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An investigation into surface energetics of rice hull ash particles using Inverse Gas Chromatography (IGC)

DEEPTANGSHU S. CHAUDHARY, MARGARET C. JOLLANDS
Rheology and Materials Processing Centre, Department of Chemical Engineering, Royal Melbourne Institute of Technology University, Melbourne, Australia 3000

Silanol groups that are present on the surface of rice hull ash or silica ash fillers can positively influence the reinforcing character of the filler. However, being hydrophilic, they present the problem of aggregation and moisture absorption. Physicochemical contributions to reinforcement, provided by silanol groups, influence the filler-polymer and filler-filler interactions. In this study, we investigated the surface energetics of silica ash particles and the effect of chemical surface modification on the free surface energy of silica ash particles was studied.

Inverse Gas Chromatography (IGC), a successful evaluation technique for the surface energy of solids, has been used at infinite dilution to determine the nature of surface interaction of various probes with a silica ash surface. The Gibbs free energies and enthalpies of specific interactions were also determined to estimate the acid-base characteristics of the surface of silica ash particles. The influence of heat treatment and surface modification upon the physicochemical parameters was also investigated. It was found that the silica ash surface is acidic in nature. Modification of the surface, by hydrophobization using silane agents, reduces the specific component of surface energy and could be expected to positively affect the reinforcing character. Surface modification reduced the specific component of surface energy by 80% and positively affects the filler-matrix interaction.

1. Introduction

Inverse Gas Chromatography (IGC) is a gas phase technique for characterising surface and bulk properties of solid materials. The principles of IGC are simple, being the inverse of a conventional gas chromatographic (GC) experiment. Fig. 1 elucidates the difference between analytical chromatography and inverse gas chromatography by schematic representation. IGC is now accepted as an efficient method for the evaluation of the surface energy of solids. The technique has been successfully applied to fibrous and particulate fillers alike.

Like other silicates, silanol groups present on the surface of silica ash fillers could contribute to the reinforcing character of silica ash by suitable modification. However, these silanol groups also increase the surface hydrophilicity and the subsequent problems of water sorption [1]. Silanol groups are also responsible for the acid-base character of silica surfaces and influence the free surface energy of the silica ash particles [2]. Since filler aggregation, filler-matrix adhesion and filler surface modification depend largely upon the strength of the acid-base interactions [3, 4], knowledge of the free surface energy of silica ash particles is essential for improving adhesion and lowering filler aggregation.

For solids, contact angle measurement is a standard technique for estimating the surface energy [5]. However, owing to their small size and difficulties in accessing their surface, this method presents difficulties in estimating surface energy values for filler particles. The term "*inverse*" in IGC indicates that the examined material is placed in a chromatographic column as the solid stationary phase and studied using known test vapours, This has proved to be an excellent quantitative evaluative technique for the surface energy of particulate solids, fibres and fillers [6–8]. These carefully selected test vapours are injected into a carrier gas stream and transported over the surface of the material, which may be particles or fibres. The retention times and the peak elution profiles that are characteristic of the probe molecules, affected by their interactions with the stationary phase, are used to estimate characteristic surface parameters of the examined materials. A series of IGC measurements with different gas phase probe molecules then allows access to a wide range of physico-chemical properties of the solid sample.

Interest lies in IGC measurements at infinite dilution—as these give the retention data that can be converted to dispersive and specific components of the surface energy. Volatile probe molecules are injected

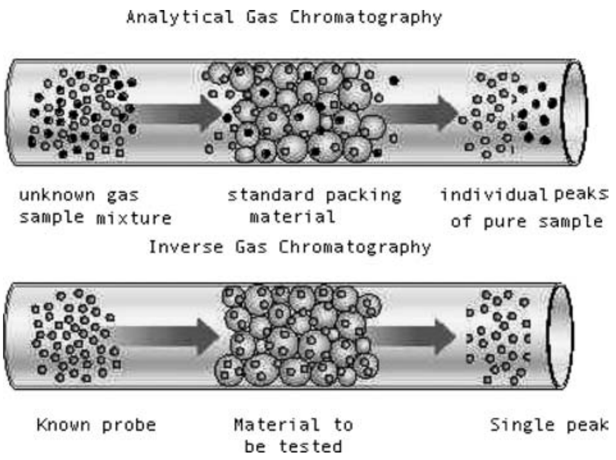

Figure 1 Schematic representation of the principle of the analytical gas chromatography compared to the inverse gas chromatography.

at infinite dilution (that assumes zero surface coverage) in order to allow stationary phase-probe molecule interactions only and to rule out probe-probe interactions. Different probe molecules have characteristic retention times, based on their interaction with the solid surface. The retention time is a measure of how strongly the probe gas interacts with the solid sample-surface and is the fundamental datum obtained from an IGC experiment. From this information, a wide range of surface and bulk properties can be calculated. In fact, the bulk adsorption of the probe continues with time, however, within the timescale of the IGC experiment, this effect can be neglected.

