Determination of Dispersive Properties of Silicas by Inverse Gas Chromatography: Variation with Surface Treatment

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The application of inverse gas chromatography (IGC) to the examination of the surface properties of untreated crystalline and fused silica and surface-treated silicas with silane coupling agents is discussed. The carbon content of the silane coupling agents adsorbed on the surface of the silicas was determined by means of a Carbon Determinator. If the assumption is made that each silane coupling agent molecule occupies an area of 0.5–1 m², the adsorption amounts show that multilayers are generally adsorbed onto the silica surfaces. This paper presents and discusses the dispersive properties expressed by \( y^D \), the dispersive component of the surface free energy, as determined at various temperatures. At the same temperature of IGC measurement, the values of \( y^D \) determined by IGC were lower for the crystalline silica than for the fused silica. This means that crystalline silica is more stable than fused silica. The silica surface-treated with \( \gamma \)-methacryloxy propyl trimethoxy silane (MTMS) shows a relatively high \( y^D \) value (42.75 mJ·m⁻² at 160°C). This means that this sample should be compatible with epoxy resin at relatively low temperatures.

Keywords: inverse gas chromatography (IGC), silica, dispersive component of the surface free energy (\( y^D \)), multilayer

1. General

1.1 Introduction

Silica has a broad variety of applications in industry. Silica has been treated with surface-modifying agents to obtain improved dispersibility, mechanical and electrical properties, water resistance and reinforcement in plastics systems. In this study, we used silane coupling agents as surface-modifying agents for silica.

The mechanical performance of a composite material strongly depends on the properties of the filler-matrix interface and, in particular, on the level of adhesion between the matrix and the reinforcing filler. The level of adhesion is determined by the surface energies of both adherents. The surface free energy, which describes the interaction potential of a given surface, has two components: the dispersive component originating from dispersive or London interactions, and the specific component due to all other types of interactions.

Inverse gas chromatography (IGC) at infinite dilution conditions may be successfully applied to the determination of the surface properties of various solids. IGC allows the detection of the solid surface properties, using molecules of known properties, or probes, which are injected into a chromatographic column filled with the solid of interest.

In this study, we chose IGC for the detection of the possible differences in the \( y^D \) values of untreated crystalline and fused silica and silicas surface-treated with silane coupling agents. The IGC results are reported in this paper.

1.2 Theory of inverse gas chromatography (IGC) at infinite dilution

In IGC under infinite dilution conditions, the retention volume \( V_N \) is computed from the following expression (1):

\[
V_N = (t_R - t_0)D_C
\]  

where \( t_R \) is the retention time of the probes, \( t_0 \) the zero retention time measured with a nonadsorbing probe such as methane, \( j \) the compressibility factor depending on the pressures at the column inlet and outlet, and \( D_C \) the corrected flow rate. Practically, the retention time and the retention volume \( V_N \) can be determined as in a current chromatographic experiment: a larger \( V_N \) will correspond to a higher affinity of the probe for the chromatographic support.

In expression (1), \( j \) was calculated by the following expression (2):

\[
j = 1.5\left[\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1}\right]
\]

where \( p_i \) is the inlet pressure of the carrier gas, and \( p_0 \) the outlet pressure of the carrier gas which usually equals atmospheric pressure.

For a test substance, the free energy of adsorption, \( \Delta G_A \), is the sum of the energies of adsorption attributable to the dispersive and specific interactions. The adsorption of non-polar probes such as n-alkanes occurs through dispersive interactions, whereas, for polar probes, both London and acid-base interactions contribute to \( \Delta G_A \). In this study, we used the model of Donnet et al., because the injected probe is in the gas state. In this model, \( \Delta G_A \) is given by the following expressions:

\[
[-\Delta G_A] = [-\Delta G^D_A] + [-\Delta G^P_A]
\]

\[
= [RT \ln V_N + C]
\]

\[
= [K \cdot (hV_S)^{1/2} \cdot \alpha_{OS} \cdot (hV_L)^{1/2} \cdot \alpha_{OL}] + [-\Delta G^P_A]
\]

