SURFACE CHARACTERISTICS OF CHEMICALLY MODIFIED NEWSPRINT FIBERS DETERMINED BY INVERSE GAS CHROMATOGRAPHY

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ABSTRACT

The surface characteristics of treated waste newsprint fibers were investigated using inverse gas chromatography (IGC). The surfaces of waste newsprint fibers were modified with γ-aminopropyltrie-thoxysilane, dichlorodiethylsilane (DCS), phthalic anhydride (PA), and maleated polypropylene. The effectiveness of these surface treatments was monitored by the IGC adsorption curves using n-alkanes and acid-base probes. The empirical acid (K_A) and base (K_D) characteristics (i.e., electron donor/acceptor abilities) of untreated and treated newsprint fibers were determined using Schultz's method and were correlated with the surface chemical compositions determined from X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The results indicated that the surface of untreated newsprint fibers had an acidic characteristic due to the electron acceptor character of the hydroxyl protons. The newsprint fibers reacted with phthalic anhydride or maleated polypropylene also exhibited an acidic surface behavior attributed to pendent carboxylic groups. Dichlorodiethylsilane produced a strong acidic surface attributed to the highly electronegative nature of the chlorine atoms of dichlorodiethylsilane. However, when the fibers were reacted with γ-aminopropyltriethoxysilane, the basic characteristic (electron donor ability) of the fiber surface was increased, presumably by the presence of attached amino groups.

Keywords: Acid-base properties, cellulosic fiber, inverse gas chromatography

INTRODUCTION

During the last decade, composites consisting of lignocellulosic fibers and synthetic thermoplastics have received substantial attention in scientific research (Woodhams et al. 1984; Kokta et al. 1990). The use of cellulosic fibers

in thermoplastic matrices is of particular interest because such fibers provide a low-cost reinforcing filler for synthetic polymers (Woodhams et al. 1984). The adhesion between hydrophilic, polar cellulosic fibers (high surface energy), and hydrophobic, nonpolar thermoplastics (low surface energy) can influence the strength and toughness of the composites (Quillin et al. 1992; Felix 1993; Kazayawoko 1996). Strong fiber-fiber interactions resulting from hydrogen bonding and physical entanglement impair the dispersion of the fibers in the viscous matrix. Coupling agents or compatibilizing agents are commonly employed to overcome these problems (Woodhams et al. 1984; Kokta et al. 1990; Felix 1993). These chemical reagents convert the hydrophilic surface of cellulosic fibers to a hydrophobic one, and the surface tension of cellulosic fibers is thereby reduced so that it approaches the surface tension of the molten polymer. As a result, the fiber-fiber hydrogen bonding is reduced, the dispersion of the fibers in the matrix is enhanced, and adhesion also is improved via the mechanisms such as entanglement, mechanical interlocking, and formation of physical or chemical bonds between treated fibers and the polymer matrix (Schultz and Lavielle 1989; Felix 1993; Kazayawoko 1996).

The adhesion of the fibers to the solidified matrix will be influenced by the chemical treatment applied to the fibers. Since a surface can be characterized by its chemical composition, surface tension, and acid-base properties, there is a strong correlation between these surface parameters and the mechanical strength of the resulting composites (Kaeble 1974; Schultz and Lavielle 1989). Therefore, the investigation of some of these surface parameters seems to be a requisite to understand the mechanism of adhesion between the fibers and the polymer. The knowledge of these surface properties would help to provide a better fundamental understanding of the relationship between surface adhesion and the mechanical properties of the composite.

Unlike cellulosic fiber/polyolefin compos-

ites, the accepted criterion of matching surface tensions by converting the hydrophilic surface of cellulosic fibers to a hydrophobic surface does not seem to be effective for enhancing the adhesion of PVC to wood-fibers (Matuana et al. 1998a). Our experimental results have suggested that other mechanisms such as acid-base characteristics of wood and PVC may also play a key role in determining the adhesion mechanism of cellulosic fiber/plastic composites. Therefore, the characterization of the acid-base characteristics of cellulosic fibers seems to be crucial to describe the adhesion between cellulosic fibers and thermoplastic polymers.

Acid-base characteristics of solids can be determined using the wetting/adsorption theory and contact angle techniques (Nguyen and Johns 1978; Schultz and Lavielle 1989; Felix 1993; Gardner 1996). Gas adsorption techniques have also been used for many years to assess adsorption properties such as the surface tension of solids independent of their morphology (Dorris and Gray 1979, 1980; Saint-Flour and Papirer 1982a, 1982b; Papirer 1986; Lavielle and Schultz 1991). The IGC technique has been widely used as one of the most valuable methods for characterization of the surface energy of solids. It applies not only for smooth surfaces but also for rough and heterogeneous surfaces such as cellulosic fibers (Dorris and Gray 1979, 1980; Kamdem and Riedl 1991a, 1991b; Chtourou et al. 1995; Garnier and Glasser 1996; Simonsen et al. 1997). It has partly replaced traditional static methods for the adsorption process because of several advantages: it is less time consuming; it does not require elaborate apparatus or vacuum; and it is accurate at low concentration (Kamdem and Riedl 1991b). Measurements can also be conducted over a wide range of temperatures.

In this context, the aim of the present study is to characterize the acid-base properties of untreated and treated cellulosic (newsprint) fibers to clarify the interfacial interactions of fibers and various thermoplastics. The surface chemical compositions of untreated and treat-

ed cellulosic materials have been characterized using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) in previous studies (Matuana et al. 1998a, 1998b, 1998c). In this study, an attempt is made to correlate the results obtained from IGC with the chemical surface compositions of the fibers determined from the XPS and FTIR studies.

