CHAPTER 12

EFFECT OF SOLVENT EXTRACTION ON SURFACE ENERGY OF KENAF POWDER

Mandla A. Tshabalala and James S. Han

ABSTRACT

The surface thermodynamic characteristics of kenaf in the form of a powder, before and after successive extraction with toluene/ethanol (2/1, v/v), followed by ethanol and water, were determined by inverse gas chromatography at infinite dilution. The dispersive component of the surface energy (γ_S^D), surface acid-base free energy of resorption (ΔG^{AB}), surface enthalpy of resorption (ΔH^{AB}), and surface acceptor (K_A) and donor (K_D) parameters were determined. The slight increase in γ_S^D after extraction was accompanied by a significant change in its rate of decrease with increase in temperature. K_A also increased significantly, while the change in K_D was insignificant. This behavior can be explained by a change in surface chemical composition caused by removal of extractives from the surface and subsequent rearrangement of surface molecules.

INTRODUCTION

Research on annual growth lignocellulosic fibers, such as kenaf, suggests that these fibers have the potential for use as reinforcing fillers in thermoplastics (Sanadi et al. 1994). Lignocellulosic fiber fillers have several advantages and disadvantages compared to traditional fiberglass fillers (Sanadi et al. 1995, Joly et al. 1996, Marcovich et al. 1996). The primary advantages of lignocellulosic fiber fillers are as follows:

- worldwide availability and low cost,
- low density, which allows attainment of high filling levels,
- biodegradability and therefore, relatively fewer disposal problems at end of lifecycle of lignocellulosic-fiber-filled composite, and

- minimal or near-zero damage by abrasion to processing equipment.

In addition, the utilization of lignocellulosic fibers together with low-value, high-volume recyclable thermoplastics has the potential of stimulating rural economies.

The primary disadvantages of lignocellulosic fiber fillers are their

- susceptibility to moisture uptake and microbial attack, and
- poor interaction with thermoplastic matrices of choice, such as polyethylene or polypropylene.

The interaction of lignocellulosic fiber fillers with the matrix can be manipulated by modifying the physical, mechanical, or chemical properties of the interface. The physical properties of the interface include such thermodynamic properties as surface energy and surface Lewis acid-base characteristics (Wennerström 1997).

The objective of the study reported here was to determine the effect of organic solvent extraction on the surface thermodynamic properties of kenaf fiber, in the form of a powder. These properties were determined by inverse gas chromatography (IGC) at infinite dilution (Saint-Flour and Papirer 1982, Lavielle and Schultz 1991, Tshabalala 1997). The surface thermodynamic properties calculated from IGC data are the dispersive component of surface energy (γ_S^D), acid-base free energy of resorption (ΔG^{AB}), acid-base enthalpy of resorption (ΔH^{AB}), and surface acceptor (K_A) and donor (K_D) parameters corresponding to acid-base surface interactions, as defined by Papirer (Saint-Flour and Papirer 1982) and elaborated by Shultz and colleagues (Shultz et al. 1987, Schultz and Lavielle 1989).

A clear understanding of the effect of organic solvent extraction is essential in the selection of appropriate solvent systems and in the design of environmentally benign extraction processes for manipulating the surface energy and surface Lewis acid-base characteristics of kenaf.

MATERIALS AND METHODS

Test Material

Kenaf powder was prepared from a cultivar grown and harvested in Mississippi by grinding in a Wiley mill. The grounds were shaken through a set of sieves for approximately 30 min, and the fraction between 250 and 212 μm (mesh sizes 60 and 80) was used for the study.

Extraction Solvents and IGC Probes

The analysis-grade toluene and ethanol used for extraction were purchased from

EM Science (Gibbstown, NJ) and Quantum Chemical Company (Tuscola, IL), respectively. The chromatography-grade solvents used as IGC probes were purchased from Sigma-Aldrich (St. Louis, MO). All solvents were used as received, without further treatment. The physiochemical properties of the IGC probes are listed in Table 12.1. Methane gas, 1.0 µg m^{-3} (1,000 ppm) in nitrogen (Aldrich Chemicals, Milwaukee, WI), was used as the IGC marker.

Table 12.1. Physiochemical properties of IGC probes used in study[a].

