Interaction of Poly(hydromethyl siloxane) and Cyclic Si-H Functional Oligomers with Metal Hydroxides

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Summary: The adsorption of oligomeric trimethyl terminated poly(methylhydrosiloxane) ($M.D(H)_{75}.M$) (PMHS) and pentamethyl-cyclopentasiloxane ($D(H)_5$) onto aluminium hydroxide ($Al(OH)_3$) and magnesium hydroxide ($Mg(OH)_2$), from heptane, has been investigated. The filler isolated from adsorption flasks was analysed using diffuse reflectance Fourier Transform infrared spectroscopy (DRIFTS) and solid-state ^{29}Si NMR. Data from the above analytical methods indicate strong adsorption of these probes on to both fillers. Adsorption of both probes occurs via formation of metal-O-Si linkages. Self condensation of Si-H groups of adsorbed PMHS was also evident. With $Al(OH)_3$, the adsorption PMHS involved a greater proportion of the Si-H groups, causing the adsorption density to be lower than with $Mg(OH)_2$.

Introduction

The surface treatment of all types of fillers has over recent years changed the role of fillers from extending agents to powerful functional additives, which can impart useful properties to polymers[1]. A classic example is the use of hydrated minerals and metal hydroxides as flame retardant and smoke suppressant additives, which are halogen free. For such applications, the high filler loading (>60% w/w) required to achieve the desired flame retardant effect[2], causes a significant reduction in mechanical properties and poor melt rheology[3]. Surface modification of the fillers primarily improves their dispersion in the polymer matrix, and in some cases, increases filler matrix interaction. This results in improved composite mechanical properties and easier processing[4].

The reaction of chlorosilanes with water, producing silanols that readily condense to form siloxanes, forms the basis of commercial silicone production. The Grignard and direct processes are the most important commercial methods for the preparation of chlorosilanes[5]. Commercial quantities of poly(methylhydrosiloxane) (PMHS), are

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obtained via hydrolysis of methyldichlorosilane ($MeHSiCl_2$)[6], a byproduct of the direct synthesis route[7]. Poly(methylhydrosiloxane) (PMHS) has up to now been an unwanted byproduct of poly(dimethylsiloxane) (PDMS) production. The unique chemistry of the Si-H bond means that they readily chemisorb onto surfaces bearing hydroxyl groups and undergo crosslinking via hydrolysis[8], features which make them potentially useful for the surface modification of fillers.

The aim of this paper is to explore the adsorption behaviour of a range of Si-H functional siloxanes onto aluminium hydroxide ($Al(OH)_3$) and magnesium hydroxide ($Mg(OH)_2$). A simple cyclic oligomer (pentamethylcyclopentasiloxane) ($D(H)_5$) and a linear methyl end blocked oligmeric PMHS ($M.D(H)_{75}.M$) will be investigated together with octamethylcyclotetrasiloxane (D_4) as a control to eliminate interaction via the siloxane linkages. Monolayer adsorption levels and the tendency for multi-layer adsorption will be assessed by determination of adsorption isotherms from heptane. Filler samples will be isolated from the adsorption flasks and the nature of probe-substrate interactions examined using infrared spectroscopy and ^{29}Si solid state NMR.

Materials

All siloxanes (D_4, $D(H)_5$, and $M.D(H)_{75}.M$) investigated were provided by Dow-Corning. The filler grade $Mg(OH)_2$ (D_{50} = 0.9 μm) used in the experiments was Magnifin H10, provided by Martinswerke via Omya-Croxton and Garry, the UK distributor. The surface area of the H10 was checked by five point N_2 BET adsorption and found to be 8.7 $m^2\ g^{-1}$. The filler grade $Al(OH)_3$ used in this study was SF-11E, (Alcan Chemicals, UK) (D_{50} = 0.7 μm, N_2 BET surface area 11.0 $m^2\ g^{-1}$). n-Heptane (HPLC grade) and KBr were supplied by the Aldrich Company.

Experimental

Adsorption isotherm studies (AIS) were carried out with 5 g of filler dispersed in 100 cm^3 heptane. Siloxane levels from 0.1 g to 5.0 g, on 100 g of filler were used. Mixtures were agitated vigorously for three hours using a laboratory shaker and then left to settle for 24 hours. The amount of siloxane adsorbed was determined by FTIR analysis of the supernatant liquor after 24 hours and after one week. The liquor samples were analysed

using a DTGS detector equipped Nicolet 510P FTIR bench and a cell with path length 0.07 mm. Calibration curves for the relevant siloxanes were constructed using standard solutions.

