Thermal stability of silane coupling agents on Nextel fibres

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The thermal stability of a series of commercially available silane coupling agents, applied to Nextel ceramic fibres, was examined using photoacoustic Fourier transform infrared spectroscopy (PA FT-IR). Quantitative analysis of the PA FT-IR data indicates that, among coupling agents with various functional groups, the highest thermal stability is achieved for silanes with aromatic and epoxy groups incorporated into one system. These coupling agents are able to withstand treatment temperatures of 550°C.

Key words: silane coupling agent; Nextel ceramic fibres; photoacoustic Fourier transform infrared spectroscopy; thermal stability

A common problem encountered when incorporating ceramic or glass fibres into composites is poor adhesion of the fibres to the polymer matrix causing low dry flexural and tensile strengths, and even lower wet flexural and tensile strengths. This problem can be overcome by treating the fibre surfaces with silane coupling agents which, through their ability to bond with both organic and inorganic surfaces, give composites increased strength. This increase in strength is emphasized more in samples that have been exposed to moisture.

A typical silane agent has the structure R-Si-X₁, where R is an organofunctional group and X is a hydrolyzable group, an ethoxy or methoxy group (in most cases). Hydrolysis is achieved by stirring the coupling agent in a slightly acidic aqueous solution. The generally accepted mechanism for the hydrolysis and condensation process is shown:

\[
\begin{align*}
\text{RSi(OH)₃} + 3\text{H₂O} & \rightarrow \text{RSi(OH)₄} + 3\text{MeOH} \\
3\text{RSi(OH)₃} & \rightarrow \text{HO-Si-O-Si-O-Si-} + 2\text{H₂O}
\end{align*}
\]

The hydrolyzed coupling agent condenses with other silane triols to form polymeric silanes of various lengths.

Current bonding theory suggests a modification of this process where the coupling agent forms a type of interpenetrating network with the polymer matrix diffusing into the partially polymerized and bonded silane coupling agent.

Although many studies have been conducted testing the dry and wet strengths of various composites treated with coupling agents, very few studies have been performed on the thermal properties of coupling agents. This aspect of coupling agent performance is addressed here. Because of the inherent thermal stability of aromatic groups, one would expect that aromatic functional coupling agents would exhibit higher thermal stability than aliphatic or amine functional coupling agents.
In this study Nextel 312 ceramic fibres, continuous polycrystalline metal oxide fibres developed for high temperature applications, were considered. Table 1 lists the fibre composition and selected properties of Nextel 312 fibers. Due to a high thermal stability, their primary use is in areas such as high temperature insulations, gaskets and seals, although the application of the fibres to thermally stable composite systems is now being explored. However, to incorporate Nextel into high temperature composites it is necessary to find a coupling agent that will remain stable at elevated temperatures. Such a coupling agent will function as a thermally stable interface only if the coupling agent by itself has a high decomposition temperature and will form a thermally stable chemical bond between the fibre surface and the matrix. Since the thermal stability of potential coupling agents as a neat liquid is only a prerequisite, the thermal stability of the coupling agents was examined after application to the fibres as that stage most closely approximates their use in composite systems.