Basic theory of IGC

Since the basic theory of the IGC technique is described in several other papers (Dorris and Gray 1980; Schultz and Lavielle 1989; Schreiber 1993), only the critical equations and assumptions are recalled in this paper. The fundamental parameter measured in IGC is the net retention volume (V_N) which is the volume of carrier gas required to elute the probes from the column. The relationship linking V_N with the surface energy of the solid is:

$$-\Delta G_A^{\circ} = RT \ln V_N + \text{constant}$$

$$= 2 \cdot N \cdot (\gamma_S^D)^{1/2} \cdot a \cdot (\gamma_L^D)^{1/2}$$

$$+ \text{constant} \tag{1}$$

where ΔG_A° is the standard free energy of adsorption per mole of "probe" molecules, R is the gas constant, T is the temperature of the column, N is Avogadro's number, and a is the surface area of the probe molecule. γ_S^D and γ_L^D are the London dispersive components of the surface energy of the solid and the probe in the liquid state, respectively.

To determine the contribution of the acid-base properties of the solid, polar probes must be injected into the column, in addition to n-alkane (nonpolar probes). By assuming that n-alkane exchanges only dispersive interactions (Fowkes 1964) and that dispersive and polar components of surface energy are additive (Fowkes 1984; Fowkes and Mostafa 1978), the alkane line may be taken as a reference for determining the dispersive component for polar probes. The difference of ordinates between the alkane straight line and the polar probe gives ΔG_{SP}°, corresponding to the spe-

cific acid-base interactions (Schultz and Lavielle 1989):

$$RT \ln \frac{V_N}{V_N^{ref}} = \Delta G_{SP}^{\circ} \tag{2}$$

From the temperature variation of the free energy of adsorption, the enthalpy of adsorption ΔH_{SP} can be obtained according to (Schultz and Lavielle 1989)

$$\Delta G_{SP} = \Delta H_{SP} - T\Delta S_{SP} \tag{3}$$

where ΔS_{SP} is the entropy of adsorption. The plot of ΔG_{SP} versus T is linear and that ΔH_{SP} can be determined from the intercept at the origin of the straight line.

Following Papirer's approach, Saint-Flour and Papirer (1982a, 1982b, 1983) Papirer (1986), Schultz and Lavielle (1989) characterized solid surfaces by the numbers describing their acidic (K_A) and basic (K_D) characteristics, using Gutmann's acid-base concepts (Gutmann 1978), and proposed the following relationship:

$$\Delta H_{SP} = K_A \cdot DN + K_D \cdot AN \tag{4}$$

where DN and AN are electron donor (base) and electron acceptor (acid) numbers of the probe, respectively. DN, expressed in kcal/mol., is the molar enthalpy of the reaction between the electron-donor with a reference acceptor, antimony pentachloride $(SbCl_5)$, in a dilute solution of 1,2-dichloroethane (Gutmann 1978). AN is in an arbitrary unit derived from the relative NMR chemical shift of ^{31}P contained in triethylphosphine oxide $(C_2H_5)_3PO$ when reacting with an acceptor solvent (Gutmann 1978).

A plot of $^{\Delta H}SP/AN$ versus $^{DN}/AN$ is actually linear and K_A and K_D can be determined from the slope and intercept at the origin of this straight line (Schultz and Lavielle 1989).

EXPERIMENTAL

Materials

A ground waste inked newsprint fiber was used as the filler. Fibers from waste newsprint were dry-shredded into feedstock in a standard

hammer mill (American Pulverizer Type M). The machine was equipped with a shift screen of openings 1 mm in diameter. After defibrating, the fibers were sieved to mesh size 60 mixture: 60% mesh 60, 20% mesh 80, 15% mesh 100, and 5% mesh 200, with a Granu Grinder (C.W. Brabender Instruments Inc.). Plasticized PVC resin was also investigated since it constitutes the thermoplastic to be compounded with waste newsprint fibers in our future work. PVC (Geon 103EPF76 K value 66) was supplied by Royal Plastics Limited and was plasticized with 7.5 phr (parts per hundred resin) Dioctyl phthalate (DOP).

γ-aminopropyltriethoxysilane ($H_2NCH_2CH_2$ CH_2)-Si-(OCH_2CH_3)$_3$ designated as A-1100 (Union Carbide Corporation), dichlorodiethylsilane (CH_3CH_2)$_2$-Si-Cl_2 designated as DCS (Dow Chemical Company), phthalic anhydride (PA, Aldrich Chemical Company), and maleated polypropylene (Epolene Wax E-43, Eastman Chemical) were used as coupling agents. Sodium carbonate (Na_2CO_3 anhydrous, J.T. Baker Chemical Co.) was used as a catalyst. All chemicals were used as received from the manufacturers.

Surface modification of fibers

Before the surface treatment, newsprint fibers were Soxhlet-extracted with acetone for 24 h to remove contaminants or impurities on the surface of fibers. This extraction also removed some acetone extractives and most of the adsorbed moisture in the fibers. After the extraction, newsprint fibers were placed in air for at least 2 weeks to allow the solvent to evaporate. The moisture content of the fibers after evaporation of the solvent was approximately 10%. Finally, the fibers were oven-dried at 60°C until constant weight was achieved.

Treatment with silanes

The treatment of newsprint fibers was carried out in a solvent-free system (dry blending) by spraying and mechanically mixing 0.1% of silanes on the surface of fibers (A-

1100 and DCS based on the weight of fibers). The treated newsprint fibers were air-dried for 30 min and then oven-dried at 60°C for 24 h. Drying was followed by Soxhlet extraction with acetone for at least 24 h to remove the silane that was not chemically bonded to fibers. After this extraction, the treated samples were air-dried for 24 h and then dried at 60°C in a circulating air oven until a constant weight was achieved.