Probe	a (Å)^2	γ_L^D (mJ x m^{-2})	AN	DN (kcal/mol)	MW	Specific character
n-hexane	51.5	18.4	0	0	86.18	neutral
n-heptane	57	20.3	0	0	100.21	neutral
n-octane	63	21.3	0	0	114.23	neutral
n-nonane	69	22.7	0	0	128.26	neutral
n-decane	75	23.4	0	0	142.29	neutral
chloroform	44	25.9	23.1	0	119.38	acid
diethyl ether	47	15.0	3.9	19.2	74.12	amphoteric
ethyl acetate	48	16.5	9.3	17.1	88.11	amphoteric
carbon tetrachloride	46	26.8	8.6	0	153.82	acid

[a]Sources: Schultz et al. 1987, Schultz and Lavielle 1989, Lavielle and Schultz 1991, Kamden et al. 1993, Tshabalala 1997.

Extraction Procedure

Samples of kenaf powder, 250- to 212-µm (60- to 80-mesh) particle size, were successively extracted for 24 h in a Soxhlet apparatus, with toluene/ethanol (2/1, v/v) followed by ethanol. Each sample was filtered under suction, rinsed with boiling water, and then transferred to an Erlenmeyer flask containing boiling water. The flask was placed in a hot water bath and left to boil for approximately 1 h. The extracted sample was filtered under suction and left to air dry for 48 h. The dry sample was stored in a sealed glass jar.

1 GC Measurements

A Hewlett Packard 5880A gas chromatography (Hewlett Packard, Bloomington, IL) equipped with a flame ionization detector was used for IGC measurements. The sample was packed in a deactivated glass column 1.2 m long with 4-mm internal

diameter (Alltech Associates, Deerfield, IL). Saturated n-alkanes were used as the neutral probes, and carbon tetrachloride, chloroform, diethyl ether, and ethyl acetate were used as the acid-base probes. The specific retention volume V_g for each probe was determined from the average of quadruplicate measurements of the corresponding retention time. The procedues for performing IGC measurements and for data reduction have been described in detail elsewhere (Tshabalala 1997). In summary, under conditions of infinite dilution or near-zero surface coverage, V_g, which is defined as the volume of carrier gas per gram of test substrate required to elute a probe from the column, can be related to various surface thermodynamic parameters. Hence, the dispersive component γ_S^D of the surface energy of kenaf powder was determined from the following relationship:

$$RT\ln V_g = 2N(\gamma_S^D)^{1/2} a(\gamma_L^D)^{1/2} + C \quad (1)$$

where R is the gas constant,

T	column absolute temperature,
N	Avogadro's number,
a	surface area of probe molecule,
γ_L^D	dispersive component of probe surface energy, and
C	a constant.

A plot of $RT\ln V_g$, versus $2Na(\gamma_L^D)^{1/2}$ should give a straight line with slope $(\gamma_S D)^{1/2}$.

The acid-base enthalpy of resorption, DH^{AB}, was calculated from the acid-base free energy of resorption DG^{AB}, which is related to V_g by the following equation:

$$RT\ln(V_g/V_g^{ref}) = \Delta G^{AB} \quad (2)$$

where V_g and V_g^{ref} are the specific retention volume of the acids-base probe and the corresponding reference n-alkane probe, respectively.

ΔG^{AB} is related to ΔH^{AB} by the following equation:

$$\Delta G^{AB} = \Delta H^{AB} - T\Delta S^{AB} \quad (3)$$

where ΔS^{AB} is the entropy of resorption of the acid-base probe. Thus, a plot of DG^{AB}/T as a function of $1/T$ should yield a straight line with slope ΔH^{AB}.

The surface acceptor (K_A) and donor (K_D) parameters are related to ΔH^{AB} by the following equation:

$$\Delta H^{AB} = K_A DN + K_D AN \tag{4}$$

where DN and AN are the literature donor and acceptor numbers, respectively, of the acid-base probe. A plot of $\Delta H^{AB}/AN$ versus DN/AN should yield a straight line with slope K_A and intercept K_D.