Initial Fourier transform infrared (FT-IR) spectroscopy studies of silane coupling agents on fibre surfaces were performed utilizing transmission spectroscopy. Ishida and Koenig conducted several studies using transmission FT-IR spectroscopy to analyse vinyltriethoxysilane and γ-methacryloyloxypropylmethoxysilane (γ-MPS) on the surface of E-glass fibres used in fibreglass reinforced plastics. The major problem with applying transmission FT-IR to fibre studies was the need to alter the samples so that the infrared beam could pass through the sample to generate a signal. Further, since transmission FT-IR is not a surface sensitive technique there was the need to run a large number of scans to obtain good resolution of the spectra and thus be able to detect surface species. More recent FT-IR studies of silane coupling agents were performed using both diffuse reflectance (DRIFT) and photoacoustic (PA) infrared spectroscopy. Although DRIFT has very good sensitivity, problems may occur in the analysis of woven fibre surfaces. For example, for highly reflective surfaces such as Nextel fibres, the diffusely scattered light may be disturbed by the specular component of the light resulting in band distortions. Therefore, a comparison of spectra for quantitative purposes may be troublesome. The method is very suitable for the analysis of powders, but unfortunately it would require alteration of the woven mats for optimum results. In the past, inherent difficulties in obtaining a good signal-to-noise ratio limited the application of PA FT-IR to surface analysis. These problems now mostly overcome, Urban and Koenig have successfully utilized PA FT-IR spectroscopy to analyse γ-MPS, γ-glycidoxypropyltrimethoxysilane (γ-GPS), and γ-aminopropyltriethoxysilane (γ-APS) coupling agents to determine their orientation as a function of concentration on the silica surface. These studies showed that, with appropriate modifications, PA FT-IR spectroscopy provides enough sensitivity to follow the changes in coupling agents deposited on the fibre surface. Some advantages of PA FT-IR are its surface sensitivity and minimal or no sample preparation requirements. The latter advantage leaves the coupling agent in its native state on the substrate. These, as well as other advantages, arise from the nature of detection since the light does not need to penetrate through the sample but simply penetrates a short distance into the surface.

The photoacoustic signal is created when intensity modulated light strikes a sample placed in an acoustically sealed chamber. Heat is generated from the sample due to absorption processes. These processes create temperature fluctuations at the sample surface which, in turn, cause pressure fluctuations (sound waves to be detected by a microphone). The generated electrical signal is Fourier transformed and recorded in the form of an infrared spectrum. Digital subtraction of spectra is possible due to the availability of software for spectral manipulation. As will be seen later, spectral subtraction is especially useful in this study since the C–H stretching band, due to structures found in the coupling agents, can be accentuated using this technique.

In this study PA FT-IR was used to analyse the thermal stability of a series of coupling agents with various functionalities deposited directly on the Nextel 312 fibre surface. The advantage of using PA FT-IR comes from the fact that the technique is nondestructive to the surface treatment and has suitable sensitivity to allow the detection of a few monolayers coverage. The resulting IR data, in turn, establishes the suitability of such coupling agents for applications in thermally stable composites.

### Experimental

#### Sample preparation

A 0.5% (wt/wt) solution of hydrolyzed coupling agent was typically prepared as follows: 49.7 g of distilled deionized water, at pH 3–4 with acetic acid, was added to 0.25 g of coupling agent. The solution was stirred for a minimum of one hour, longer as necessary, for complete hydrolysis, which was indicated by a clear solution. In some cases it was necessary to use a stronger acid, such as formic acid, or to initially dissolve the coupling agent in alcohol or add small amounts of surfactant to the solution to fully hydrolyze the coupling agent. The exact amounts of each reactant for all the coupling agent solutions along with the manufacturer’s described structure or functionality are listed in Table 2.

The samples for spectroscopic analysis were prepared by cutting circular mats of heat-cleaned Nextel 312 cloth with a size 5 cork borer. The mats were placed in

### Table 1. Physical properties of Nextel 312 fibres

<table>
<thead>
<tr>
<th>Property (units)</th>
<th>Property (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre composition</td>
<td>62% Al₂O₃, 24% SiO₂, 14% B₂O₃</td>
</tr>
<tr>
<td>(wt%)</td>
<td>(μm)</td>
</tr>
<tr>
<td>Use Temperature</td>
<td>1200</td>
</tr>
<tr>
<td>(°C)</td>
<td>(MPa)</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>2.70</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>1720</td>
</tr>
<tr>
<td>Tensile modulus of elasticity (GPa)</td>
<td>152</td>
</tr>
</tbody>
</table>

The samples for spectroscopic analysis were prepared by cutting circular mats of heat-cleaned Nextel 312 cloth with a size 5 cork borer. The mats were placed in
Table 2. List of tested coupling agents and their preparation parameters