Treatment with phthalic anhydride (PA) and maleated polypropylene (E-43)

Newsprint fiber samples were immersed in a toluene solution containing 2 moles of PA at 100°C for 20 min. Na_2CO_3 (10% by the weight of fibers) was used as catalyst. The treatment of newsprint fibers with E-43 was performed in a solvent system without a catalyst. The newsprint fibers were immersed in a 100-ml toluene solution containing 3% of E-43 (by weight of fibers) at 100°C for 20 min. These treatments were followed by a Soxhlet extraction of treated newsprint fibers with toluene for at least 24 h, evaporating the solvent in air for 24 h and finally oven-drying at 60°C until a constant weight was achieved.

Chromatographic conditions

Inverse gas chromatography measurements were made using a Beckman GC-65 gas chromatograph equipped with a flame ionization detector of high sensitivity (FID, Dani FID control 331). A copper column 60 cm in length with an internal diameter of 4 mm was packed with 2 to 2.5 g of fibers used as the stationary phases. Nitrogen was used as a carrier gas and air as a noninteracting marker, i.e., to determine the dead volume. The flow rate of the carrier gas (N_2) was 32.5 ml/min. The injector port and detector temperatures were 175°C and 200°C, respectively, to insure flash vaporization of the probes. The column was conditioned overnight under a steady flow of nitrogen at 90°C prior to use. A 1-μl Hamilton gas tight syringe was used to inject a trace amount of vapors into the column through the

TABLE 1. *Characteristics of probes used in IGC experiments (Gutmann 1978; Schultz and Lavielle 1989).*

Probes	a $(Å^2)$	$\gamma_l{}^D$ $(mJ\cdot m^{-2})$	DN (kcal/mol)	AN	Specific characteristics
C_7H_{16}	57.0	20.3	—	—	Neutral
C_8H_{18}	62.8	21.3	—	—	Neutral
C_9H_{20}	68.9	22.7	—	—	Neutral
$C_{10}H_{22}$*			—	—	Neutral
Ethyl-Acetate (EA)	48.0	19.6	17.1	9.3	Amphoteric
Acetone	42.5	16.5	17.0	12.5	Amphoteric
THF	45.0	22.5	20.0	8.0	Base
DEE	47.0	15.0	19.2	3.9	Base
$CHCl_3$	44.0	25.9	0	23.1	Acid

* The value of $(a\gamma_l{}^D)^{1/2}$ in Figure 1 (x-axis) for $C_{10}H_{22}$ was estimated to be 358.2 mJm^{-2}Å^2 (Mukhopadhyay and Schreiber 1993).

injection port, and at least 5 separate vapor injections were made for each probe. The n-alkane probes (C_6-C_{10}) were used to measure the dispersive interactions. On the other hand, several acid-base probes used for the nondispersive interactions were chosen either for their strong donor (base) characteristic or a strong acceptor (acid) characteristic, or both characteristics simultaneously (amphoteric). These probes listed in Table 1 included acetone, tetrahydrofuran (THF), diethylether (DEE), ethyl acetate (EA), and chloroform ($CHCl_3$). Retention data were recorded on a Fisher Recordall 5000 chart recorder. Symmetrical elution peaks were obtained, and the peak maxima method was used to obtain the retention times from the chromatographs.

RESULTS AND DISCUSSION

The effectiveness of the modifications made on the surfaces of newsprint fibers following the treatments with A-1100, DCS, PA, and E-43 was investigated in previous studies (Ma-

tuana et al. 1998a, 1998b, 1998c). The XPS and FTIR results based on the elemental and functional compositions of the untreated and treated newsprint fibers indicated that modifications were made on the fiber surface.

The effectiveness of the treatment of fiber with coupling agents was monitored by the changes in the relative atomic ratios of oxygen-to-carbon, silicon-to-carbon, and nitrogen-to-carbon on the surface of the fibers (Table 2). In addition, the treatment of newsprint fibers with coupling agents caused an increase in the concentration of unoxidized carbon (C1 component), and consequently, a significant decrease of the O/C atomic ratio, as expected from compounds rich in carbon-containing groups. For the treatment with silanes, this decreased O/C atomic ratio (or increased concentration of unoxidized carbon) arose from the aliphatic hydrocarbon chains (-CH_2-)$_3$ and (CH_3–CH_2)$_2$ that serve to attach the functional groups to the silicon atom, whereas for the treatments with PA and E-43, the increased

TABLE 2. *Elemental surface composition and analysis of high resolution C_{1s} peaks of untreated and treated newsprint fibers determined from XPS (Matuana et al. 1998b, 1998c).*

Newsprint fibers	Elemental composition (%)				O/C	Analysis of C_{1s} peaks (%)			
	O	C	Si	N		C1	C2	C3	C4
Untreated	35.6	60.7	3.7	0.0	0.59	48.6	43.5	7.9	0.0
Treated with									
A-1100	25.1	55.1	11.9	7.9	0.46	72.0	23.0	5.0	0.0
DCS	19.8	68.7	11.5	0.0	0.29	86.7	8.7	4.6	0.0
PA	30.9	69.1	0.0	0.0	0.45	52.7	34.5	7.9	4.9
E-43	30.8	69.2	0.0	0.0	0.45	62.3	25.6	6.9	5.2

concentration of unoxidized carbon must have originated from the aliphatic carbons of polypropylene chains of E-43 and from the carbons of the aromatic ring of PA. The decrease in the O/C ratio of newsprint fibers following the treatments was a clear indication of the attachment of the coupling agents to the surface of newsprint fibers. The IGC experiments were conducted in the present study to examine the acid-base characteristics of the untreated and treated waste newsprint fibers. An attempt was made to correlate the IGC results with surface chemical compositions determined from previous XPS and FTIR spectroscopy studies.

Effects of treatment on $\gamma^D{}_S$ of the fibers

The mechanism of probe retention by various substrates is of prime importance for any IGC data and may involve either diffusion of the probe into the bulk of the solid or surface adsorption. If the former mechanism can be avoided during IGC experiments, valuable surface properties of the solid can be quantified from the IGC data.