The treated filler obtained by AIS was isolated by Buchner filtration, and washed on the funnel to remove loosely bound adsorbate with 3 x 25 cm^3 of fresh heptane, then dried to constant mass at 70 °C. The washings were also analysed under the same conditions as the supernatant liquors in order to detect possible removal of loosely bound adsorbate.

The dried filler samples were then examined using diffuse reflectance Fourier Transform infrared spectroscopy (DRIFTS) and solid-state ^{29}Si NMR spectroscopy.

The samples for DRIFTS analysis were diluted to 5% w/w with KBr and then analysed using a DTGS detector equipped Nicolet 510P FTIR bench fitted with a Spectra-Tech DRIFTS cell. Spectra were made up of 168 scans with resolution set to 4 cm^{-1}. Control samples, treated in exactly the same manner as the other samples, but with no added adsorbate, were also analysed.

The ^{29}Si cross polarisation/magic angle spinning (CP/MAS) NMR spectrscopy was carried out on undiluted samples using a JEOL 400 MHz Lambda NMR spectrometer. All chemical shifts are given relative to tetrakis(trimethylsilyl)silane, which is the accepted NMR chemical shift reference standard for ^{29}Si NMR[9].

The conditions used are given in Table 1.

Table 1: ^{29}Si CP/MAS conditions.

Parameter	Value
Observation frequency	79.38 MHz
Rotation frequency	5 kHz
Sweep width	32 kHz
Number of scans	13620-16202
Relaxation delay	5 s
Contact time	5 ms

Results and Discussion

The adsorption isotherms for $D(H)_5$ and $M.D(H)_{75}.M$ (Figures 1-2) and the resultant monolayer adsorption levels (Table 2) were determined using the symmetric ($-CH_3$) deformation band (1261 cm^{-1})[10]. FTIR analysis of the solvent used to wash the filler on the Buchner funnel after isolation shows very little evidence of probe removal.

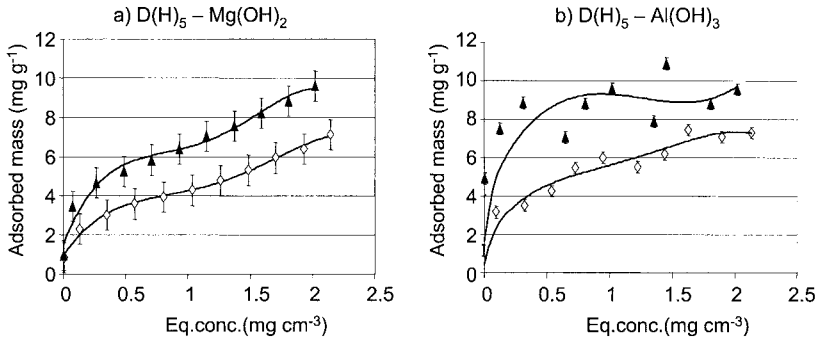


Figure 1: Adsorption isotherms of $D(H)_5$ from heptane obtained after 24 h (◇) and 1 week (▲), a) on $Mg(OH)_2$, b) on $Al(OH)_3$.

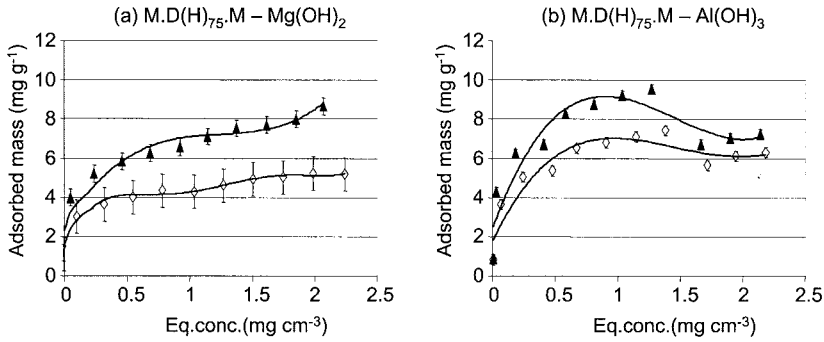


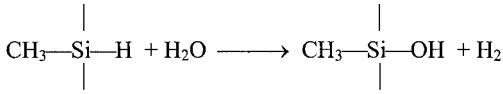
Figure 2: Adsorption isotherms of $M.D(H)_{75}.M$ from heptane obtained after 24 h (◇) and 1 week (▲), a) on $Mg(OH)_2$, b) on $Al(OH)_3$.