<table>
<thead>
<tr>
<th>Name</th>
<th>Coupling agent (g)</th>
<th>Water (g)</th>
<th>Acid (type g⁻¹)</th>
<th>Alcohol (type g⁻¹)</th>
<th>Surfactant* (g)</th>
<th>Structure</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1100</td>
<td>0.25</td>
<td>49.75</td>
<td></td>
<td></td>
<td></td>
<td>γ-amino-propyltriethoxysilane</td>
<td>Union Carbide</td>
</tr>
<tr>
<td>Y-9576</td>
<td>0.25</td>
<td>48.175</td>
<td>Acetic/1.325</td>
<td></td>
<td>Phenylaminolauryltriethoxysilane</td>
<td>Union Carbide</td>
<td></td>
</tr>
<tr>
<td>X1-6125</td>
<td>0.25</td>
<td>49.0</td>
<td>Formic/0.09</td>
<td>Methanol/0.75</td>
<td>50% N-beta-aminoethyl-gamma-amino-propyltrimethoxysilane</td>
<td>Dow Corning</td>
<td></td>
</tr>
<tr>
<td>X1-6100</td>
<td>0.25</td>
<td>49.5</td>
<td>Formic/0.09</td>
<td>Methanol/0.25</td>
<td>50% Phenyltrimethoxysilane</td>
<td>Dow Corning</td>
<td></td>
</tr>
<tr>
<td>X1-6106</td>
<td>0.25</td>
<td>49.75</td>
<td>Acetic/pH 3.8</td>
<td></td>
<td>Alkoxy-silanes</td>
<td>Dow Corning</td>
<td></td>
</tr>
<tr>
<td>Z-6032²</td>
<td>0.59</td>
<td>49.38</td>
<td>Acetic/0.03</td>
<td></td>
<td>Organotrimethoxysilane</td>
<td>Dow Corning</td>
<td></td>
</tr>
<tr>
<td>P-0320</td>
<td>0.25</td>
<td>49.5</td>
<td>Formic/0.05</td>
<td>Methanol/0.25</td>
<td>N-2-(vinylbenzylamino)-ethyl-3-amino-propyltrimethoxysilane monohydrogen chloride</td>
<td>Dow Corning</td>
<td></td>
</tr>
<tr>
<td>Prosil 2107</td>
<td>0.25</td>
<td>49.5</td>
<td>Acetic/pH 3.2</td>
<td>Isopropyl/0.25</td>
<td>Phenyltrimethoxysilane</td>
<td>Petrarch</td>
<td></td>
</tr>
<tr>
<td>Prosil 2212</td>
<td>0.25</td>
<td>49.5</td>
<td>Acetic/pH 3.2</td>
<td>Isopropyl/0.25</td>
<td>Epoxy and methoxy functional silanes</td>
<td>PCR</td>
<td></td>
</tr>
<tr>
<td>Prosil 9214²</td>
<td>0.29</td>
<td>49.5</td>
<td>Acetic/pH 3.2</td>
<td>Isopropyl/0.46</td>
<td>Polyimide</td>
<td>PCR</td>
<td></td>
</tr>
<tr>
<td>Prosil 9102</td>
<td>0.25</td>
<td>49.5</td>
<td>Acetic/pH 3.2</td>
<td>Isopropyl/0.50</td>
<td>Trialkoxysilylacid silane</td>
<td>PCR</td>
<td></td>
</tr>
</tbody>
</table>

* Triton X-100, Rham and Haas
² 40% Coupling agent in methanol, prepared as a prehydrolyzate solution as per company literature
²² Supplied prehydrolyzed at 0.43% by weight
²²² Supplied 80% (wt/wt) in methanol

the bottom of a sintered glass filter and the hydrolysed coupling agent solution was poured through the filter twice giving a total contact time with the mats of about 90 seconds. The treated samples were dried and cured in a heated vacuum desiccator at 50°C for six hours, followed by storage in a room temperature desiccator.

Samples were heated at the selected temperatures for one hour in a Thermolyne type 1300 furnace. Temperatures used for the first set of sample heatings were 100°C, 200°C, 300°C and 400°C ± 20°C. Two cloth samples with each coupling agent were prepared with no exposure to heat except during drying. For samples prepared with 1% (wt/wt) solutions heating temperatures included 350°C, 450°C, 500°C and 550°C. For subtraction purposes, untreated Nextel mats were also heated at each of the selected temperatures to use as a reference.