Figures 1 (a–f) are illustrative plots of $RTlnV_N$, a measure of the free energy of adsorption, versus $a \cdot (\gamma^D{}_L)^{1/2}$ obtained at 60°C for untreated and treated newsprint fibers with silanes (A-1100, DCS), PA, E-43, and plasticized PVC. Similar results were obtained at 70 and 80°C (not shown). As reported by Schultz and Lavielle (1989), a linear relation for n-alkanes (C_7-C_{10}) was observed, suggesting surface adsorption as the only mechanism of alkane probe retention by the fibers and plasticized PVC. As shown in Fig. 2, the magnitude of the free energy of adsorption (ordinate) for n-alkane probes increased after surface treatment of newsprint fibers and plasticized PVC, indicating a strong interaction of these materials with n-alkane probes. In addition, the slope of the straight lines (measure of $\gamma^D{}_S$) changed. These differences are indicative of the effectiveness of the surface modification of the newsprint fibers.

The London dispersive components of the surface free energy $\gamma^D{}_S$ of the fibers determined from the slope of the relationship $RTlnV_N$ versus $a \cdot (\gamma^D{}_L)^{1/2}$ are listed in Table 3. The value of $\gamma^D{}_S$ related to the untreated newsprint fibers is relatively lower than others observed values at 25°C (Kamdem and Riedl 1991b; Dorris and Gray 1980) but agrees well with those reported in the literature for explosion pulps and Kraft pulps in the range of temperatures investigated in this study (Chtourou et al. 1995). The causes of the low dispersive energy for untreated newsprint fibers are unknown at the moment but will be investigated. When $\gamma^D{}_S$ is regressed down to room temperature, a value of around 22 mJ/m² is obtained for dispersive energy. From a practical standpoint, the low surface energy may make these fibers compatible with low energy materials. However, the surface treatments of the fibers resulted in significant changes in $\gamma^D{}_S$. The treated fibers showed higher $\gamma^D{}_S$ than the untreated ones, implying the modification made on the surface of the fibers. This significant increase in the $\gamma^D{}_S$ after treatment indicated a strong interaction of treated fibers with n-alkane probes. Since n-alkanes are able to interact only through dispersion interactions, the increased $\gamma^D{}_S$ for treated fibers was an indication that the fibers had become more hydrophobic. This observation is consistent with the increase of unoxidized carbon atoms C1 (or decrease of O/C atomic ratio) on the surface of treated fibers as revealed in the XPS analysis (Matuana et al. 1998b, 1998c).

It should be noted that the surface energy determined from Eq. (1) has been criticized for violating the thermodynamic phase rule for capillary systems by requiring more degrees of freedom than are available for a two-components solid-liquid-vapor system (Spelt et al. 1984; Kwok and Neumann 1994). The Fowkes approach does not give the overall surface tension of the solid. Only the London dispersive component of surface tension can be determined from the slope of this relationship. However, the effect of surface treatment of the present study on the surface tension of wood has been previously investigated (Matuana et
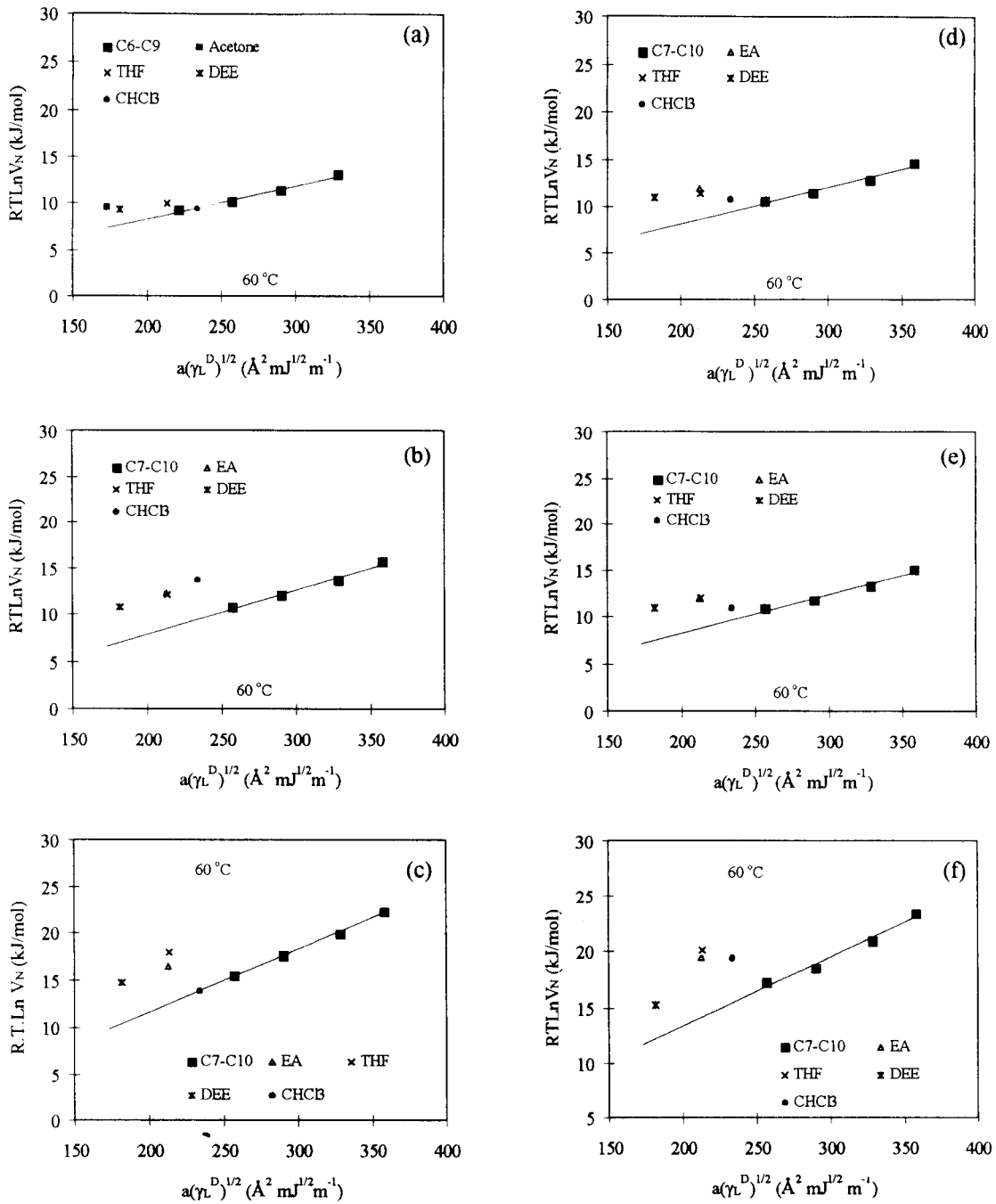
FIG. 1. $RTLnV_N$ versus $a \cdot (\gamma^D_L)^{1/2}$ of dispersive and nondispersive probes for (a) untreated newsprint-fibers, newsprint-fibers treated with (b) A-1100, (c) DCS, (d) PA, (e) E-43, and (f) plasticized PVC. Column temperature: 60°C.
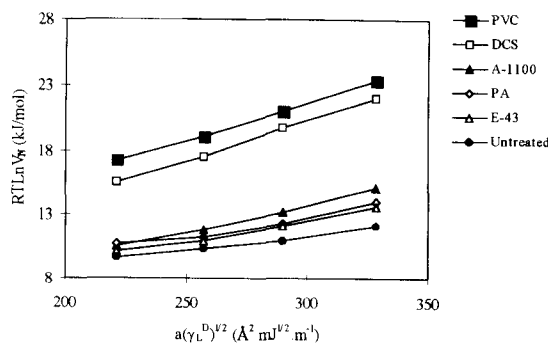
FIG. 2.   RTLnV$_N$ versus a·$(\gamma^D_L)^{1/2}$ of dispersive probes for untreated newsprint-fibers, treated newsprint-fibers, and plasticized PVC.

