PMMA-based composite materials with reactive ceramic fillers
Part 1.—Chemical modification and characterisation of ceramic particles

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Polymerisable organic silane molecules [3-(trimethoxysilyl)propyl methacrylate, γ-MPS] have been grafted onto the surface of ceramic oxide powders (Al_2O_3, ZrO_2, TiO_2), *via* hydroxy groups of the latter oxides, in order to obtain organic–inorganic hybrid 'macromonomers'. Densities of surface hydroxy groups have been determined using thermogravimetry (TG) and chemical titration. Quantification of γ-MPS grafting has been determined by FTIR spectroscopy, elemental analysis and TG. Typical grafting yields up to 6 μmol m^{-2} were obtained. The influence of the relative amount of silane used has been studied. Silane multilayers and/or aggregates are formed as observed in ^{29}Si CP MAS NMR spectroscopy.

Ceramic oxide fillers are often added to polymers in order to obtain composite materials with better (mechanical, thermal, electrical, magnetic, *etc*.,) properties than those exhibited by their constitutive components. An important feature for obtaining an improvement in the properties (in particular mechanical) is a strong interface adhesion between filler particles and the polymer matrix.[1]

A solution for improving interface adhesion consists in establishing covalent chemical bonding between the two phases. This can be achieved through the grafting of a polymerisable group onto the oxide surface (*via* hydroxy groups) followed by its copolymerisation with organic monomers, a process that is expected to result in the formation of inorganic–organic hybrids (Scheme 1).

Although much information is available in the literature on the use of silane coupling agents with glass or silica powders[2–11] (mainly for chromatography or reinforced plastics applications), less attention has been paid to the silanisation of other ceramic oxides, in particular Al_2O_3,[1,12–17] TiO_2[18–20] and ZrO_2. Moreover, little information exists concerning the copolymerisation with organic monomers.[10,21]

The present study deals with the surface modification of ceramic oxide particles Al_2O_3, TiO_2 and ZrO_2 through grafting of 3-(trimethoxysilyl)propyl methacrylate (γ-MPS) as depicted in Scheme 2 and the corresponding characterisation.

This paper is the first of a series dealing with [ceramic oxide powder]–[PMMA] composites. Further papers addressing the free-radical copolymerisation of these modified ceramic oxides with (meth)acrylic monomers and the mechanical characterisation of resulting inorganic–organic hybrid materials will follow.

Experimental

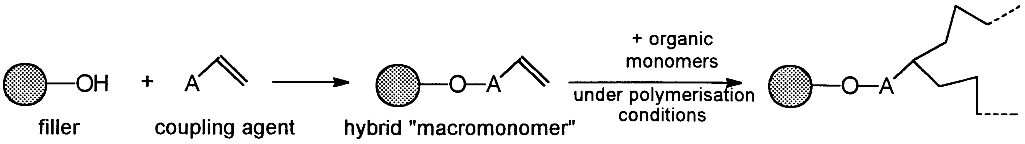
Materials

Table 1 lists the physical properties for the commercial oxide powders Al_2O_3, ZrO_2 and TiO_2 used in this study. The powders were dried at 130 °C under vacuum for 15 h prior to any characterisation or use. 3-(Trimethoxysilyl)propyl methacrylate (γ-MPS) from Fluka Chem. and 99.8% toluene from Sigma–Aldrich were used in the grafting experiments. Triethylaluminium (TEA) (1.0 M solution in heptane) and 99% anhydrous heptane both from Aldrich were used in chemical titration experiments without further purification.

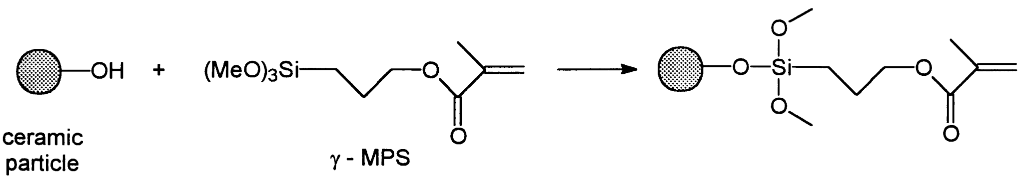
Chemical titration of hydroxy groups

Reaction with TEA was used to determine the hydroxy surface density in oxide powders, as already described.[22,23] The reaction takes place according to Scheme 3.