RESULTS AND DISCUSSION

Dispersive Component of Surface Energy

There was a measurable difference between extracted and unextracted kenaf powder for the dispersive component γ_S^D as a function of temperature (Figure 12.1). For comparison, Figure 12.1 also shows linear regression lines for this relationship. Although solvent extraction increased γ_S^D below 40°C to 50°C, γ_S^D of extracted kenaf also showed a relatively greater rate of decrease with increased temperature compared to that of unextracted kenaf. Hence, at temperatures greater than 40°C, the surface energy of extracted kenaf was lower than that of unextracted kenaf. This behavior appears to be consistent with the speculation that solvent extraction may have resulted in structural rearrangement of the surface molecules, which would allow for more freedom of movement at higher temperatures to satisfy the thermodynamic requirement of minimization of the surface free energy (Gunnells et al. 1994). Possible structural rearrangements may be modification of the crystalline structure of the cellulose chains, phase transition of the lignin matrix, migration of short hemicellulose chains to the surface, or deposition of low energy, low molecular weight compounds on the surface (Owen et al. 1988).

Surface Acid-Base Characteristics of Kenaf Powder

The effect of solvent extraction on the surface acid-base characteristics (ΔG^{AB}, ΔH^{AB}, K_A, and K_D) is evident from a comparison of Figures 12.2 and 12.3, which show plots of $\Delta G^{AB}/T$ versus $1/T$ for extracted and unextracted kenaf powder, respectively. For the extracted kenaf, these plots show a strong linear coefficient of determination (r^2), ranging from 0.8322 to 0.976, for all the acid-base probes. For unextracted kenaf, on the contrary, only one probe (chloroform) showed a strong linear coefficient of determination (0.9525).

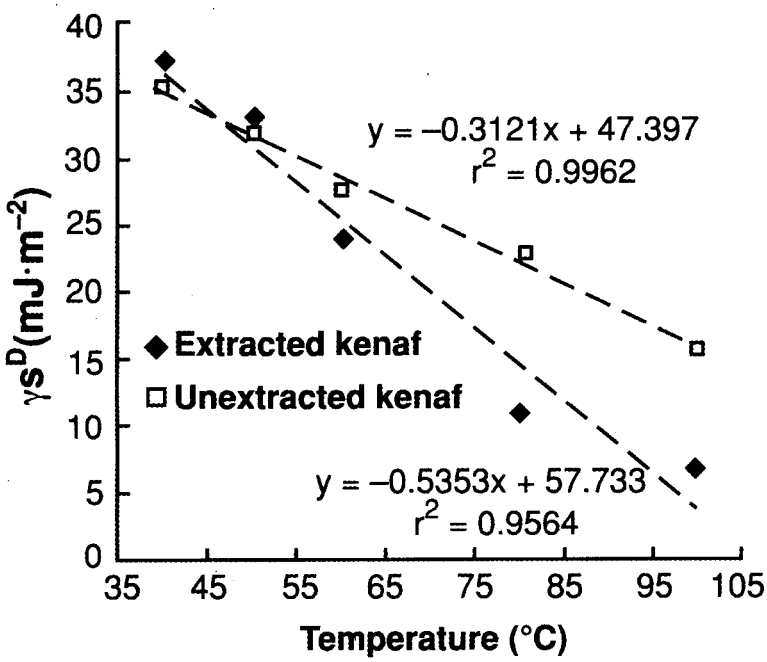

Figure 12.1. $\gamma_S{}^D$ versus temperature for extracted and unextracted kenaf powder.