al. 1998a) using the equation of state for interfacial tensions where the predicted number of degrees of freedom of this equation from the capillary system has been shown to agree well with the experimental results (Kwok and Neumann 1994).

Effect of treatment on acid-base characteristics of fibers

Figure 1 shows that the points corresponding to the acidic, basic, and amphoteric probes clearly lie on or above the n-alkane reference lines, indicating that nondispersive or polar interactions were present. Unlike the newsprint fibers treated with aminosilane (A-1100), the interactions of the overall newsprint fibers and plasticized PVC were greater for the basic probes, whereas the newsprint fibers treated with A-1100 interactions were greater for acidic probes. From these observations, it can be confirmed on a qualitative basis that news-

print fibers treated with aminosilane had basic surfaces, whereas the untreated newsprint fibers, the newsprint fibers treated with dichlorosilane, phthalic anhydride, maleated polypropylene, and the plasticized PVC all had predominantly acidic surface characteristics.

To quantify the acid-base surface characteristics of untreated and treated newsprint fibers and PVC, i.e., K$_A$ and K$_D$, the values of ΔG°_{SP} were plotted against the temperature. This was done to determine the enthalpies of adsorption ΔH_{SP} corresponding to the specific interactions. Figure 3 shows the temperature dependence of the specific component of ΔG°_{SP} for the adsorption of an acidic probe ($CHCl_3$) and a basic probe (THF) on the surfaces of untreated and treated newsprint fibers and plasticized PVC. Similar plots were obtained with other probes, i.e., DEE and EA. The values of ΔG°_{SP} corresponding to the specific acid-base interactions of the fibers were determined from the vertical distance between the n-alkane line and the polar probes from Fig. 1.

Figure 3 illustrates that ΔG°_{SP} varied linearly with temperature. This linear relationship for acid-base probes implies that adsorption was the dominant mechanism of probe retention by the fibers. The slope of the straight line in Fig. 3 is proportional to the entropy of adsorption (ΔS_{SP}), while the intercept determines the enthalpy of adsorption (ΔH_{SP}). It should be noted that the lines for the untreated newsprint fibers and those treated with DCS overlapped in Fig. 3 (a) because they both had $\Delta G^\circ_{SP} = 0$.

ΔH_{SP} constitutes an important parameter since it is a measure of the specific work en-

TABLE 3.   *Surface characteristics of newsprint-fibers and plasticized PVC determined by IGC.*

| Samples	γ_S^D (mJ/m²)			K$_A$ acid	K$_D$ base	Coefficient of correlation %	K$_D$/K$_A$	Surface characteristics
	60°C	70°C	80°C					
Untreated newsprint fibers	8.8	5.4	3.5	0.65	0.16	95	0.25	Acidic
Treated newsprint fibers with								
A-1100	15.7	12.9	6.8	0.57	0.96	99	1.68	Basic
DCS	30.0	29.6	27.1	1.41	0.05	100	0.04	Acidic
PA	10.8	6.7	3.9	0.87	0.20	97	0.23	Acidic
E-43	11.7	7.9	5.8	0.68	0.35	94	0.51	Acidic
Plasticized PVC	26.1	23.4	22.2	1.43	0.65	98	0.43	Acidic
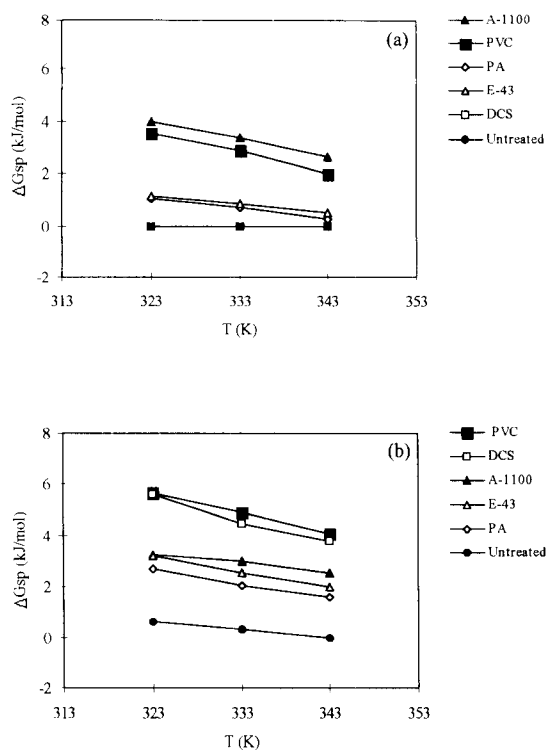
FIG. 3. The temperature dependence of the specific component of ΔG°_{SP} for the adsorption of (a) an acidic probe ($CHCl_3$) and (b) a basic probe (THF) on the surface of untreated and treated newsprint-fibers and plasticized PVC.