Experiments were carried out at 25 °C in dry heptane under an argon atmosphere. An excess of TEA (1 ml) was added to



Scheme 1

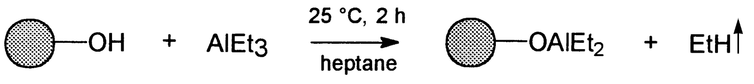


Scheme 2

Table 1 Physical properties of ceramic powders

ceramic powder	supplier	commercial name or reference	purity (%)	crystallographic form	particle size distribution (sedigraph) d_{50}/μm	specific surface area/$m^2\ g^{-1}$
Al_2O_3	Baikowski Chimie	CR30	99.9	α	0.5	26 ± 1
		CR15	99.9	α	0.40	15 ± 1
		GE30	99.9	α	13	26 ± 1
		CRT30	97	θ	0.19	31
		D65CR	97	δ	0.24	66
	Degussa	C	99.6	δ	0.013	100 ± 15
ZrO_2	Magnesium Elektron	G10	99	monoclinic	14[a]	3 ± 1
	Degussa	VP	96	monoclinic	0.03	40 ± 10
TiO_2	Aldrich	23,203–3	99.9	anatase	0.2	10

[a] Determined by laser coulter technique.



Scheme 3

a stirred suspension of 0.2 g of oxide powder in 20 ml of heptane and the volume of produced ethane gas measured in a gas burette. The experiments were repeated four times to check the reproducibility.

Grafting of γ-MPS onto ceramic particles

Grafting was carried out under an argon atmosphere according to the work of Tsubokawa *et al.*,[24] that is to say without catalyst. The reaction mixture consisted of an excess of silane (deduced from the measured hydroxy group surface density), 200 ml of toluene and 10 g of ceramic powder. After dispersing the powder in toluene, silane was added and the resulting solution refluxed under a stream of argon for 15 h. The modified powder was then poured off and washed with 300 ml of fresh toluene in a Soxhlet apparatus for 24 h. Finally, the powder was dried at 110 °C for 3 h under vacuum.

Characterisation techniques

IR characterisation of pristine and modified powders were performed using a Bruker IFS Equinox 55 FTIR spectrometer (signal averaging 30 scans at a resolution of $4\ cm^{-1}$). KBr pellets containing *ca.* 2 mass% of material were analysed.

Thermogravimetry (Setaram MTB 10–8) of 75–100 mg of both modified and non-modified powders was performed in static air at a ramp rate of $240\ °C\ h^{-1}$ to 1150 °C.

Pyrolysis/mass spectrometry experiments were carried out using a Fisons Autospec EQ-Q apparatus under electron impact conditions (70 eV, 100–200 μA ionising current) at a rate of $30\ °C\ min^{-1}$ at 10^{-5} Torr. Elemental analyses were performed by Centre d'Analyse du CNRS.

^{29}Si CP MAS NMR spectra were obtained on a Bruker MSL 200 spectrometer at 39.76 MHz. The samples were spun at 10 kHz using zirconium oxide 4 mm rotors. The spectral width was 8 kHz and pulse interval time 5 s. Single contacts were used with a contact time of 5 ms. All chemical shifts were referred to tetramethylsilane (TMS). As a consequence of the rotor size capacity (permitting the analysis of only 75 mg of powder) and the low % of ^{29}Si, more than 27 000 FIDs had to be accumulated.

Results and Discussion

Our investigation started by the characterisation of the native hydroxy functions present on the surface of the various ceramic particles (Table 1). Then, the grafting process was studied and the modified powders were characterised.

Characterisation of hydroxy groups on dried pristine powders

IR spectra revealed the presence of numerous hydroxy groups as indicated by the large OH stretching band at *ca.* $3500\ cm^{-1}$ [Fig. 1(*a*)] mainly due to physisorbed water. The presence of 'free' hydroxy groups (chemisorbed water) is sometimes reported,[25,26] but was not observed under our experimental conditions. The very weak absorption band that is seen at *ca.* $2900\ cm^{-1}$ (CH stretching) was assigned to organic surface contaminants.

In order to quantify, to a reasonable extent, the amount of γ-MPS required for grafting, it is first necessary to determine the surface density of hydroxy groups. Thermogravimetry and/or TEA chemical titration were used to quantify the hydroxy group density for each powder studied (Table 2). Three domains can be distinguished in the thermograms obtained for pristine powders: 100–400 °C, 400–800 °C and 800–1100 °C [see Fig. 2(*a*) for Al_2O_3]. Between 100 and 400 °C the main mass loss can be assigned to the desorption of physisorbed water. Above 400 °C dehydration occurs according to reaction Scheme 4.