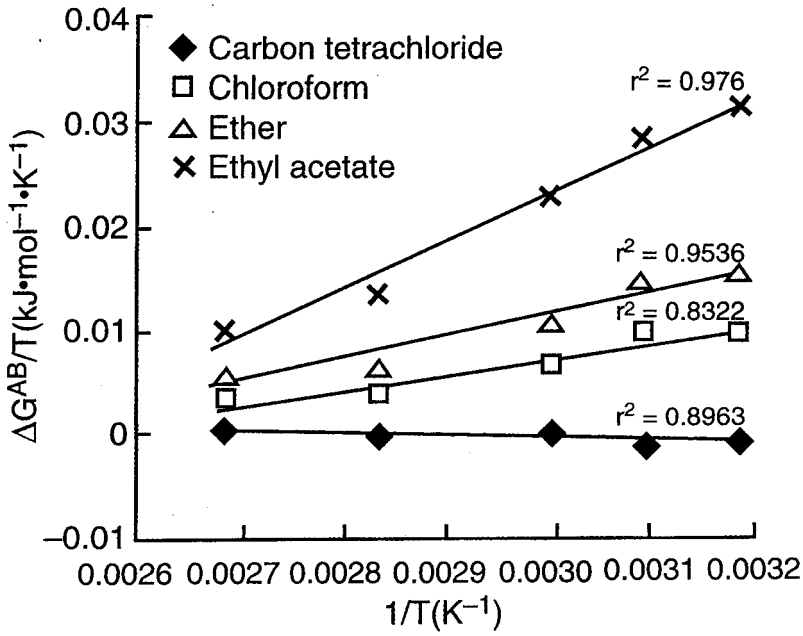

Figure 12.2. $\Delta G^{AB}/T$ versus 1/*T* for acid-base probes on extracted kenaf.

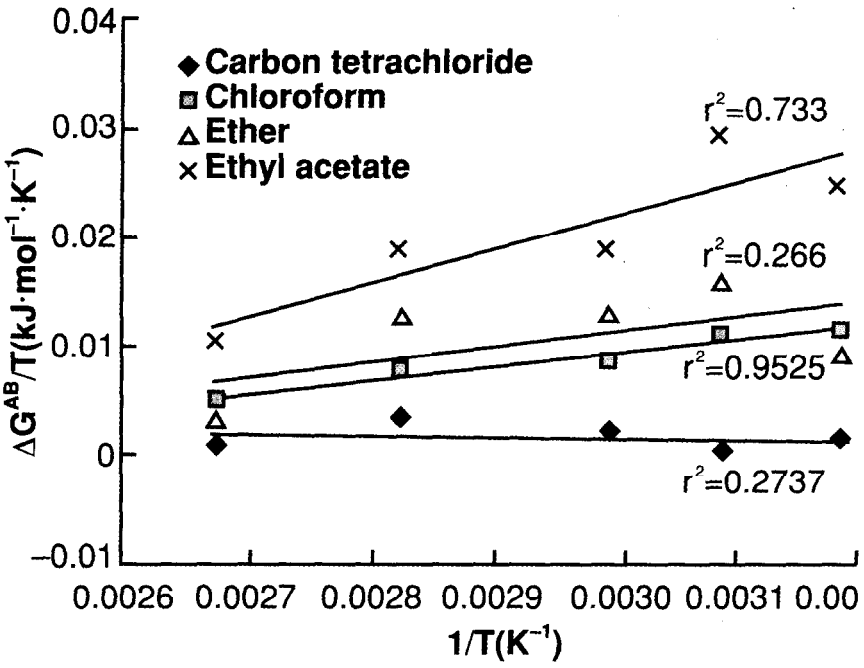

Figure 12.3. $\Delta G^{AB}/T$ versus $1/T$ for acid-base probes on unextracted kenaf powder.

As noted, according to Equation (3), ΔH^{AB} is determined from the slope of the plot of $\Delta G^{AB}/T$ versus $1/T$. As shown in Figure 12.4, the AH^{AB} values for unextracted kenaf do not show a well-defined trend. By contrast, the values for extracted kenaf increased with an increase in the amphoteric character of the probe. A possible explanation for these differences is that the surface of unextracted kenaf powder was apparently covered by a substance or substances that had repulsive interaction with the ether probe. The likelihood of such a possibility appears to be confirmed by a comparison of the acceptor and donor parameters (K_A and K_D) of extracted and unextracted kenaf, calculated according to Equation (4) (Figure 12.5). The surface of unextracted kenaf appears to be covered by a substance or substances that have relatively low donor (0.12) and acceptor (0.08) parameters compared to the donor (0.16) and acceptor (0.27) parameters of the extracted kenaf.