By using IGC, this study focuses on the determination of: (1) How the surface treatment of silica ash with organosilanes affects surface energies (2) How temperature influences surface energies (3) How the information about the surface energies can help us understand filler reinforcement character in polymeric composites. Investigation of the composite mechanical properties is currently being carried out and the results will be published in due course.

2. Theory

The fundamental retention parameter in IGC—the retention time—is used to estimate the net retention volume of the volatile probe, V_n, which corresponds to the volume of the carrier gas required to elute a zone of test vapour. Of greater importance is the specific retention volume, V_g, which can be defined as V_n per unit mass of stationary phase.

For surface adsorption,

$$V_g = K_s S = \frac{V_n}{g} \tag{1}$$

Here K_s is the surface partition coefficient, defined as the ratio of the probe-gas concentration in the stationary phase to that in the mobile phase.

From K_s and its temperature dependence, thermodynamic data describing the probe retention process may be derived. At a given temperature, T, the standard free energy in isothermal transfer of a mole of vapour from the gas phase to a standard state on the surface, or the adsorption energy (ΔG°), is given by

$$\Delta G^\circ = -RT \log_n \left(\frac{K_s P_o}{P} \right) \tag{2}$$

Here, R is the gas-constant, P_o is the reference pressure and P is the equilibrium pressure of gas at the adsorbed state. When De-Boer's constant is taken as reference state of the surface, the change in standard free energy becomes

$$\Delta G^\circ = -RT \log_n \left(\frac{B V_n}{Sg} \right) \tag{3}$$

Here, B is the De-Boer's constant and the value of $B = 2.99 \times 10^2$, S is the specific area of the adsorbent (m^2/g), g is adsorbent mass in column (gram), V_n is net retention volume (cm^3).

For a given system thus, B, S and g are constant and we have

$$\Delta G^\circ = -RT \log_n (V_n) + constt \tag{4}$$

The value of the constant depends on the arbitrary chosen reference state of the adsorbed molecule. The net retention volume was calculated after incorporating the necessary corrections for flow-rate and pressure drop as

$$V_n = Dj(t_r - t_m) \frac{273.15}{T_c} \tag{5}$$

Here D = uncorrected flow rate (cm^3/min), t_r = retention time of probe (min), t_m = dead time of marker (min), j = James-Martin correction factor for gas compressibility = $j = 1.5\left(\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right)$, P_i = pressure of carrier gas at inlet of column (bar), P_o = pressure of carrier gas at column outlet (bar), T_c = column temperature in °C.

Accurate measurement of the retention times is critical as these are directly related to the specific retention volume of the individual test vapours. Adsorbate-adsorbent interaction can be either dispersive (Van der Waals) or specific (acid-base, hydrogen bonding, etc.). As a first approximation, the free energy of adsorption, ΔG°, on a solid surface can be expressed as follows [9, 10]

$$\Delta G^{o} = \Delta G^{d} + \Delta G^{sp} \tag{6}$$

Here ΔG^d and ΔG^{sp} are the dispersive and specific components of the surface energy, respectively.

When the free energies of adsorption of a series of homologous alkanes vary linearly with the number of carbon atoms, the free energy of adsorption corresponding to one methylene group (CH_2) is calculated as

$$\Delta G_{CH_2} = -RT \log_n \frac{V_{N(n)}}{V_{N(n+1)}} \tag{7}$$

Here $V_{N(n)}$ and $V_{N(n+1)}$ are the retention volumes of n-alkanes with n and $n+1$ carbon atoms, respectively.