ergy of adhesion for phases similar to the probe. Once again, Fig. 3 shows that fibers having strong acidic surface characteristics had greater affinity for the basic probe (THF) compared to the acidic probe ($CHCl_3$) and vice-versa. The values of $^{\Delta H}SP/_{AN}$ were plotted versus $^{DN}/_{AN}$ in Fig. 4 to obtain the expected linear relationship. The acid (K_A) and base (K_D) surface characteristics of untreated and treated newsprint fibers and plasticized PVC were determined from the slope and intercept at the origin of these straight lines and are summarized in Table 3. The quantitative results of K_A and K_D listed in this table corroborated the conclusions drawn from the qualitative observations. It should be noted that ethyl acetate was not used as an amphoteric probe for untreated fibers in calculating K_A and K_D, because the elution of peaks was not

symmetrical. Similarly, acetone was not used because it did not produce symmetrical peaks for treated fibers.

The acidic nature of untreated newsprint fibers may be attributed to the electron acceptor character of the hydroxyl protons. Newsprint fibers have a higher O/C atomic ratio as cellulose and hemicelluloses are rich in oxygen. The XPS results showed that the newsprint fiber surface had 43.5% of C2, 7.9% of C3, and 35.6% of O components (Table 2). So there are more hydroxyl groups than carboxyl groups at the surface and this suggests a more acidic character of the newsprint fiber surface. Similar results have been reported in the literature for cellulose fibers (Schreiber 1993; Garnier and Glasser 1996). The lignin and fatty acids may also contribute to the acidic character of the untreated newsprint fibers. The acidic characteristics of newsprint fibers treated with dichlorosilane (DCS) and plasticized PVC were attributed to the highly electronegative nature of the chlorine atoms (Schreiber 1993). The basic surface of newsprint fibers after treatment with aminosilane (A-1100) was attributed to the presence of the amine groups on the surface of the fibers as measured from the XPS high-resolution spectra of N_{1s} (Matuana et al. 1998b). Because aminosilanes react with hydroxyl groups of the fibers, the surface of the fibers was covered with amine groups (which are known electron donors). The acidic characteristics observed with newsprint fibers treated with maleated polypropylene (E-43) were not in good agreement with the neutral characteristics of cellulose-fibers treated with E-43 as reported by other investigators (Felix 1993). This discrepancy may be explained either by the difference in the nature of the fibers used and/or the nature of chemical reaction between the maleate groups of E-43 and the hydroxyl groups of the fibers. It is possible that there is an optimum quantity of E-43 wherein all the maleate groups are attached to the surface of the fibers and exposing a polypropylene surface (Fig. 5a), i.e., reaction of maleate groups with hydroxyl groups of the fiber to form a diester during esterifi-
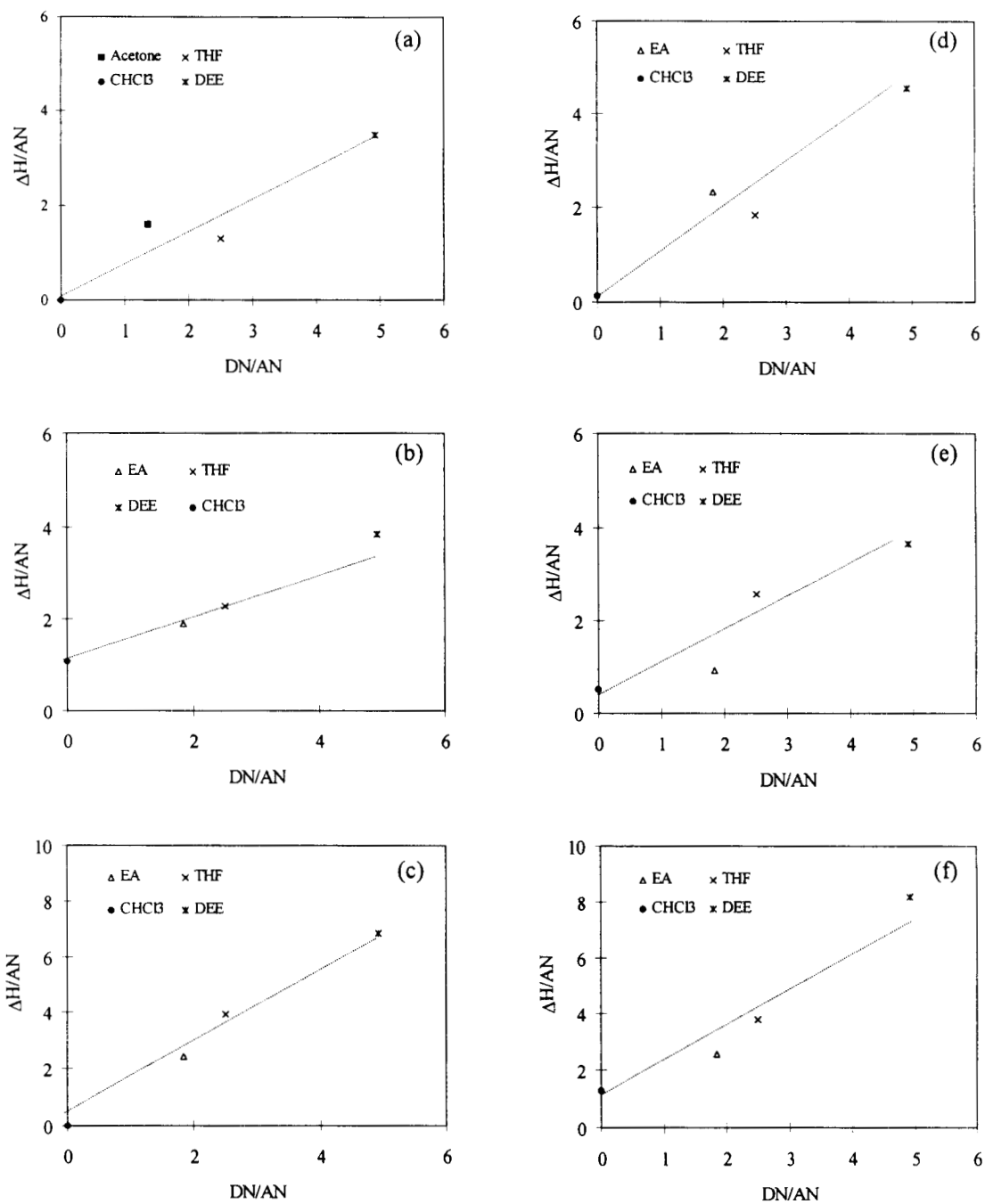
FIG. 4. ΔH/AN versus DN/AN for (a) untreated newsprint-fibers, treated newsprint-fibers with (b) A-1100, (c) DCS, (d) PA, (e) E-43, and (f) plasticized PVC.
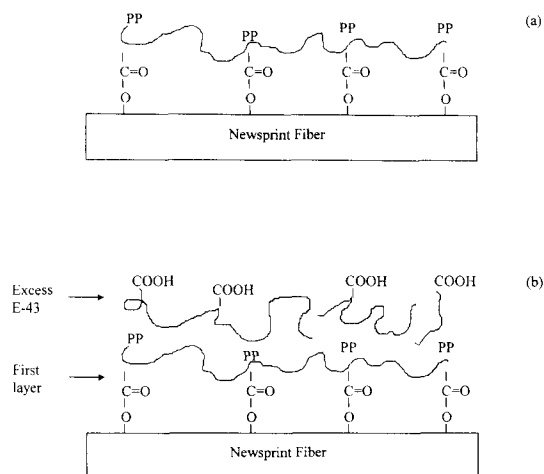
FIG. 5. Chemical reaction of maleated polypropylene with the surface hydroxyl groups of newsprint fibers.