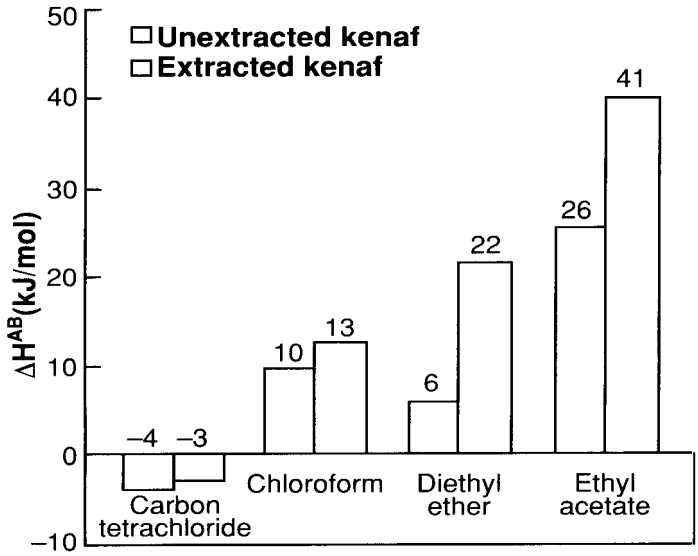

Figure 12.4. Enthalpy of resorption ΔH^{AB} of acid-base probes from extracted and unextracted kenaf powder.

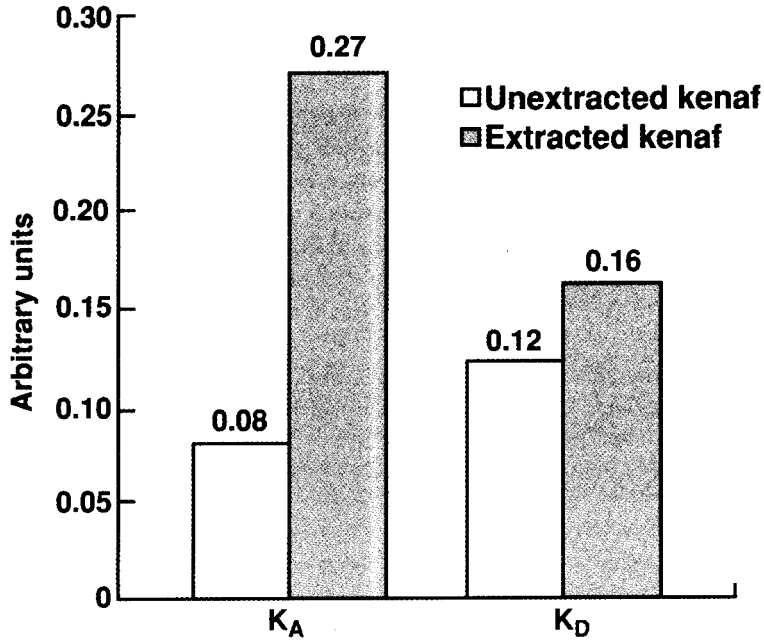

Figure 12.5. Comparison of surface acid-base parameters K_A and K_D for extracted and unextracted kenaf powder.

CONCLUSIONS

The successive extraction of kenaf with toluene/ethanol (2/1 v/v), followed by ethanol and water led to a significant change in the surface thermodynamic parameters of kenaf powder as determined by IGC.

- The dispersive component, γ_S^D, of the surface energy of extracted kenaf was slightly increased relative to that of unextracted kenaf. This increase in γ_S^D was also accompanied by a significant change in the rate of decrease of γ_S^D with increased temperature.
- The surface acid-base free energy of desorption, ΔG^{AB}, of extracted kenaf was significantly different from that of unextracted kenaf. Whereas the $\Delta G^{AB}/T$ versus $1/T$ plots for extracted kenaf were well-behaved straight lines for all the acid-base probes, the same was not true for unextracted kenaf, which showed a well-behaved straight line for only one probe.
- The surface acid-base enthalpy of resorption, ΔH^{AB}, for extracted kenaf showed an increase with increased amphoteric character of the acid-base probes. By contrast, ΔH^{AB} for unextracted kenaf did not show any well-defined trend.
- The acceptor parameter (K_A) of extracted kenaf was significantly increased compared to K_A of unextracted kenaf, but the change in the donor parameter (K_D) was insignificant.

The results of this study have demonstrated that solvent extraction of kenaf may be a viable approach to manipulating its surface thermodynamic characteristics. The significant increase in the acceptor parameter K_A suggests that extracted kenaf may interact more strongly with a matrix, such as a polyester (Marcovich et al. 1996), or a coupling agent, such as m-phenylene bismaleimide (Sain et al. 1993), both of which contain carbonyl functional groups that have high donor numbers. On the other hand, the increase in the donor parameter K_D of the extracted kenaf surface may also render it more susceptible to interaction with moisture compared to unextracted kenaf, since water has a relatively high acceptor number (54.8) (Riddle and Fowkes 1990).

DISCLAIMER

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