The n-alkanes exchange only non-specific interactions giving a straight line relationship whereas the polar probes have specific interactions. Therefore, the corresponding surface energies lie above the n-alkane reference line. The adhesion work, W_a , between a non-polar liquid and a surface, when there is no polar interaction taking place between them [10, 11], is given by

$$W_a = 2\left(\gamma_l^d \gamma_s^d\right)^{0.5} \tag{8}$$

Here γ_l^d and γ_s^d are the surface dispersive energies of the liquid and the solid, respectively.

Under conditions of non-specific adsorption, Dorris and Gray proposed that, to a first approximation, the adhesion work is related to the free energy increment of adsorption associated with a methylene group [12], and thus

$$\frac{\Delta G_{\mathrm{CH_2}}}{Na_{\mathrm{CH_2}}} = 2\left(\gamma^d_{\mathrm{CHh_2}} \gamma_s^d\right)^{0.5} \tag{9}$$

Here N = Avogadro's number; $a_{\mathrm{CH_2}} = 0.06$ nm^2; $\gamma_{\mathrm{CH_2}} = 35.6 + 0.058(20 - T)$ mJ/m^2, T in °C.

As shown in Fig. 2, apolar probes (n-alkanes) exchange only dispersive interactions with the solid surface, whereas for polar probes, the interactions are a combination of specific acid base interactions and dispersive interactions. Since one chromatographic signal is recorded for a given probe, one has to find a method to distinguish between the dispersive and the specific contributions to ΔG° (refer to Equation 6). A widely used approach is plotting the free energy of adsorption, ΔG°, versus a given physicochemical property of the probes (such as the vapour pressure, the boiling point, the product of cross-sectional area (a) and the square root of the dispersive contribution to the surface energy of probes ($[\gamma_l^d]^{0.5}$), for which a linear relationship is obtained between surface energy of the solid and the physicochemical property of the apolar probes.

This straight line acts a reference state for estimating the extent of specific interactions of the polar probes given that they exchange acid-base interactions with the solid surface. Correspondingly, the values of ΔG° for polar probes lie above the straight line and the specific component of the free energy can be estimated as

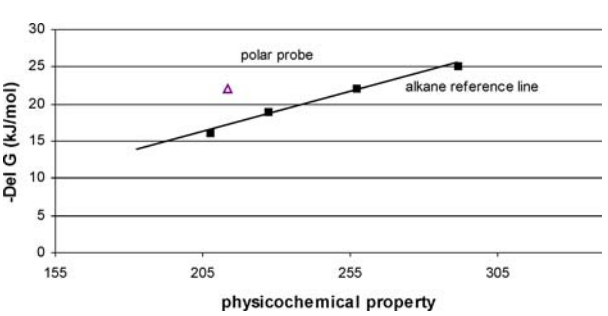

Figure 2 Plot showing the linear relationship between the surface energy of the test solid material and a physicochemical parameter of a series of n-alkanes.

$$-\Delta G^{sp} = -(\Delta G^\circ - \Delta G^d) \tag{10}$$

The γ_l^d values are highly temperature dependent, more than that of the molecular cross-sectional area, and there is lack of data on γ_l^d of probes at various temperatures. In such a situation, the theoretical molecular area (a) can be taken as a probe property as long as the surface energy of the solid bears a linear dependency on it, as shown earlier [13]. Then, the difference in ordinate between the point corresponding to the specific probe and the reference alkane line leads to the value of specific free energy of the adsorption, ΔG^{sp}. Now the specific work of interaction, or the specific interaction per unit surface, I_{sp}, can be calculated as,

$$I_{\mathrm{sp}} = \frac{\Delta G^{sp}}{Na} \tag{11}$$

Here, the numerator is the difference between the surface energy of a polar probe and the surface energy of a hypothetical probe (n-alkane) having the same molecular cross-sectional area as the polar probe. The surface area of the probe molecules can be calculated from the liquid density and the molecular weight [14].

Also, at zero surface coverage, the enthalpy of adsorption, ΔH, can be identified with the differential heat of adsorption and can be calculated from the temperature dependence of the ΔG^{sp} [15] as

$$\Delta H = -\frac{d(\Delta G^{sp}/T)}{d(1/T)} \tag{12}$$

Finally, the acid-base properties of the surface can be correlated to the enthalpy of adsorption by using the acceptor-donor number approach as [15, 16] that gives

$$-\Delta H = K_D(AN) + K_A(DN) \tag{13}$$

Here, *AN* and *DN* are the acceptor and donor numbers, respectively of the probe molecules. Parameter K_D and K_A reflect the ability of the surface to act as electron donors or as electron acceptors, respectively.