Table 2: Monolayer adsorption levels for the Si-H functional siloxanes determined from adsorption isotherms.

Sample	After 24 hours	After one week
D_4 on $Mg(OH)_2$	0.00 mg m^{-2}	0.00 mg m^{-2}
$D(H)_5$ on $Mg(OH)_2$	0.46 mg m^{-2}	0.81 mg m^{-2}
$D(H)_5$ on $Al(OH)_3$	0.54 mg m^{-2}	0.82 mg m^{-2}
$M.D(H)_{75}.M$ on $Mg(OH)_2$	0.58 mg m^{-2}	0.92 mg m^{-2}
$M.D(H)_{75}.M$ on $Al(OH)_3$	0.64 mg m^{-2}	0.82 mg m^{-2}

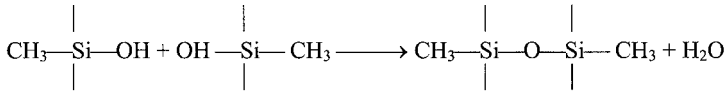
This shows that the adsorption reactions are slow and that some rearrangement takes place after adsorption therefore allowing more efficient packing of the adsorbate molecules. Determination of levels of adsorption of $M.D(H)_{75}.M$ using the Si-H stretching bands (at 2274 cm^{-1} and 2171 cm^{-1})[10] gave higher levels of adsorption than

those calculated from the methyl C-H deformation band (1261 cm^{-1}). This observation confirms that mutual reaction of the Si-H groups (forming Si-O-Si linkages), and reaction of Si-H groups with the filler surface (forming Si-O-Metal linkages), occurred (Schemes 1 to 3).



Scheme 1: Formation of silanol groups by pre-hydrolysis of Si-H by water (from the filler surface).

The second stage is self-condensation of Si-OH to form siloxane linkages[5] (Scheme 2):



Scheme 2: Formation of siloxane linkages via condensation of silanols.

After one day, the adsorption isotherms for $D(H)_5$ and $M.D(H)_{75}.M$ on both fillers were broadly similar and were generally of the Langmuir form with the exception of $D(H)_5$ on magnesium hydroxide where no distinct plateau was observed. However, after one week of treatment the levels of adsorption were higher in all cases and adsorption onto magnesium hydroxide showed a reduction in Langmuir character[11] where the level of adsorption increased steadily within the equilibrium concentration range investigated. The aluminium hydroxide surface appeared to be more active towards the Si-H group as steeper isotherms were observed with the first inflexion being reached at lower equilibrium concentration than was the case with equivalent isotherms for magnesium hydroxide. Solid-state ^{29}Si NMR spectroscopy of the siloxane treated fillers revealed fewer unreacted Si-H groups on aluminium hydroxide (36 ppm) than magnesium hydroxide, and thus confirmed that the former filler has greater reactivity towards Si-H groups. Adsorption studies using an equivalent dimethyl siloxane cyclic model compound (D_4) shows no adsorption at all. This observation demonstrates that the p d π-bonding system of the siloxane bond plays a negligible part in the adsorption of the siloxanes investigated.

Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) analysis of washed filler samples from the adsorption flasks, shows a reduction of the $Si\text{-}H/CH_3$