cation reaction (Matuana et al. 1998c). In this case, the treatment will reduce the acidic characteristics of the fiber because of the neutral behavior of the exposed polypropylene chains of E-43. If excess or unreacted maleate groups are present, the unreacted or exposed maleate groups will be exposed (Fig. 5b), accounting for the discrepancy. However, the acidic surface characteristics of newsprint fibers treated with E-43 observed in this study can be attributed to the introduction of carboxylic species on the surface of the fibers as evidenced by FTIR absorption spectra (Matuana et al. 1998c). The FTIR spectroscopy results showed that anhydride moieties of both phthalic anhydride and maleated polypropylene entered into the esterification reaction with the surface hydroxyl groups of the newsprint fibers. These reagents have been reacted with the surface of newsprint fibers to form a monoester, i.e., the formation of esterified fibers bearing pendent carboxylic groups as illustrated in Fig. 5b. The newsprint fibers treated with PA also exhibited acidic surface characteristics attributable to the pendent carboxylic functional groups. This strong acidity of newsprint fibers treated with PA is reflected by the ratio K_D/K_A being less than unity.

CONCLUSIONS

The acid-base surface characteristics of untreated newsprint fibers, treated newsprint fibers, and plasticized PVC have been investigated using the IGC technique. Newsprint fibers were surface modified with γ-aminopropyltriethoxysilane, dichlorodiethylsilane, phthalic anhydride, and maleated polypropylene.

Based on the K_D and K_A values, the surface of untreated newsprint fibers has an acidic characteristic due to the electron acceptor character of hydroxyl protons. The newsprint fibers reacted with phthalic anhydride or maleated polypropylene exhibited an acidic surface attributed to pendent carboxylic groups, the presence of which were confirmed by FTIR spectroscopy. Aminosilane treatment produced a basic surface due to the incorporation of amine substituents on the surface of the fibers. Dichlorosilane produced a strong acidic surface. Plasticized PVC exhibited an acidic surface because of the electronegative nature of the chlorine atoms.

Inverse gas chromatography at infinite dilution has been found to be a valuable tool for investigating the interfacial acid-base properties of surface modified newsprint fibers, which can then be correlated with the mechanical properties of such composites.

REFERENCES

CHTOUROU, H., B. RIEDL, AND B. V. KOKTA. 1995. Surface characterization of modified polyethylene pulp and wood-fibers using XPS and inverse gas chromatography. J. Adhes. Sci. Technol. 9(5):551–574.

DORRIS, G. M., AND D. G. GRAY. 1979. Adsorption, spreading pressure, and London force interactions of hydrocarbons on cellulose and wood fiber surfaces. J. Colloid Interface. Sci. 71(1):93–106.

————, AND ————. 1980. Adsorption of n-alkanes at zero coverage on cellulose paper and wood fibers. J. Colloid Interface. Sci. 77:353–362.