3. Experimental

3.1. Surface modification of silica ash

Aminopropyltriethoxy silane (APTS) and Vinyltrimethoxy silane (VTMS) were obtained from Sigma-Aldrich Chemicals, New South Wales. Both silanes were 99.99% pure grades and were used as supplied. Measured quantities of each silane (based on weight percentage of silica ash) were added to a 95% aq. ethanol solution while continuously stirring. After about 10 minutes, a known quantity of silica ash, previously washed in acidic aqueous solution (pH ∼ 4.5) and rinsed with de-ionised (DI) water, was charged in an open bench-top mixer (with stainless-steel container) and the silane solution mixture was added. This mixture was agitated for at least 30 minutes before subjecting it to heat treatment to achieve the ultimate silane condensation step. The heat treatment was carried out at 110°C for 2 hours and the samples were stored in sealed containers.

3.2. Column packing

A nickel-stainless steel column was used (L = 304.8 mm, ID = 2.48 mm). To begin packing the column, stainless steel tubing was straightened, glass wool was used to plug one end, weighed and this same end was attached to a water aspirator. The column was fed with small amounts of silica ash sample and a mechanical vibrator was used to obtain uniform packing in the column. This was done until the column was filled and the unplugged end was also sealed with glass wool. The weight of the packed column was noted to obtain the mass of the silica ash sample in the column.

3.3. Chromatographic measurements

The column was coiled and connected with the chromatograph inlet port and helium was used to purge overnight at 150°C (flow rate = 10 cm^3/min). The column was usually conditioned at a higher temperature than the working temperature. Helium was used as the carrier gas for chromatographic measurements. During each experiment, the flow rate of carrier gas was corrected for pressure drop and for temperature changes in the column by use of the *James-Martin* factor. For experiments with infinite dilution, flame ionisation detector (FID) was used in the IGC experiments. Further, the injection and detector temperature were maintained at approx. 220°C throughout the experiment to prevent any temperature gradient at inlet and outlet of column.

Table I lists the various probes used in the study. To measure the retention time, a small amount of the probe was injected with a 0.5 μL syringe into the chromatograph. Methane was used as the marker probe. The characteristic elution curves were plotted on the chromatogram and the retention times were determined graphically. The procedure was repeated until consecutive injections showed no dependence of the retention column on the amount of probe in the column. A set of retention volumes for 3 different temperatures was obtained by repeating the experiments at those temperatures.

TABLE I The different probes used in the study along with their characteristics. The molecular cross-sectional area values were obtained from elsewhere [17]

Probe	Molecular Weight (g/mol)	Molecular cross-sectional area (nm^2)	γ_l (mJ/mol)
Pentane	60	4.78	18.82
Hexane	72	5.15	19.41
Heptane	84	5.71	20.37
Octane	96	6.30	21.33
Acetone	58	4.25	16.52
Chloroform	65.5	4.42	25.91
Tetrahydrofuran	72	4.51	22.56

TABLE II Retention data and free energies of various apolar and polar probes used

	Temperature, °C					
	60		80		100	
Probe	T_r, min	$-\Delta G^o$, kJ/mol	T_r, min	$-\Delta G^o$, kJ/mol	T_r, min	$-\Delta G^o$, kJ/mol
C5	0.89	16.25	0.29	13.05	0.15	9.86
C6	2.21	19.02	0.91	17.19	0.32	14.06
C7	6.99	22.31	3.16	21.09	1.12	18.75
C8	20.46	25.31	12.34	25.16	4.20	23.03
THF	7.25	22.41	2.54	20.43	1.65	20.02
$CHCl_3$	1.79	18.39	0.69	16.31	0.30	13.88
Acetone	1.77	18.36	0.97	17.41	0.55	16.26

4. Results and discussion

4.1. Thermodynamic parameters of adsorption of probes on untreated silica ash

The retention time at infinite dilution (Henry's law region) was found graphically and the ΔG^o values for various test vapours were calculated at 60, 80 and 100°C. Table II gives the retention time and the corresponding free energy of adsorption of various probes on untreated silica ash, at the mentioned temperatures.