Between 800 and 1100 °C, isolated hydroxy groups migrate on the surface and are consumed *via* the same reaction. Therefore, surface hydroxy groups available for reaction with γ-MPS are uniquely those found between 400 and 1100 °C.

The densities of OH obtained are higher than those generally reported for such oxides: 4–7 $\mu mol\ m^{-2}$ for Al_2O_3[27,28] and 5–9 $\mu mol\ m^{-2}$ for TiO_2,[18,19,26] but lower than Pesek's TG values[14] (40 $\mu mol\ m^{-2}$ for Al_2O_3). As compared with the TG results, slightly higher values are obtained using TEA chemical titration. As a matter of fact, both TG and chemical titration may give overestimated results. Indeed, TG does not distinguish between OH groups present on the particle surface

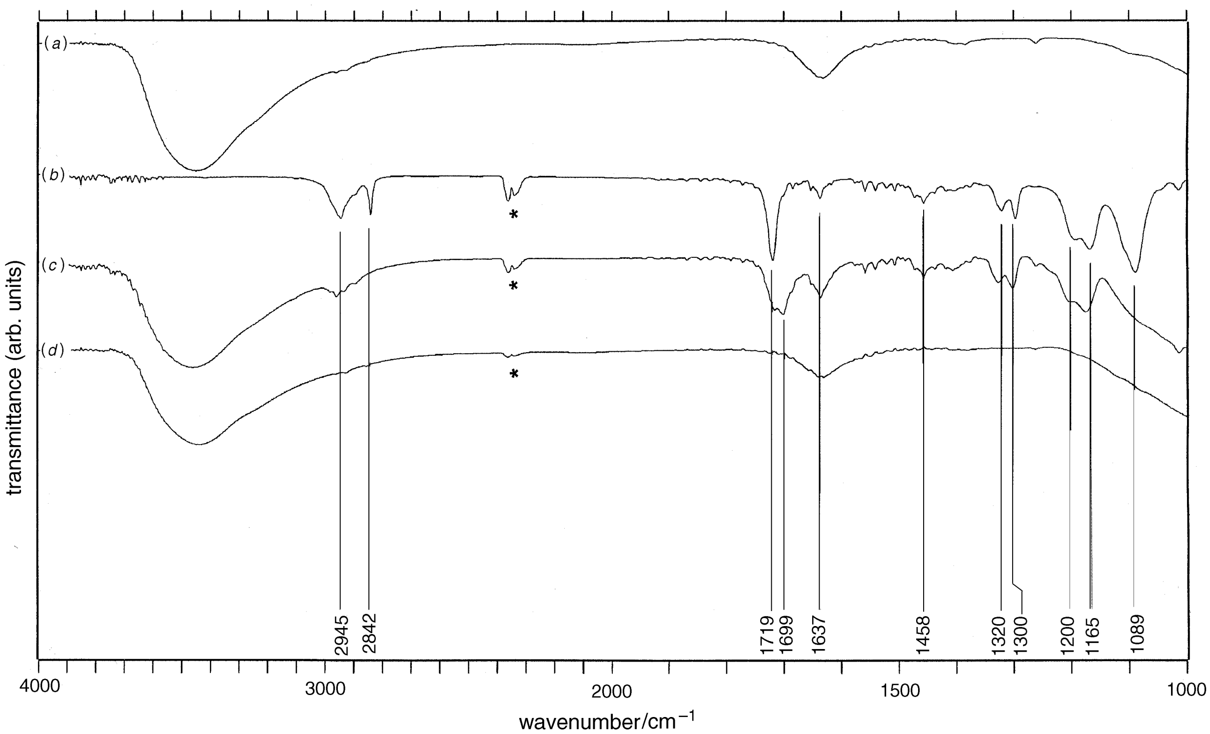
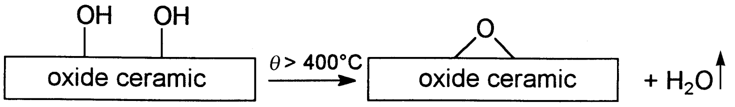


Fig. 1 IR spectra of: (*a*) pristine C alumina, (*b*) γ-MPS reagent, (*c*) γ-MPS-modified C alumina, (*d*) γ-MPS-modified C alumina following pyrolysis at 650 °C (*, atmospheric CO_2)