where \( \Delta G^D_A \) and \( \Delta G^P_A \) are the dispersive and specific components of the free energy of adsorption, respectively. The value of the constant, \( C \), in expression (4) depends on the arbitrarily chosen reference state of the adsorbed molecule. In expression (5), \( K \) is a constant, \( h \) Planck’s constant, and \( \alpha_0 \)
the deformation polarizability of the molecules. Subscripts $S$ and $L$ refer to solid and liquid, respectively. In the case of $n$-alkanes, $\Delta G_A$ is equal to the free energy of adsorption corresponding to the dispersive interactions, $\Delta G_A^D$, only, i.e., $[−\Delta G_A^{SP}]=0$ in expression (5). The term $\left[K \cdot \langle hV_s \rangle^{1/2} \cdot \alpha_{0s}\right]$ is characteristic of a given solid surface and is related to $\Delta G_A^D$. Consequently $[RT \ln V_s + C]$, between an adsorbate and an adsorbent, appears as a linear equation of the parameter $[(hV_s)^{1/2} \cdot \alpha_{0s}]$, and $[K \cdot \langle hV_s \rangle^{1/2} \cdot \alpha_{0s}]$ becomes the slope of the linear equation.

The above method has been used to characterize silicas, modified silicas, oxides, various minerals and solid polymers.5–11

2. Experimental

2.1 Materials

Natural crystalline and fused silica were used in this work, and the chemical compositions and physical properties of these silicas are shown in Table 1. The chemical names and structures of the silane coupling agents used in the adsorption experiment are shown in Table 2. The silane coupling agents contain three hydrolysable substituents on the right side of each silicon center(Table 2), which, in principle, would enable the formation of a chemisorbed crosslinked siloxane network by the condensation of adjacent adsorbed silantriols with each other as well as with the surface hydroxyl groups as shown in Fig. 1. The silane coupling agents also contain one or more nonhydrolyzable alkyl or aryl groups which are used to provide compatibility with organic matrices. These may also contain substituent groups that can provide reactive centers for graft formation between a polymeric matrix and the mineral surface. These reactive substituents can be tailored for specific applications and include vinyl, acrylate and methacrylate, chloro, amino, epoxy, and mercapto groups.12

2.2 Adsorption experiment

We used methanol and distilled water as the solvent and acetic acid as the catalyst to hydrolysis. The experiment designed to modify the crystalline and fused silica surface was performed as follows. Solvent (100 mL), silane coupling agents (0.2, 0.3, 0.4, 0.6, 0.8, 1.0 and 2.0 g) and silicas (30 g) were stirred by a magnetic bar stirrer for an hour and then separated into solid and liquid components by a centrifugal

![Fig. 1 Schematic diagram for the reaction of alkoxy silanes with hydroxylated silica surface.](image)

Table 1 Chemical compositions and physical properties of samples.

<table>
<thead>
<tr>
<th>Chemical composition (mass%)</th>
<th>Crystalline silica</th>
<th>Fused silica</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{SiO}_2$</td>
<td>99.7</td>
<td>$\text{SiO}_2$</td>
</tr>
<tr>
<td></td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>0.1561</td>
<td>$\text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td></td>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>0.0098</td>
<td>$\text{Fe}_2\text{O}_3$</td>
</tr>
<tr>
<td></td>
<td>$\text{Na}_2\text{O}$</td>
<td>0.0214</td>
<td>$\text{Na}_2\text{O}$</td>
</tr>
<tr>
<td>Maximum diameter((\mu)m)</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Mean diameter((\mu)m)</td>
<td>13.55</td>
<td>14.21</td>
<td>13.55</td>
</tr>
<tr>
<td>BET Surface Area(m²/g)</td>
<td>2.2654</td>
<td>2.9894</td>
<td>2.2654</td>
</tr>
<tr>
<td>Average Pore Diameter(nm)</td>
<td>4.9484</td>
<td>7.3271</td>
<td>4.9484</td>
</tr>
</tbody>
</table>

Table 2 Chemical names and structures of the silane coupling agents.