Fig. 3 shows the change in free energies of adsorption of a series of n-alkanes against their carbon numbers. The observed linear relationship is characteristic of non-specific adsorption and thus, it is confirmed that the interaction of n-alkanes with solid silica ash surface is only possible via dispersive forces. Further, it is seen that with increase in temperature, the free energy of adsorption decreases. This effect could be attributed to the increased degree of freedom at higher temperatures that causes adsorption to be difficult.

4.1.1. Dispersive component of surface energy

The linearity between the free energy of adsorption and the carbon atom number of a series of n-alkane (as shown in Fig. 3) allows the dispersive component of the solid surface energy to be calculated from the increment in the free energy of adsorption per methylene (CH_2) group. This is obtained from the slope of line relating ΔG^d of n-alkanes to the number of carbon atoms (#) in

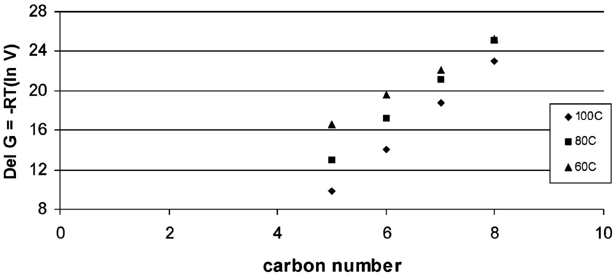

Figure 3 Plot showing the linear relationship of the surface energy (ΔG^o) of silica ash surface and the carbon number of a series of n-alkanes at various temperatures. Since n-alkanes are able to exchange only dispersive interactions, $\Delta G^o = \Delta G^d$.

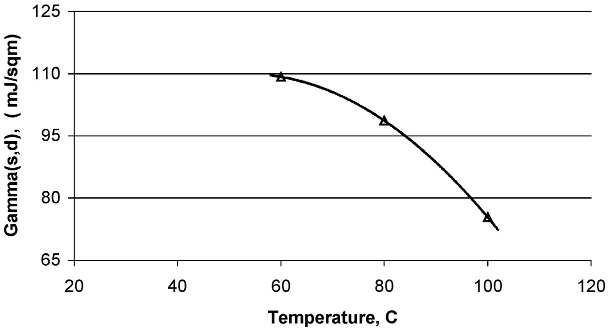

Figure 4 Plot showing the variation in dispersive interaction, γ_s^d, against temperature for untreated silica ash.

their molecules. Equations 7–9 are used to determine the dispersive component of surface energy at various experimental temperatures.

The changes in dispersive interaction component, determined at temperatures ranging from 60 to 100°C, are shown as a function of temperature in Fig. 4. The dispersive interaction component decreases with increase in temperature as highlighted by the figure, which follows the decrease in the net surface energy with increasing temperature. However, the decrease in γ_s^d is not linear as seen in Fig. 7 and it was found that the temperature dependence of γ_s^d is

$$\frac{d\gamma_s^d}{dT} = -0.0159T + 1.072\ \text{mJ/m}^2{}^\circ\text{C} \qquad (14)$$

Here T is the temperature (°C). It also shows that for anhydrous surfaces, lower energy is required for dispersive interactions. It is possible that the density of hydroxyl group is not the only major factor in determining the dispersive interaction component. Other factors could include the increasing freedom with increasing temperatures and possible changes on the solid surface makes the non-specific adsorption difficult, thus reducing the dispersive component of the surface energy.

4.1.2. Specific component of surface energy

At infinite dilution, with the probe concentration becoming zero in the solid phase, the interaction between the probe and the surface can be taken as a reversible physical exchange. With an additional specific component in the interaction, the values lie above the alkane reference line on the 'ΔG^o' *versus*' a' plot as shown in Fig. 5.

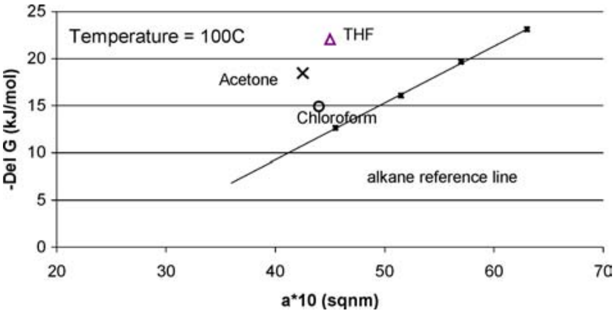

Figure 5 Variation in free energy of adsorption versus the molecular cross-sectional area of various probes on silica ash surface at 100°C.