Table 2 Hydroxy groups and grafted γ-MPS surface densities for Al_2O_3, ZrO_2 and TiO_2 powders

		hydroxy groups surface densities		γ-MPS surface densities	
ceramic powder	commercial name or reference	measured by TG/ μmol m^{-2}	measured by chemical titration/ μmol m^{-2}	added amount/ μmol m^{-2}	grafted amount measured by TG/ μmol m^{-2}
Al_2O_3	CR30	10.4	12.6	12.3	6.1
				24.5	7.3
	CR15	12.4	—	15.8	6.6
	GE30	9.6	—	24.8	7.5
	CRT30	32.8	—	9.4	4.8
				12.3	5.3
	D65CR	12.1	—	12.2	4.6
	C	7.8	12.1	31.6	6.2
ZrO_2	G10	16	—	35	2.8
				140	3.0
	VP	17.1	24.9	40	5.7
TiO_2	23,203-3	23.0	—	42	5.8



Scheme 4

from those within micropores. The latter will not react with γ-MPS and are therefore of little interest in the present investigation. TEA chemical titration may give overestimated OH surface densities owing to the presence of physisorbed water which is not completely removed during the initial drying process at 130 °C.

To verify this assumption, chemical titration experiments were performed on α-alumina (CR30) powder, after a heat treatment from ambient to 400 °C under an anhydrous argon atmosphere corresponding to the experimental conditions used for TG measurements. A value of 1.9 μmol m^{-2} was obtained which is definitely lower than the previously mentioned values of 10–12 μmol m^{-2} for Al_2O_3. The value of 1.9 μmol m^{-2} is more representative of the actual density of hydroxy groups accessible to chemical reagents.

Therefore, all densities given in Table 2 are more likely overestimates of the true values of surface reactive hydroxy groups and are not representative of OH groups uniquely available for the reaction. Thus, the amount of γ-MPS (based on such determinations) used in the following section represents more likely an excess.

Results reported for alumina in Table 2 also show that the hydroxy surface density depends upon the crystal structure. Better correlation would have required a more detailed investigation which was not our main purpose.

Control of γ-MPS grafting

Prior to the grafting of γ-MPS, pristine powders were partially dried at 130 °C in order to safeguard one or two physisorbed water layers. Thus, the hydrolysis of silane methoxy groups, generating Si—OH groups, occurs near the powder surface just before condensation with single M—OH groups. Anhydrous toluene was used in order to prevent γ-MPS homopolycondensation and promote local hydrolysis followed by condensation.

As indicated by the significant mass loss in the TG analysis of modified powders (Fig. 2), the grafting of γ-MPS successfully occurred for all of the ceramic powders treated. Effective silanisation is also evident from the FTIR data of modified powders. Fig. 1 displays FTIR spectra obtained for both pristine and modified C alumina powders. In the spectrum of modified powders [Fig. 1(*c*)], strong α,β-unsaturated ester bands at 1699, 1302 and 1200 cm^{-1} and methyl bands at *ca.* 2900 cm^{-1} are observed. In particular, a stretching vibration at 1699 cm^{-1} with a shoulder at 1716 cm^{-1} can be seen. As already observed,[7] the main band at 1699 cm^{-1} attests to the formation of hydrogen bonding between most of the carbonyl groups and unreacted Al—OH or generated Si—OH groups. The shoulder at 1716 cm^{-1}, comparable with the similar stretching band at 1719 cm^{-1} in pure γ-MPS [Fig. 1(*b*)], is relative to the 'free' counterparts of C=O groups.

Quantification of γ-MPS grafting

The grafting reaction may involve one, two or three vicinal (eventually geminal) hydroxy groups present at the surface of the oxide particles for every grafted γ-MPS molecule, as reported by De Haan *et al.* for the grafting on silica gel.[7] They showed that monodentate and bidentate structures are mainly formed upon reaction of γ-MPS in dry toluene. For this reason, grafting yields are impossible to evaluate and we considered silane surface density rather than grafting yields based upon hydroxy density data.