**Spectral analysis**

All samples were analysed by photoacoustic FT-IR spectroscopy. The PA FT-IR spectra were recorded on a Digilab FTS-10M Fourier transform infrared spectrometer equipped with a photoacoustic cell (Digilab). All spectra were collected at a 4 cm⁻¹ resolution with a mirror velocity of 0.3 cm s⁻¹. In order to improve the signal-to-noise ratio, 400 scans were collected for each sample and ratioed against carbon black powder. The instrument was continuously purged with dry nitrogen. The PA cell was purged with dry helium for ten minutes and pressurized before each data collection.

**RESULTS AND DISCUSSION**

In order to analyse spectroscopically the various coupling agents deposited on the Nextel surface it is necessary to find a spectral region which would be common for studied samples and, at the same time, would represent thermal stability of the coupling agent on the Nextel surface. Fig. 1 illustrates the PA FT-IR spectrum of untreated Nextel fibre. Below 1600 cm⁻¹ the presence of heavily overlapping bands, due to the metal oxides forming the fibres, makes the analysis of coupling agents difficult in this region. However, all the analysed silanes contain organic groups which absorb in the 3000 cm⁻¹ region of the infrared spectrum due to absorption of the C–H stretching modes. Thus, this region was used for the analysis of thermal stability. The graphs discussed in the following section were
obtained by plotting the percent intensity loss of the aliphatic C–H stretching band as a function of the treatment temperature of the sample. Percent intensity loss was determined by normalizing the peak intensities for each temperature to the intensity of the non-heat-treated sample.

Fig. 2 shows the results for the γ-APS silane coupling agent, also known as A-1100. Initially, the decrease in the relative amount of coupling agent found on the fibre is attributed to the loss of non-polymeric silanes from the fibre surface. As the temperature increases, a loss of the coupling agent is observed due to either decomposition or volatilization caused by the exposure to elevated temperatures. The γ-APS coupling agent is no longer detected on the surface of the fibre when the treatment temperature reaches 300°C. This behaviour is attributed to the fact that γ-APS has both aliphatic and amine functionalities which are not expected to provide high thermal resistance. Ideally, an initial drop in the relative amount of coupling agent on the fibre surface due to the loss of non-polymerized low molecular weight species would be observed, while at high temperatures the concentration should remain constant, indicating thermal stability. Although it might be deduced that upon silane oxidation the surface of the Nexel fibres should contain an increased amount of SiO₂, a heavy overlap of the metal-oxide bands of Nexel makes the analysis unreliable. Depending upon the thermal stability of the surface polymerized silanes, it is also possible that the decomposition of polymer may lead to volatilization of larger segments from the surface.

The results for X1-6125 and Z-6032 coupling agents are also shown in Fig. 2. The X1-6125 is a mixture with 50% aromatic containing coupling agent and 50% aliphatic and amine functional coupling agent whereas Z-6032 is an aliphatic-bridged aromatic silane coupling agent. In spite of the presence of aromatic groups, these coupling agents also lose their thermal resistance under 300°C. Because of the presence of the aromatic groups in the coupling agents one would expect that both samples should exhibit higher thermal stability.

However, this is not observed in the X1-6125 treated samples where the aliphatic coupling agent is lost by 300°C and the aromatic containing coupling agent cannot be detected because of a relatively low concentration of the aromatic groups on the fibre surface and a low extinction coefficient for the aromatic C–H stretching modes in this system. This is supported by the difficulty in detecting the aromatic C–H stretching band in the PA FT-IR spectrum of the coupling agent alone. For the Z-6032 samples, previous studies have shown that aliphatic-bridged aromatic coupling agents exhibit intermediate thermal stability, less than that of coupling agents with the aromatic group bonded directly to the silane.