<table>
<thead>
<tr>
<th>Expressions in this paper</th>
<th>Chemical name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTMS</td>
<td>$\gamma$-Methacryloxy propyl trimethoxy silane</td>
<td>$\text{CH}_3$ $\text{O}$ $\text{CH}_2=\text{C} \text{CO(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3$</td>
</tr>
<tr>
<td>GMS</td>
<td>$\gamma$-Glycidoxy propyl trimethoxy silane</td>
<td>$\text{CH}_2\text{CH}=\text{CH}_2\text{O(CH}_3\text{)}_2\text{Si(OCH}_3\text{)}_3$</td>
</tr>
<tr>
<td>MCMS</td>
<td>$\gamma$-Mercapto propyl trimethoxy silane</td>
<td>$\text{HS(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3$</td>
</tr>
<tr>
<td>AES</td>
<td>$\gamma$-Amino propyl triethoxy silane</td>
<td>$\text{NH}_2\text{(CH}_2\text{)}_3\text{Si(OCC}_2\text{H}_5\text{)}_3$</td>
</tr>
</tbody>
</table>
separator. A suitable amount of acetic acid specially was added before stirring in accordance with the type of coupling agents to obtain a reasonable pH value for hydrolysis, because the pH value is the most important factor in the hydrolysis of silane coupling agents. The conditions used in the adsorption experiment are shown in Table 3. The separated silicas were then dried for 8 hours at 105 °C. The various samples were prepared in this way for the IGC study at infinite dilution viz. the untreated crystalline and fused silicas, four types of silane coupling agents-treated crystalline and fused silicas.

### Table 3 Adsorption experimental conditions.

<table>
<thead>
<tr>
<th>Silane coupling agent</th>
<th>Solution</th>
<th>pH</th>
<th>Remarks</th>
<th>Silica weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTMS</td>
<td>Methanol(80 v.%)</td>
<td>3.53~3.58</td>
<td>Acetic acid catalyzed</td>
<td></td>
</tr>
<tr>
<td>GMS</td>
<td>Distilled water(20 v.%)</td>
<td>5.66~6.88</td>
<td>Natural</td>
<td>30 g</td>
</tr>
<tr>
<td>MCMS</td>
<td>Methanol(80 v.%)</td>
<td>4.72~4.76</td>
<td>Acetic acid catalyzed</td>
<td></td>
</tr>
<tr>
<td>AES</td>
<td>Distilled water(20 v.%)</td>
<td>9.95~10.66</td>
<td>Natural</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4 Carbon content of four silane coupling agents adsorbed on the surface of silicas.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silane coupling agent</th>
<th>Experimental concentration</th>
<th>C content (w/w%)</th>
<th>The number of adsorption layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline silica</td>
<td>MTMS</td>
<td>1.0 g/100 mL</td>
<td>0.2109</td>
<td>3.33~6.67</td>
</tr>
<tr>
<td></td>
<td>GMS</td>
<td>1.0 g/100 mL</td>
<td>0.2005</td>
<td>3.7~7.4</td>
</tr>
<tr>
<td></td>
<td>MCMS</td>
<td>1.0 g/100 mL</td>
<td>0.0748</td>
<td>2.76~5.52</td>
</tr>
<tr>
<td></td>
<td>AES</td>
<td>1.0 g/100 mL</td>
<td>0.0905</td>
<td>3.34~6.68</td>
</tr>
<tr>
<td>Fused silica</td>
<td>MTMS</td>
<td>1.0 g/100 mL</td>
<td>0.1364</td>
<td>1.63~3.27</td>
</tr>
<tr>
<td></td>
<td>GMS</td>
<td>1.0 g/100 mL</td>
<td>0.1466</td>
<td>2.05~4.1</td>
</tr>
<tr>
<td></td>
<td>MCMS</td>
<td>1.0 g/100 mL</td>
<td>0.1518</td>
<td>4.25~8.49</td>
</tr>
<tr>
<td></td>
<td>AES</td>
<td>1.0 g/100 mL</td>
<td>0.1139</td>
<td>3.18~6.37</td>
</tr>
</tbody>
</table>