TABLE III The specific free energy of adsorption for polar probes at various experimental temperatures

	$-\Delta G^{sp}$ (kJ/mol)		
Polar probe	60°C	80°C	100°C
THF	7. 19	8.95	12.01
$CHCl_3$	4.07	5.61	6.72
Acetone	5.52	8.64	11.24

TABLE IV Specific interaction parameter, I_{sp}, for different polar probes at various temperatures

	I_{sp}, mJ/sqm		
Temperature (°C)	THF	$CHCl_3$	Acetone
60	37.95	14.65	33.44
80	33.84	13.33	32.83
100	28.95	10.16	32.05

In Fig. 5, the tendency of the solid surface to accept or donate an electron in an interaction is represented by the n-alkane straight line and is zero at the line (having only dispersive interactions). Further, depending upon the nature of the polar probe molecule, the solid surface accepts or donates electron and therefore, the polar probes lie above the n-alkane line (having dispersive and specific interactions). One finds that chloroform, which is a Lewis acid probe, is situated near the alkane line, whereas THF, a Lewis base, lies well above the reference line. This is suggestive of the greater interaction of THF with silica ash surface compared to $CHCl_3$. Table III shows the specific free energy of adsorption, ΔG^{sp}, values for the different experimental temperatures. Using these values and Equation 11, the specific interaction parameter, I_{sp}, was calculated. Table IV shows the values of specific interactions for various polar probes, at different experimental temperatures.

The data in Table IV are suggestive of the acidic nature of silica ash surface. The higher I_{sp} of silica ash with THF or acetone relative to $CHCl_3$ probe is an indication of the higher surface polarity, mainly due to the acidic silanol groups and also due to impurity and surface irregularity. Also, as seen for other silicates [18], the specific interaction parameter also decreases with temperature in a way that is similar to its dispersive counterpart, indicating that both parameters are highly temperature dependent. Both THF and acetone have Lewis basic character, and therefore, show considerable interaction with the silica ash surface as compared to $CHCl_3$, which has an acidic character.

Interestingly, the limited dispersion characteristics of the untreated silica ash can now be represented by a low γ_s^d/I_{sp} ratio. Though other silicates, such as precipitated silica, also have a high specific component of surface energy [7], silica ash suffers from a poor specific surface area and an irregular topography making its reinforcing character inferior to that of precipitated or fumed silicas [19]. The specific interaction capability of the silica ash surface can also be represented through Lewis acid-base characteristics, reported in terms of the

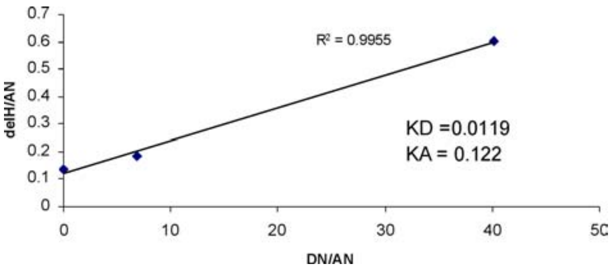

Figure 6 Graphical determination of K_A and K_D values for the silica ash surface.

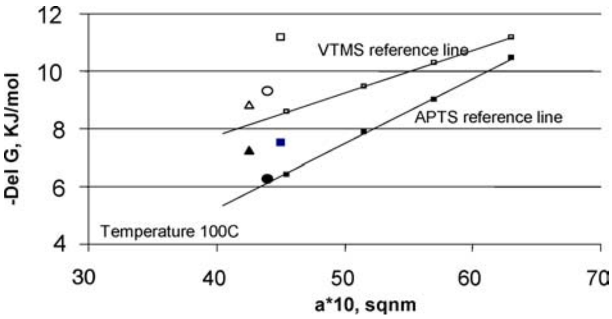

Figure 7 Plot of the surface energy V_s cross-sectional area of *n*-alkane probes for APTS and VTMS modified silica ash. Filled and unfilled points represent probes for APTS and VTMS, respectively. (■ - THF, Δ/▲ - Acetone, O/● - $CHCl_3$).

