Surface Characterization of Pulp Paper Fibres Using Inverse Gas Chromatography

Alireza Shakeri*1,i and Korosh Tabar-Haidar2

(1) Department of Composites, Faculty of Processing, Iran Polymer and Petrochemical Institute
P.O. Box: 14965/115, Tehran, I.R. Iran
(2) Center of Research Chemical and Chemical Engineering, P.O. Box: 14335/186
Tehran, I.R. Iran

Received 14 July 2003; accepted 1 June 2004

ABSTRACT

The surface characteristics of treated pulp paper fibre were investigated using inverse gas chromatography (IGC). The surface of pulp paper fibres was modified with \(\gamma\)-aminopropyl-triethoxysilane, dichlorodiethylsilane and vinyl triethoxysilane. The effectiveness of these surface treatments was monitored by 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 pulp papers fibres were determined using Schultz’s method and were correlated with the surface chemical compositions determined from Fourier transform infra-red spectroscopy (FTIR) technique. The results indicated that the surface of untreated pulp paper fibres had an acidic characteristic due to the electron acceptor character of the hydroxyl protons. \(\gamma\)-Aminopropyl triethoxysilane produced a basic surface behaviour attributed to the electron donor ability of the amino groups. Dichlorodiethylsilane produced a strong acidic surface attributed to the highly electronegative nature of the chlorine atoms. When the fibres were treated with vinyl triethoxysilane, an acidic surface was observed.

INTRODUCTION

Cellulosic-fibre plastic composites have been extensively studied in recent years [1]. These materials offer many potential benefits, such as low cost, increased stiffness, recyclability, ease of processing, flexible design of properties, and higher strengths compared to unreinforced plastic. Although in many respects the properties of these composites have improved, but the lack of adhesion between the wood fibre and plastic still remains a problem. The adhesion between hydrophilic, polar cellullosic...
fibres (high surface energy), and hydrophobic, non-polar thermoplastics (low surface energy) can influence the strength and toughness of the composites. The adhesion of the fibres onto the solidified matrix is influenced by the chemical treatment applied to the fibres. Since a surface can be characterized by 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 [2]. Therefore, the investigation of some of these surface parameters seems to be a requisite to understand the mechanism of the adhesion between the fibres 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.

Acid-base characteristics of solids can be determined using the wetting/adsorption theory and contact angle techniques [3, 4]. Gas adsorption techniques have also been used for many years to assess adsorption properties such as the surface tension of the solids independent of their morphology [5, 6]. 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 fibres [7-11]. 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 [11]. Measurements can also be made over a wide range of temperatures.

The dispersive component, $\gamma_D$, of fibre surface energy is determined by injecting alkane probes in the column. The general equation is given by:

$$RT \ln N + \text{constant} = 2 \times N \times (\gamma_D^{1/2}) \times a \times (\gamma_L^{1/2}) + \text{constant}$$

$R$ being the gas constant, $T$ the column temperature, $N$ is Avagadro’s number, and $a$ is the surface area of the probe molecule, $\gamma_L$ is the London dispersive components of the surface energy of the probe in liquid state.

According to Gutman’s approach [12], the probes are characterized by their donor-acceptor numbers, DN and AN (Table 1).

Following Papirer’s approach characterized solid surface by the numbers describing their acidic ($K_A$) and basic ($K_D$) characteristics [5], Using eqn (2):

$$\Delta H_{sp} = K_A \times DN + K_D \times AN$$

Where $\Delta H_{sp}$, the enthalpy of adsorption corresponding to the specific interactions, $K_A$ and $K_D$ are, equivalent to AN (acceptor number) and DN (donor number) of molecules, respectively.

With acid and base probes, the difference of ordinates between the experimental point and the reference line corresponding to alkanes give an evaluation of the specific free energy $\Delta G_{sp}^c$.

From temperature variation of the free energy of adsorption, the enthalpy of adsorption $\Delta H_{sp}$ can be obtained according to:

---

Table 1. Characteristics of probes used in IGC experiments [2,16].