2.3 IGC experiment conditions

Since the particle size of the silica was too small to make chromatographic supports, silica disks were prepared by compression of the powders in an IR die under a pressure of $10^5$ Pa. The disks were then hand-crushed and sieved to select the fraction of particles having diameters between 250 and 425 μm. Particles of the correct size were introduced into a stainless steel column, 50 cm long and 3.17 mm in diameter. Approximately 1 g of each sample was used as the filling of the chromatographic column. Each column, filled with the sample, was conditioned at 200 °C for 24 hours to remove any impurities in it. The IGC measurements were performed with a Hewlett Packard 6890 GC system equipped with a highly sensitive flame ionization detector (FID). The carrier gas was nitrogen (N$_2$) and the flow rate was 10 mL/min. The temperature of the IGC measurement was varied from 70 to 180 °C. Very small amounts of the probes were injected using the following stratagem: 1 to 5 μL of the probe was introduced via a septum into a 1 L flask, which was flushed with N$_2$, after which about 0.3 mL of the diluted probe was injected into the GC system. A homologous series of n-alkanes, C$_3$ to C$_{10}$, were used as the probe in the IGC experiment.

2.4 Analysis instruments

We used a Mastersizer of Malvern Co. for the particle size analysis, an ICP-7500 of Shimadzu Co. for the chemical analysis of the samples, an ASAP 2010 of Micromeritics for the BET surface area, a WR-112 Carbon Determinator of Leco Co. for the carbon analysis and an HP 6890 Plus of Hewlett Packard Co. for the IGC experiment.

3. Results and Discussion

3.1 The number of adsorption layers

We performed the hydrophobic experiment of all of the samples to generally examine which concentration was achieved monolayer adsorption at. It was found that the MTMS- and MCMS-treated samples with a concentration of 0.8 g/100 mL and above completely floated on the water. However, the hydrophobic experiment of the samples surface-treated with GMS and AES was unable to be performed, because both of these samples have hydrophilic properties. Consequently, we chose the samples at a concentration of 1 g/100 mL as the standard samples for the IGC experiment, because it was considered that higher than monolayer adsorption of the silane coupling agents was achieved at this concentration.

We performed the carbon analysis to calculate the number of layers adsorbed on the surface of the standard samples. The carbon analysis results of the standard samples are presented in Table 4. The molecular possession area of silane coupling agents is approximately 0.5 to 1 nm$^2$. If we choose the crystalline silica surface-treated with MCMS,
because its carbon content is the lowest, the number of adsorption layers can be calculated as follows.

**BET surface area of crystalline silica = 2.2654 m²/g**  
(Table 1)

Mass of carbons in functional group of MCMS: C₃ = 36 g/mol  
Carbon content per 100 g of the crystalline silica surface-treated with  
MCMS = 7.48 × 10⁻² g (Table 4)

This can be changed to mole numbers as follows.

\[ 7.48 \times 10^{-2} \text{ g} \times \frac{\text{mol}}{36 \text{ g}} \approx 0.208 \times 10^{-2} \text{ mol} \]

\[ = 20.8 \times 10^{-4} \text{ mol} \]

That is, the mole number per 1 g of the crystalline silica surface-treated with MCMS = 20.8 × 10⁻⁶ mol

This can be changed to molecular numbers as follows.

\[ 20.8 \times 10^{-6} \text{ mol} \times \frac{6.02 \times 10^{23}}{\text{mol}} = 125.22 \times 10^{17} \]

If the molecular possession area of the silane coupling agent(0.5 to 1 nm²) is 0.5 nm², the total molecular possession area is:

\[ 125.22 \times 10^{17} \times 50 \times 10^{-20} \text{ m}^2 = 6.261 \text{ m}^2/\text{g} \]

Finally, the number of adsorption layers is as follows.