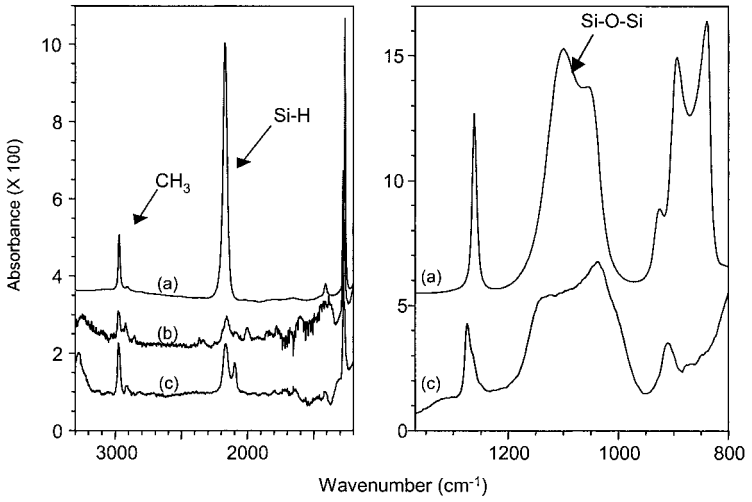
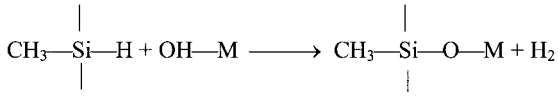
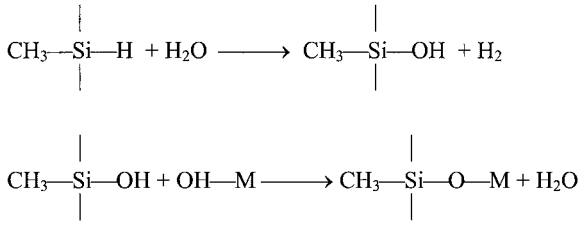


Figure 3: (a) IR spectrum of M.D(H)75.M, (b) substrate subtracted DRIFTS spectra of $Al(OH)_3$ treated with M.D(H)75.M, (c) substrate subtracted DRIFTS spectra of $Mg(OH)_2$ treated with M.D(H)75.M. (b) is not shown in the 1400-800 cm^{-1} region due to interference from $Al(OH)_3$ absorption bands (that could not be eliminated by subtraction).



Scheme 3: Reaction of Si-H with M-OH.



Scheme 4: Reaction of Si-H with M-OH preceded by hydrolysis of Si-H.

absorbance ratio for the adsorbed $M.D(H)_{75}.M$ on the surfaces of both fillers in relation to the same absorbance ratio for unbound $M.D(H)_{75}.M$. (Figure 3). This is clear evidence of self-condensation of Si-H (Schemes 1+2) and Si-H + Metal-OH (M-OH) reactions (Schemes 3+4), forming Si-O-Si and Si-O-Metal linkages, respectively. The broadening, shifting and attenuation of the Si-O-Si asymmetric stretching bands (1200-1000 cm^{-1}) observed in the DRIFTS spectrum of $M.D(H)_{75}.M$ treated $Mg(OH)_2$ indicate

self condensation of the Si-H groups and interaction of PMHS with the filler surface via Si-O-Mg linkages (Figure 3(c)). The latter bonds probably absorb at ca. 1000 cm^{-1}, where there is a weak shoulder. The changes in position and relative intensities of the two major components of the Si-O-Si asymmetric stretching band envelope, resulting from adsorption associated interactions, afford insight into the new species formed[12]. A reversal of the relative intensity of the higher (1100 cm^{-1}) and lower energy (1050 cm^{-1}) components (and slight shift of the latter component to lower energy (ca. 1040 cm^{-1})) may be due to the presence of unreacted silanol groups[12]. However, this could not be confirmed due to interference from the OH stretching bands of the $Mg(OH)_2$. The shift of the higher energy component (1100 cm^{-1}) to even higher energy (1150 cm^{-1}) is likely to be related to increased structuring[12], possibly associated with self-condensation of Si-H groups. Size exclusion chromatography investigations (not shown) on the supernatant liquors indicated that the self-condensed species remained on the filler surface.

The solid-state ^{29}Si NMR analysis of the $M.D(H)_{75}.M$ treated $Al(OH)_3$ and $Mg(OH)_2$ (Figure 4) shows that in both cases T_2 (-56ppm) and T_3 (-67ppm) units have been formed[9]. A T_3 unit is a silicon atom attached to three (-O-Si) groups and one methyl group, whilst a T_2