TABLE V The specific work of interaction, I_{sp}, for APTS and VTMS modified silica ash for various polar probes at different experimental temperatures

	I_{sp} (mJ/sqm)					
	APTS modified silica ash			VTMS modified silica ash		
T (°C)	THF	$CHCl_3$	Acetone	THF	$CHCl_3$	Acetone
60	8.58	11.64	10.38	9.58	5.89	11.08
80	6.83	8.34	8.69	9.06	4.26	6.44
100	4.03	4.82	5.73	8.79	3.59	2.77

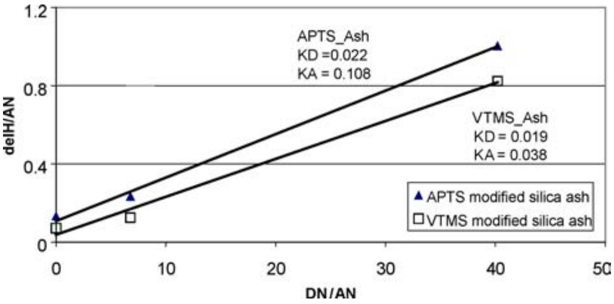

Figure 8 Determination of K_A and K_D values of the APTS and VTMS modified silica ash surface.

electron acceptor-donor capabilities. Using the temperature dependency of ΔG^{sp} as given in Equation 12 and using an earlier mentioned approach [15], a plot can be generated, as shown in Fig. 6, which readily gives the K_A and K_D in the form of the slope and the intercept, respectively. The large value of $S_c = K_A/K_D$ also confirms the acidic nature of the silica ash surface.

4.2. Interaction of surface treated silica ash with polar probes

The contrasting difference between the modified silica ash and the unmodified silica ash samples is that for modified silica ash, the net surface energy of the solid surface is considerably reduced and therefore the ΔG^{o} values of the polar probes lie closer to the alkane reference line as seen in Fig. 7.

More interestingly, the reduction in the free energy of adsorption of the polar probes on VTMS treated ash and on APTS treated silica ash also results in the reduction in the corresponding specific interaction parameter. Table V reveals the improvement that surface modification can achieve in terms of reduction of the filler-filler interaction. Comparing the specific interaction parameters for untreated silica ash (shown in Table IV) to the values shown in Table V, it is evident that about 80% reduction in I_{sp} is achieved by surface treatment with either silane.

However, these values are still higher than those for carbon black and commercial precipitated silicas [18]. It is thought that the silica ash surface irregularity causes only partially 'capping' of silanol groups by the silane molecules. This leaves scope for further reduction in the specific work of interaction. Further, it is also seen that the reduction obtained in case of $CHCl_3$ is quite insignificant, leading to the conclusion that the interactions of the acidic probe were insignificant. Table V also provides a comparison between APTS and VTMS and suggests that VTMS achieves an overall better surface modification.

Further, a better indication of the modification achieved by either silane can be obtained from the acid-base characteristics of the modified silica ash. Fig. 8 shows a plot of $\Delta H/AN$ Vs *DN/AN*, similar to one shown in Fig. 6. A comparison of the K_A values for APTS and for VTMS modified silica ash indicates that the silica ash achieved better overall modification with VTMS than with APTS.

A low value of the specific component of surface energy is preferred as it reduces the filler-filler interactions. Also, with increasing surface modification, filler-matrix adhesion increases since the filler surface provides increasing numbers of hydrophobic sites with which polymeric chains can interact. However, since silane application reduces the total free surface energy, the accompanying dispersive component also decreases, which is undesirable. Therefore, a compromise on the extent of surface modification of the silica ash needs to be reached.

5. Conclusion

Significant strong interactions were observed between a number of test vapours and the unmodified silica ash. As expected, the surface energy decreased with increasing temperature. The dispersive component of the surface energy for unmodified silica ash was significantly affected by changes in temperature. The high values of K_A signified that the silica ash surface is acidic in character.

After surface modification, the specific component of the surface energy is significantly reduced (∼80%), showing that filler-filler interactions are significantly reduced by application of coupling agents. This would in turn contribute to filler-matrix adhesion. A comparison of the surface modification achieved in silica ash by APTS and VMTS, in terms of the specific component of surface energy, shows that the modifier (silane agent) significantly reduced the magnitude of specific interactions. This was attributed to the reduction in the free silanol groups on the silica ash surface. Further, it was also found that the modification achieved by VMTS is better compared to APTS.

Acknowledgements

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