If the molecular possession area of the silane coupling agent is 1 nm², the number of adsorption layers will be twice that. The number of adsorption layers calculated using the above method is presented in Table 4. That is, the results presented in Table 4 suggest that the above monolayer adsorption of the silane coupling agents was achieved for all of the samples. A schematic diagram of the multilayer is shown in Fig. 1. The surface properties of the samples reflect the innate characteristics of the functional group of each silane coupling agent, regardless of the number of adsorption layers, because the functional groups protrude from the layer as shown in Fig. 1.

### 3.2 The dispersive component of the surface free energy  
(\( \gamma_D^S \))

The dispersive component of the surface free energy, \( \gamma_D^S \), is obtained by injecting a homologous series of \( n \)-alkanes into the column and determining their retention characteristics. Dorris and Gray used the incremental amount of free energy of adsorption corresponding to the adsorption of one CH₂ group, \( \Delta G_{A_{CH_2}} \), to determine the value of \( \gamma_D^S \):²¹

\[ \gamma_D^S = 1 \left[ \frac{\Delta G_{A_{CH_2}}}{N \cdot a_{CH_2}} \right]^2 \]

where \( \gamma_{CH_2} \) is the surface energy of a solid composed solely of -CH₂ groups, i.e., a surface analogous to polyethylene, N Avogadro’s number, and \( a_{CH_2} \) the cross sectional area of an adsorbed -CH₂ group (0.06 nm²).²¹ The variation of \( \gamma_{CH_2} \) with the temperature is given by:

\[ \gamma_{CH_2} = 35.6 + 0.058(293 - T) \text{ in mJ·m}^{-2} \]

where \( T \) is the temperature in K.

Generally, the logarithm of \( V_N \) varies linearly with the number of carbon atoms of the injected \( n \)-alkanes. Therefore, it becomes possible to define the free energy of adsorption, \( \Delta G_{A_{CH_2}}^S \), of one methylene group, which no longer depends on the arbitrary choice of the reference state:

\[ \Delta G_{A_{CH_2}}^S = -RT \ln \left( \frac{V_{N+1}^n}{V_N^n} \right) \]

In the IGC experiment, the retention time and volume are associated with the \( \gamma_D^S \) of the solid. That is, RT\( \ln V_N \) varies linearly with the number of carbon atoms of the injected \( n \)-alkanes, as shown in Fig. 2.

In Fig. 2, \( \Delta G_{A_{CH_2}}^S \) is the slope of the line obtained from expression (8). Therefore, the \( \gamma_D^S \) values of the solid are computed by expression (6).

Figures 3 and 4 display the variation of [RT \( \ln V_N \)] vs. the carbon number of the \( n \)-alkanes used to probe the surface properties of the untreated crystalline and fused silica. Figures 5 and 6 display the variation of [RT \( \ln V_N \)] vs. the carbon number of the \( n \)-alkanes used to probe the surface properties of the crystalline and fused silica surface-treated with MTMS. Each line in the above graphs indicates the variation according to the temperature of the IGC measurement. The \( \gamma_D^S \) values of the untreated crystalline, fused and surface-treated silicas were computed by the above method for each line.

The \( \gamma_D^S \) values of the samples were computed at various measuring temperatures between 70 and 180° C. The calculated values of \( \gamma_D^S \) are presented in Table 5. The range of temperature used for the IGC measurement was different for each sample, as shown in Table 5. This means that the range of temperature which is suitable for the IGC measurement is
different for each sample because their surface properties are different.

The $\gamma_S^D$ values of the crystalline and fused silica are lower than those of the other fillers. There have been several papers that presented the $\gamma_S^D$ values for synthetic silica. The $\gamma_S^D$ values of crystalline and fused silica in this paper are similar to those of these previous studies. The $\gamma_S^D$ values of synthetic silica were as follows: 40 ± 4 mJ·m⁻² at 80°C, 40 mJ·m⁻² at 150°C, 46 mJ·m⁻² at 80°C.