<table>
<thead>
<tr>
<th>Probe</th>
<th>$a$ ($A^2$)</th>
<th>$\gamma_D$ (mJ.m$^{-2}$)</th>
<th>DN (kcal/mol)</th>
<th>AN</th>
<th>Specific characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_7H_{16}$</td>
<td>57.0</td>
<td>20.3</td>
<td>---</td>
<td>---</td>
<td>Neutral</td>
</tr>
<tr>
<td>$C_8H_{18}$</td>
<td>62.8</td>
<td>21.3</td>
<td>---</td>
<td>---</td>
<td>Neutral</td>
</tr>
<tr>
<td>$C_9H_{20}$</td>
<td>68.9</td>
<td>22.7</td>
<td>---</td>
<td>---</td>
<td>Neutral</td>
</tr>
<tr>
<td>$C_{10}H_{22}$</td>
<td>76.9</td>
<td>24.9</td>
<td>---</td>
<td>---</td>
<td>Neutral</td>
</tr>
<tr>
<td>Ethyl acetate (EA)</td>
<td>48.0</td>
<td>19.6</td>
<td>17.1</td>
<td>9.3</td>
<td>Amphoteric</td>
</tr>
<tr>
<td>Acetone</td>
<td>42.5</td>
<td>16.5</td>
<td>17.0</td>
<td>12.5</td>
<td>Amphoteric</td>
</tr>
<tr>
<td>THF</td>
<td>45.0</td>
<td>22.5</td>
<td>20.0</td>
<td>8.0</td>
<td>Base</td>
</tr>
<tr>
<td>DEE</td>
<td>47.0</td>
<td>15.0</td>
<td>19.2</td>
<td>3.9</td>
<td>Base</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>44.0</td>
<td>25.9</td>
<td>0</td>
<td>23.1</td>
<td>Acid</td>
</tr>
</tbody>
</table>
\[ \Delta G_{sp}^o = \Delta H_{sp} - T\Delta S_{sp} \]  

(3)

Where \( \Delta H_{sp} \) is the adsorption entropy. The plot of \( \Delta G_{sp}^o \) versus \( T \) is linear and that \( \Delta H_{sp} \) can be determined from the intercept at the origin of the straight line.

Dorryis and co-workers [13] extended the IGC technique to the study of fibres. Further development of the theory allowed the thermodynamic functions of adsorption to be derived from retention volume data. The aim of the present study is to characterize the acid-base properties of untreated and treated cellulosic (pulp paper) fibres to clarify the interfacial interaction of fibres and various thermoplastics. The surface chemical compositions of untreated and treated pulp paper fibres have been characterized using FTIR in previous studies [14].

In this study, an attempt is made to correlate the results obtained from IGC with the chemical surface compositions of the fibres determined from FTIR studies.

**EXPERIMENTAL**

**Materials**

The hard wood (beach and hornbeam), natural sulphite semi-chemical pulp paper (NSSC) commercial product of Mazandaran Wood and Paper Mill Co. was used as a filler. The average length and aspect ratio of the fibres before mixing was 1.1mm and 90, respectively. The fibres were sieved to mesh size 35 mixture: 60% mesh 35, 10% mesh 60, 15% mesh 80 and 5% mesh 100, with a Granu Grinder (C.W Brabender Instrument Inc.). \( \gamma \)-Aminopropyl triethoxysilane (H\( \text{2NCH}_2\text{CH}_2\text{CH}_2 \)-Si-(OCH\(_2\text{CH}_3\)_3 designated as A-1100 (Union Carbide Corporation), dichlorodiethyilsilane (CH\(_3\)CH\(_2\)_2Si-Cl\(_2 \) designated as DSC and vinyl triethoxysilane (CH\(_2\)=CH)-Si(OCH\(_2\text{CH}_3\)_3 designated as A-172 (Aldrich Chemical Co.), were used as coupling agents.

**Treatment of Fibre with Coupling Agent**

Prior to surface treatment, fibres were soxhlet-extracted with acetone for 24 h to remove contaminants or impurities on the surface of fibres. Following the extraction, pulp paper specimens were kept placed under ambient conditions for at least one week in order to allow the solvent to evaporate. Finally, the fibres were oven dried at 70 C until constant weight was achieved. The silane treatment of fibres was carried out in a solvent-free system (dry blending) by spraying and mechanically mixing 0.5 % of silanes (on the weight of fibres) on the surface of the fibres. The treated fibres were air-dried for 1 h and then oven-dried at 70 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 fibres. After this extraction, the treated samples were air-dried for 24 h and then dried at 70 C in an oven with circulating air until a constant weight was achieved.