FELIX, J. 1993. Enhancing interactions between cellulose fibers and synthetic polymers. Ph.D. Thesis, Department of Polymer Technology, Chalmers University of Technology, Göteborg, Sweden.

FOWKES, F. M. 1964. Attractive forces at interfaces. Ind. Eng. Chem. 56(12):40–52.

————. 1984. Acid-base contributions to polymer-filler interactions. Rubber Chem. Technol. 57:328–343.

————, AND M. A. MOSTAFA. 1978. Acid-base interactions in polymer adsorption. Ind. Eng. Chem. Prod. Res. Dev. 17(1):3–7.

GARDNER, D. J. 1996. Applications of the Lifshitz-Van der Waals acid-base approach to determine wood surface tension components. Wood Fiber Sci. 28(4):422–428.

GARNIER, G., AND W. G. GLASSER. 1996. Measuring the surface energies of spherical cellulose beads by inverse gas chromatography. Polym. Eng. Sci. 36(6):885–894.

GUTMANN, V. 1978. The donor-acceptor approach to molecular interactions. Plenum Press, New York, NY. 267 pp.

KAEBLE, D. H. 1974. A relationship between the fracture mechanics and surface energetics failure criteria. J. Appl. Polym. Sci. 18:1869–1889.

KAMDEM, D. P., AND B. RIEDL. 1991a. Characterization of wood fibers modified by phenol-formaldehyde. Colloid Polym. Sci. 269(6):595–603.

————, AND ————. 1991b. IGC characterization of PMMA grafted onto CTMP fiber. J. Wood Chem. Technol. 11(1):57–91.

KAZAYAWOKO, M. 1996. Surface modification and adhesion mechanisms in woodfiber-polypropylene composites. Ph.D. Thesis, Faculty of Forestry, University of Toronto, Toronto, Ontario, Canada.

KOKTA, B. V., D. MALDAS, C. DANEAULT, AND P. BÉLAND. 1990. Composites of polyvinyl chloride-wood-fibers. III: Effects of silanes as coupling agent. J. Vinyl Technol. 12(3):146–153.

KWOK, D. Y., AND A. W. NEUMANN. 1994. Fowkes' surface tension component approach revisited. Colloids Surfaces A: Physicochem. Eng. Aspects. 89:181–191.

LAVIELLE, L., AND J. SCHULTZ. 1991. Surface properties of carbon fibers determined by inverse gas chromatography: Role of pretreatment. Langmuir 7(5):978–981.

MATUANA, L. M., J. J. BALATINECZ, AND C. B. PARK. 1998a. Effect of surface properties on the adhesion between PVC and wood veneer laminates. Polym. Eng. Sci. 38(5):765–773.

————, ————, ————, AND R. N. S. SODHI. 1998b. X-ray photoelectron spectroscopy study of silane-treated newsprint fibers. Wood Sci. Technol. (in press).

————, R. N. S. SODHI, AND C. B. PARK. 1998c. Surface characterization of esterified cellulosic fibers by XPS and FTIR spectroscopy. Wood Sci. Technol. (in press).

MUKHOPADHYAY, P., AND H. P. SCHREIBER. 1993. Inverse gas chromatography for polymer surface characterization above and below Tg. Macromolecules 26(24):6391–6396.

NGUYEN, T., AND W. E. JOHNS. 1978. Polar and dispersion force contributions to the total surface free energy of wood. Wood Sci. Technol. 12:63–74.

PAPIRER, E. 1986. Characterization of fibers and fillers for composite materials using inverse gas chromatography. Pages 203–214 in H. Ishida and J. L. Koenig, eds. Composite interfaces. Elsevier Science Publishing Co., Inc., New York, NY.

QUILLIN, D. T., D. F. CAULFIELD, AND J. A. KOUTSKI. 1992. Surface energy compatibility of cellulose and polypropylene. Pages 113–126 in R. M. Rowell, T. L. Laufenberg, and J. K. Rowell, eds. Materials interactions relevant to recycling of wood-based materials. Proc. Materials Research Society Symposium, San Francisco, CA.

SAINT-FLOUR, C., AND E. PAPIRER. 1982a. Gas-solid chromatography: A method of measuring surface free energy characteristics of short glass fibers. 1. Through adsorption isotherms. Ind. Eng. Chem. Prod. Res. Dev. 21(2):337–341.

————, AND ————. 1982b. Gas-solid chromatography: A method of measuring surface free energy characteristics of short glass fibers. 2. Through retention volumes measured near zero surface coverage. Ind. Eng. Chem. Prod. Res. Dev. 21(4):666–669.

————, AND ————. 1983. Gas-solid chromatography: A quick method of estimating surface free energy variations induced by the treatment of short glass fibers. J. Colloid Interface. Sci. 91(1):69–75.

SCHREIBER, H. P. 1993. Aspects of component interactions in m polymer systems. Pages 21–59 in G. Akovali, ed. The interfacial interactions in polymeric composites. Kluwer Academic Publishers, Netherlands.

SCHULTZ, J., AND L. LAVIELLE. 1989. Interfacial properties of carbon fiber-epoxy matrix composites. Pages 185–202 in D. R. Lloyd, H. P. Schreiber, and T. Ward, eds. Inverse gas chromatography: Characterization of polymers and other materials. ACS Symposium Series No. 391, American Chemical Society, Washington, DC.

SIMONSEN, J., Z. HONG, AND T. G. RIALS. 1997. The properties of the wood-polystyrene interphase determined by inverse gas chromatography. Wood Fiber Sci. 29(1):75–84.

SPELT, J. K., D. R. ABSOLOM, AND A. W. NEUMANN. 1984. Solid surface tension: The interpretation of contact angles by the equation of state approach and the theory of surface tension components. Langmuir 2(5):620–625.

WOODHAMS, R. T., G. THOMAS, AND D. K. RODGERS. 1984. Wood fibers as reinforcing fillers for polyolefins. Polym. Eng. Sci. 24:1166–1171.