The P-0320 silane coupling agent, phenyltriethoxysilane, shows slightly improved thermal stability over the previous coupling agents and, as illustrated in Fig. 3, retains its thermal stability to between 300°C and 400°C. This is shown spectroscopically by the subtraction spectra in Fig. 4. This shows the spectrum of untreated Nexel fibres subtracted from that of treated fibres, both heat at the same temperature. A steady decrease in the intensity of the band at 2880 cm⁻¹ indicates the loss of low molecular weight species from the surface of the fibre as that band is attributed to the symmetric C–H stretching vibrations of the –CH₂–CH₃ groups not hydrolyzed during the initial preparation of the coupling agent. The presence of a weak band at 3050 cm⁻¹ due to aromatic C–H stretching vibrations indicates that polymeric siloxane is still present on the fibre surface. Although the band at 3050 cm⁻¹ can still be observed upon heat treatment at 300°C, its intensity is diminished to zero by 400°C. In order to narrow down the region of thermal stability for the coupling agent, the fibres were treated with a 1% (wt/wt) solution of P-0320 and heated at 350°C and 450°C in addition to the previous temperatures. This experiment indicated that loss of the P-0320 coupling agent from the fibres occurred somewhere between 300 and 350°C. However, data published earlier indicates that P-0320 has a thermal stability limit of 550°C. A failure to detect
the presence of the coupling agent is perhaps attributable to the low extinction coefficient of the aromatic C–H stretching modes and the absence of the aliphatic C–H structures. The latter bands would enable tracking of any remaining coupling agent on the fibre surface.

Prosil 2107 is stated by the manufacturer to be an epoxy functional coupling agent, although FT-IR and NMR data indicate the presence of an aromatic group in the structure. The results of analysis of this coupling agent are shown in Fig. 3. Prosil 2107 exhibits near ideal behaviour, with an initial decrease in concentration on the fibre surface and then a levelling off at higher treatment temperatures. This can be seen more clearly in Fig. 5, which illustrates results obtained for 1% (wt/wt) Prosil 2107 deposited on the fibre surface. This plot illustrates that Prosil 2107 remains on the fibre surface even after treatment at 550°C. This is shown spectroscopically in Fig. 6 where the band at 2925 cm$^{-1}$ due to aliphatic C–H stretching modes is present even after treatment at 550°C. A weaker band at 3050 cm$^{-1}$ due to aromatic C–H stretching vibrations can be seen in the subtraction spectra (Fig. 6) at 300°C after which it becomes difficult to differentiate from
noise. This disappearance could be attributable to complete loss of aromatic species from the coupling agent but is more likely due to the low extinction coefficient for these species in this region of the spectrum.

The presence of an aromatic group in the polymer backbone or as a side group has long been known to provide increased thermal stability to a fibre system. Examples of this are seen in engineering polymers such as polycarbonates, polysulfones, polyethers, polysulfides and polyamides which all contain aromatic groups that function as chain stiffeners and provide increased resistance to degradation and softening at elevated temperatures. However, this is not the case for X1-6125 and Z-6032 coupling agents; the increase in thermal stability attributed to aromatic functionality is system dependent, i.e. the aromatic groups must have appropriate positioning in the chain in order to be effective chain stiffening components. In the case of P-0320 and Prosil 2107 the thermal stability afforded by aromatic groups in polymers also appears to contribute to an increase in the thermal stability of coupling agents. This study shows that the inclusion and appropriate positioning of aromatic groups in a coupling agent can increase the thermal stability of the system. When an aromatic group is coupled with epoxy functionality the thermal resistance can be increased to an even greater extent.

CONCLUSION

In this work, PA FT-IR was employed to monitor the thermal stability of commercially available silane coupling agents. Using PA FT-IR, it is possible to follow semi-quantitatively the loss of these coupling agents, with increasing temperature, in their native state on the surface of Nextel ceramic fibres. Table 3 summarizes the results for all of the coupling agents examined in this study although only a representative few were presented in the previous discussion. The coupling agent yielding the best thermal stability, Prosil 2107, contains both aromatic and epoxy functionality in its composition. This coupling agent can still be detected on the Nextel fibre after treatment at 550°C.

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