**Chromatographic Condition**

Inverse gas chromatography measurements were conducted using a Beckman GC-65 gas chromatograph equipped with a flame ionization detector. A copper column 60 cm in length with an internal diameter of 4 mm was packed with 2 to 2.5 g of pulp paper fibres used as stationary phase. Nitrogen was used as a carrier gas and air, a non-interacting 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 were set at 180 and 200 C, respectively, to ensure flash vaporization of the probes. The column was conditioned overnight under a steady flow of nitrogen at 90 C prior to use. A 1-\( \mu \)L Hamilton gas tight syringe was used to inject a trace amount of vapours into the column through the injection port, and at least 5 separate vapour injections were made for each probe. The alkane probes (C\(_7\)-C\(_{10}\)) were used to measure the dispersive interactions. On the other hand, several acid-base probes used for the non-dispersive interaction were chosen either for the strong donor (base) characteristic or for a strong acceptor characteristic, or both characteristics simultaneously (amphoteric). These probes listed in Table 1 included acetone, chloroform (CHCl\(_3\)), diethylether (DEE), ethyl acetate (EA) and tetrahydrofuran (THF). Symmetrical elution peaks were obtained, and the peak maximum method was used to obtain the retention times from the chromatographs. The retention volume (\( V_N \)) was calculated by eqn (4):

\[ V_N = F_j (t_R - t_m) \]  

(4)

Where \( F \) is a corrected flow rate of the carrier gas and \( j \) is a pressure-gradient correction factor for gas com-
pressibility, \( t_R \) is the retention time of the gaseous probe molecule on the surface and \( t_m \) is the time necessary for a non-adsorbing probe (methane) to flow through the column [15].

RESULTS AND DISCUSSION

The effectiveness of the modifications made on the surfaces of pulp paper fibres following the treatments with A-1100 and A-172 was investigated in a previous study [14]. The FTIR results based on the functional composition of the untreated and treated pulp paper fibres indicated that modifications were made on the fibres surface.

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 1a-d are illustrative plots of \( RT \ln V_N \), a measure of the free energy of adsorption, versus \( a \times (\gamma D)^{1/2} \) obtained at 40 C for untreated and treated pulp papers fibres (NSSC) with silanes (A-1100, A-172 and DSC). Similar results were obtained at 50 C, 60 C and 70 C (not shown). As reported by Schultz and Lavielle,
a linear relation for alkanes (C_7-C_{10}) was observed, suggesting surface adsorption as the only mechanism of alkane probe retention by the fibres. As shown in Figure 2, the magnitude of the free energy of adsorption (ordinate) for n-alkane probes increased after surface treatment of pulp papers, indicating a strong interaction of these materials with n-alkane probes. In addition, the slope of the straight lines (measured $\gamma^D_S$) changed. These differences are indicative of the effectiveness of the surface modification of the pulp paper fibres. The London dispersive components of the surface energy, $\gamma^D_S$, of the fibres determined from the slope of the relationship $RT\ln V_N$ versus $a \times (\gamma^D_L)^{1/2}$ are listed in Table 2.

The surface treatments of the fibres resulted in significant changes in $\gamma^D_S$. The treated fibres showed higher $\gamma^D_S$ than the untreated ones, implying the modification made on surface of the fibres. This significant increase in the $\gamma^D_S$ after treatments indicated a strong interaction of treated fibres with n-alkane probes. Since n-alkane probes are able to interact only through dispersion interactions, the increased $\gamma^D_S$ for treated fibres was an indication that the fibres had become more hydrophobic [10].

It should be noted that the surface energy determined from eqn (1) has been criticized for violating the thermodynamic phase rule for capillary systems by requiring more degrees of freedom than are available for two-component solid-liquid-vapour system [18]. 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. 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 [17].

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 non-dispersive or polar interaction were present. Unlike the pulp paper fibres treated with aminosilane (A-1100), the interactions of the overall pulp paper fibres were greater for the basic probes, whereas the pulp paper fibres treated with A-1100 interactions were greater for acidic probes. From these observations, it can be confirmed, on a qualitative basis, that pulp paper fibres treated with aminosilane had basic surface, whereas the untreated pulp paper fibres, the pulp paper fibres treated with dichlorosilane and vinyl triethoxysilane all had predominantly acidic surface characteristics.

To quantify the acid-base surface characteristics of untreated and treated pulp papers fibres, i.e., $K_A$ and $K_D$.