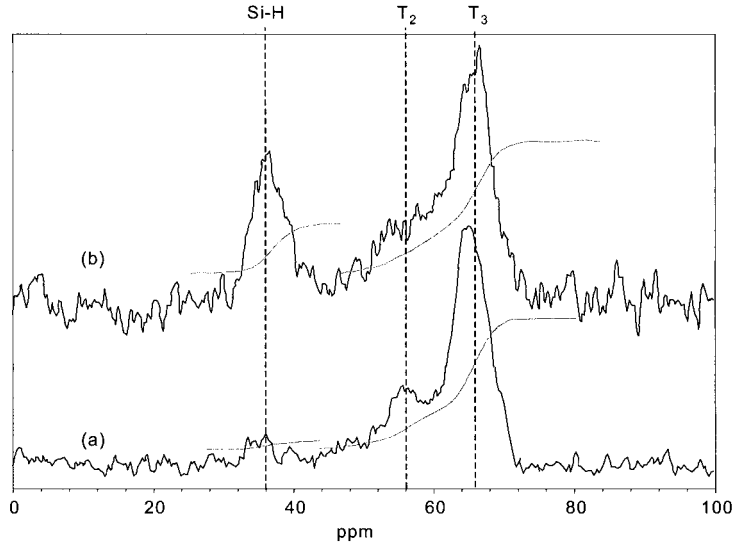


Figure 4: (a) ^{29}Si NMR spectra of $Al(OH)_3$ treated with M.D(H)75.M, (b) ^{29}Si NMR spectra of $Mg(OH)_2$ treated with M.D(H)75.M.

unit is a silicon atom attached to two (-O-Si) groups, one OH group and one methyl group. The level of unreacted Si-H (36 ppm) in the adsorbed siloxanes was determined relative to the combined level of T_2 (ca. 64 ppm) and T_3 (ca. 74 ppm) units.

The Si-H/(T_2+T_3) ratio for $Al(OH)_3$ was 0.06 for the $Al(OH)_3$ and 0.37 $Mg(OH)_2$. It must be emphasised that these values are comparable in relative terms but are not absolute; this is because CP/MAS causes the Si-H group to produce a stronger signal than T_2 and T_3 units. The difference in the relative amount of Si-H reacted can be related to the surface area normalised monolayer levels of adsorption (Table 2) and in turn to the mode of adsorption. On $Al(OH)_3$ more self condensation of $M.D(H)_{75}.M$ and/or formation of Si-O-Al linkages occurred than with $Mg(OH)_2$, this led to a flatter adsorption with the molecule taking up more space on the surface, this effect is manifested in the slightly lower adsorption density of $M.D(H)_{75}.M$ on $Al(OH)_3$ after one week.

The weaker basicity of $Al(OH)_3$ relative to $Mg(OH)_2$ makes this result somewhat surprising, though with $Al(OH)_3$ there is a greater chance of sodium contamination. SF11-E is a low sodium grade $Al(OH)_3$ intended for electrical applications, however, the washing process used to remove the sodium may still leave sodium trapped in the sub-surface structure. In time, the latter sodium may migrate to the surface forming very strongly basic sites that are absent on $Mg(OH)_2$. These sites may explain the higher level of Si-H reaction on $Al(OH)_3$. The possibility of reaction of both fillers with atmospheric carbon dioxide cannot be ignored; in the case of $Mg(OH)_2$ magnesium carbonate will form. Formation of aluminium carbonate is unlikely, however, any sodium oxide that migrates to the surface will be converted to sodium carbonate. Magnesium carbonate is insoluble and weakly basic, whereas sodium carbonate is soluble and strongly basic. Therefore, the surface of the $Al(OH)_3$ may feature strongly basic adsorption sites despite reaction with carbon dioxide. Further work is, however, needed to verify this idea.

Conclusion

Pentamethylcyclopentasiloxane ($D(H)_5$) and oligomeric poly(methylhydrosiloxane) ($M.D(H)_{75}.M$) chemically adsorbed onto $Mg(OH)_2$ and $Al(OH)_3$. Adsorption isotherm studies and ^{29}Si CP/MAS solid state NMR, clearly indicated a lower adsorption density of $M.D(H)_{75}.M$ onto $Al(OH)_3$ and involvement of a greater proportion of the Si-H

groups per molecule adsorbed, relative to equivalent adsorption on to $Mg(OH)_2$. This implied flatter adsorption on to $Al(OH)_3$. NMR revealed a higher level of unreacted Si-H groups in $M.D(H)_{75}.M$ on $Mg(OH)_2$ an observation, which together with increased adsorption density, suggests slightly more loop adsorption. DRIFTS analysis of filler samples isolated from the adsorption flasks confirmed adsorption via the Si-H groups (forming Si-O-Metal) and self-condensation of Si-H groups (forming Si-O-Si). Octamethylcyclotetrasiloxane (D_4) showed no adsorption on either filler, thus confirming that the siloxane linkages do not play a significant role in the adsorption of methylhydrosiloxanes under these conditions.

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