The $\gamma_S^D$ values of the untreated fused silica shown in Table 5 were slightly higher than those of the untreated crystalline silica at the same measuring temperature. This means that crystalline silica is more stable than fused silica. The $\gamma_S^D$ values of the silicas surface-treated with MTMS were higher than those of the silicas surface-treated with the other silane coupling agents at the same measuring temperature. The MTMS agent is compatible with polyester, having a $\gamma_S^D$ value of 27 ± 3 mJ·m⁻² at 290°C. The $\gamma_S^D$ values of the silicas surface-treated with GMS were approximately 30 mJ·m⁻² at 160°C. It is estimated that the GMS agent is suitable for most polymers, because it has a $\gamma_S^D$ value of around 30 mJ·m⁻² at 140°C. The $\gamma_S^D$ values of the crystalline silica surface-treated with MCMS was about 30 mJ·m⁻² at 150°C. The $\gamma_S^D$ values of the silicas surface-treated with AES were around 30 mJ·m⁻² in the relatively low temperature range. Consequently, the AES agent is compatible with epoxy resin, having a $\gamma_S^D$ value of 40 mJ·m⁻² at 80°C.
4. Conclusions

Crystalline and fused silica were subjected to surface treatment with four types of silane coupling agent: MTMS, GMS, MCMS and AES. The treatment of the crystalline and fused silica by these silane coupling agents modified their surface energy. We examined the number of layers adsorbed on the surface of the silicas by carbon analysis and the surface properties of these silicas according to $\gamma_D$ using IGC. The present study produced the following conclusions:

1. By assuming that the molecular possession area of the silane coupling agent is 0.5 to 1 nm$^2$, it was determined that multilayer adsorption was achieved on the surface of the silicas by carbon analysis.

2. The values of $\gamma_D$ decreased with increasing IGC measuring temperature in all cases. Silica is an oxide with a relatively low surface energy. The $\gamma_D$ values of the crystalline silica were lower than those of the fused silica at the same measuring temperature. This means that crystalline silica is more stable than fused silica from the surface energetic point of view.

3. The $\gamma_D$ values of the silicas surface-treated with MTMS were higher than those of the others, while the $\gamma_D$ values of the silicas surface-treated with AES were the lowest at the same measuring temperature. This result indicated that while the AES-surface-treated silica is suitable for polymers such as epoxy resin, the MTMS-surface-treated silica is suitable for polymers such as polyester. The silicas surface-treated with GMS and MCMS are suitable for most polymers, because their $\gamma_D$ value is close to that of almost all resins at 160°C (30 mJ·m$^{-2}$).

### Table 5 Dispersive component ($\gamma_D$) of the surface free energy of untreated and silane coupling agents-treated silicas at various temperatures.

<table>
<thead>
<tr>
<th>Silane</th>
<th>Sample</th>
<th>Concentration</th>
<th>$\gamma_D$ (mJ·m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>70°C</td>
</tr>
<tr>
<td></td>
<td>GMS</td>
<td>1.0 g/100 mL</td>
<td>54.69</td>
</tr>
<tr>
<td></td>
<td>Fused</td>
<td>1.0 g/100 mL</td>
<td>50.78</td>
</tr>
<tr>
<td></td>
<td>MTMS</td>
<td>1.0 g/100 mL</td>
<td>49.07</td>
</tr>
<tr>
<td></td>
<td>Fused</td>
<td>1.0 g/100 mL</td>
<td>54.05</td>
</tr>
<tr>
<td></td>
<td>MCMS</td>
<td>1.0 g/100 mL</td>
<td>49.65</td>
</tr>
<tr>
<td></td>
<td>Fused</td>
<td>1.0 g/100 mL</td>
<td>54.10</td>
</tr>
<tr>
<td></td>
<td>AES</td>
<td>1.0 g/100 mL</td>
<td>40.12</td>
</tr>
<tr>
<td></td>
<td>Fused</td>
<td>1.0 g/100 mL</td>
<td>38.60</td>
</tr>
</tbody>
</table>

### REFERENCES