM probe in contact with a flat surface. They found that a relative humidity of less than 75% has little effect on the capillary force. However, as the surrounding environment approaches to the point of saturation, significant capillary condensation occurs which affects nano-scale properties. A hydrophilic surface may expedite this process. Again, when the radius of curvature of the probe tip

is large enough, the effect of capillary condensation is negligible.[47]

As the relative humidity of the laboratory was maintained at around 40% RH and the radius of the probe tip was large enough, it is expected that the effect of capillary condensation is negligible. To minimize the effect of electrostatic force during adhesion force measurement, the experimental setup was periodically discharged and ground connected to prevent the buildup of excess charge. As a result, the effect of electrostatic force was also negligible. The single flax fibers were dry enough to prevent the formation of chemical bonding such as hydrogen or hydrophilic bonding between the tip and the fiber surface. Hence, the adhesion force measured by AFM is expected to be arising from mainly due to the van der Waals interactions between the probe tip and the fiber surface.

Conclusion

In this work, the dispersive component of surface free energy of a single flax fiber was determined by AFM through the direct measurement of fiber-tip adhesion force. The value of γ_2^d was evaluated to be $32.9 \pm 2.1\,\mathrm{mJ/m^2}$. Compared with other measurement methodologies, AFM is proven to be a powerful tool in measuring the surface free energy of flax fibers. No additional surface preparation is required and flax fibers are in its natural state, which is essential for understanding its surface characteristics for manufacturing bio-composite materials. The measurement of adhesion force may also predict the surface wettability of single flax fibers. Thus, the method shown in this paper may serve as a useful tool for investigating the fiber-matrix adhesion properties of natural fiber reinforced composite materials.

Author's contributions

S Ahmed prepared the sample, carried out the experiment, analyzed data, and drafted the manuscript. X Wang and C Ulven supervised and guided the overall project and involved in drafting the manuscript. K Li performed the MATLAB coding and involved in sample preparation.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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