**Table 2.** Surface characteristics of pulp paper fibres (NSSC) determined by IGC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma^D_S$ (mJ/m²)</th>
<th>$K_A$ acid</th>
<th>$K_D$ base</th>
<th>$K_D/K_A$</th>
<th>Surface characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Untreated fibres</td>
<td>7.4</td>
<td>6.1</td>
<td>5.2</td>
<td>3.41</td>
<td>0.71</td>
</tr>
<tr>
<td>Treated fibres with A-1100</td>
<td>15.1</td>
<td>12.4</td>
<td>7.5</td>
<td>6.5</td>
<td>0.56</td>
</tr>
<tr>
<td>A-172</td>
<td>12.3</td>
<td>8.6</td>
<td>6.5</td>
<td>5.1</td>
<td>0.68</td>
</tr>
<tr>
<td>DSC</td>
<td>27.8</td>
<td>26.5</td>
<td>25.4</td>
<td>22.8</td>
<td>1.43</td>
</tr>
</tbody>
</table>
KD, the values of $\Delta G_{sp}^{c}$ were plotted against the temperature. This was done to determine the enthalpies of adsorption $\Delta H_{sp}$ corresponding to the specific interactions. Figure 3 shows the temperature dependence of the specific component of $\Delta G_{sp}^{c}$ for the adsorption of an acidic probe (CHCl$_3$) and a basic probe (THF) on the surfaces of untreated and treated pulp papers fibres. Similar plots were obtained with other probes, i.e., DEE and EA. The values of $\Delta G_{sp}^{c}$ corresponding to the specific acid-base interactions of the fibres were determined from the vertical distance between the n-alkane line and the probes from Figure 1.

Figures 3 illustrates that $\Delta G_{sp}^{c}$ varied linearly with temperature. This linear relationship for acid-base probes implies that adsorption was the dominant mechanism of probe retention by the fibres. The slope of the straight line in Figure 3 is proportional to the entropy of the adsorption ($\Delta S_{sp}$), while the intercept determines the enthalpy of adsorption ($\Delta H_{sp}$). $\Delta H_{sp}$ constitutes an important parameter since it is a measure of the specific work energy of adhesion for phases similar to the probe. Figure 3 shows that fibres 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 Figure 4 to obtain the expected linear relationship. The acid (K$_A$) and base (K$_D$) surface characteristics of untreated and treated pulp papers fibres were determined from the slope and intercept at the origin of these straight lines and are summarized in Table 2. The quantitative results of K$_A$ and K$_D$ listed in this table corroborated the conclusions drawn from the qualitative observation.

The acidic nature of untreated pulp papers fibres may be attributed to the electron acceptor character of the hydroxyl protons. The lignin and fatty acids may also contribute to the acidic characteristics of pulp papers fibres. So there are more hydroxyl groups than carboxyl groups at the surface and this suggests more acidic character of the pulp paper fibres surface. Similar results have been reported in the literature for cellulose fibres [18, 8]. The acidic characteristic of pulp paper fibres treated with dichlorosilane (DSC) is attributed to the highly electronegative nature of the chlorine atoms [18]. The basic surface of pulp paper fibres after treatment with aminosilane (A-1100) was attributed to the presence of the amine groups on the surface of the fibres as measured from FTIR spectroscopy [14]. Because hydroxyl groups of the fibres react with aminosilanes, the surface of the fibres was covered with amine groups (which are known electron donors). Pulp paper fibres treated with vinyl triethoxysilane showed less acidic characteristics. In this case, the treatment reduced the acidic characteristics of the fibre because of the neutral behaviour of the exposed vinyl of A-172.

All the results which have been obtained confirmed the previously untreated and treated cellulosic fibre surface properties [14]. In accordance with Garnier and Mantuana and co-workers [8,10], we have found that treatment with coupling agent can modify the surface properties of pulp paper fibre.
CONCLUSION

The acid-base surface characteristics of untreated and treated pulp paper fibres have been investigated using the IGC technique. The pulp paper fibres were surface modified with \( \gamma \)-aminopropyl triethoxysilane, dichlorosilane and triethoxyethyl silane. Based on the \( K_A \) and \( K_D \) values; the surface of untreated pulp paper fibres had an acidic characteristic due to the electron acceptor character of hydroxyl protons. Aminosilane treatment produced a basic surface due to the incorporation of amine subsistent on the surface of the fibres. Vinyl triethoxysilane produced an acidic surface but dichlorosilane produced a strong acidic surface.

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

REFERENCES

3. Nguyen T. and Johns W.E., Polar and dispersion force contribution to the total surface free energy of wood,