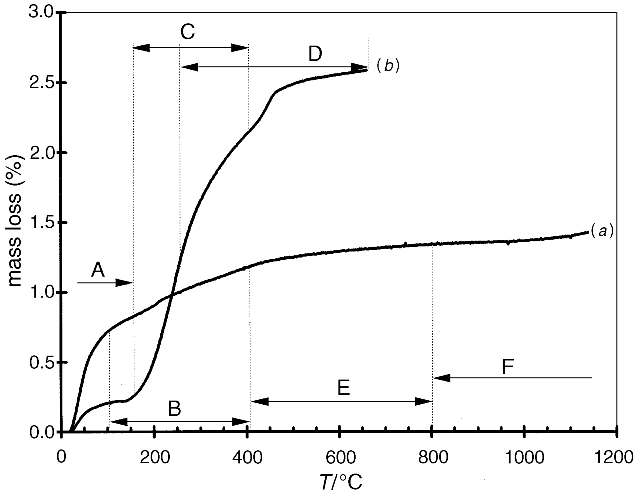


Fig. 2 Thermogravimetry of : (*a*) pristine CR 30 alumina, (*b*) γ-MPS-modified CR 30 alumina. A, gas desorption; B, physisorbed water desorption; C, methacrylic acid loss; D, allylic radical loss; E, adjacent hydroxy group desorption; F, isolated hydroxy group diffusion and desorption.

Quantification of the amount of grafted γ-MPS was calculated from TG mass losses considering that thermal degradation proceeds as follows: initially there is a cleavage of C—O bonds (methacrylic acid loss by McLafferty rearrangement) followed by the cleavage of Si—C bonds (allylic radical loss) as depicted in Scheme 5.

Such a mechanism is based upon pyrolysis/mass spectrometry results for modified CR30 Al_2O_3 powders. The analysis showed the loss of a methacrylic acid unit ($m/z = 86$) between 150 and 400 °C and the loss of an allylic radical ($m/z = 41$) between 250 and 650 °C. No loss of Si-containing fragments was observed during mass spectrometry experiments. This suggests that strong covalent Al—O—Si bonds are established between the organic silane and alumina surface.

γ-MPS quantification by TG was confirmed by elemental analysis for CR 30 alumina samples, whose initial purity was >99.9% (Table 3). Such experiments yielded a value of 5.8 µmol m^{-2} grafted γ-MPS, which is close to the value of 6.1 µmol m^{-2} obtained from TG experiments. The observed molar ratio $C/Si = 7.5$ shows that practically all carbon atoms present on the surface belong to the γ-methacryloylpropyl group. This suggests that 0.5 methoxy groups for every γ-MPS molecule was not hydrolysed during the grafting reaction. We also observed that more than 80% of the carbon content is removed after pyrolysis at 650 °C, thus confirming the degradation mechanism depicted in the previous scheme.

The amount of grafted γ-MPS generally remains constant or levels off independently of the excess of γ-MPS used during processing as seen in Table 2.

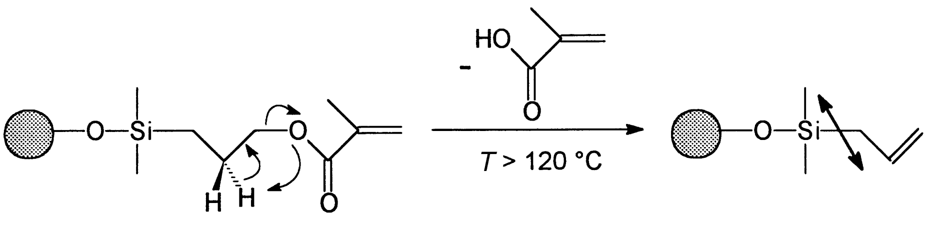
If a molecular area of 0.60 nm^2 is assumed for γ-MPS,[7] a silane single coating would result in a maximal surface density of 2.8 µmol m^{-2}. As a much higher density was measured, we can envisage either the formation of γ-MPS multicoatings or the aggregation of γ-MPS on the surface.

Characterisation of grafted γ-MPS

Evidence of the hydrophobic characteristics of γ-MPS is displayed in the TG plot in Fig. 2(*b*). The mass loss for the modified curve is significant only above 150 °C while in the pristine powders significant mass loss occurs below 150 °C (due to physisorbed water loss).

Information on the bond formation was obtained from ^{29}Si CP MAS NMR spectroscopy data for the case of modified Degussa C Al_2O_3 powder (Fig. 3). ^{29}Si magnetisation occurs *via* proton magnetisation and therefore depends upon the proton environment. We considered that all ^{29}Si atoms are approximately equivalent since they are originating from γ-MPS for which proton polarisation mainly occurs through Si—C—H bonds in the γ-methacryloylpropyl group.

In the case of γ-MPS grafted onto porous silica surfaces,



Scheme 5

Table 3 Elemental analysis results for Si and C in γ-MPS grafted CR 30 alumina and subsequent calculated surface densities

pyrolysis treatment	Si (mass%)	C (mass%)	silicon surface density/ μmol m^{-2}	carbon surface density/ μmol m^{-2}	C/Si molar ratio
none	0.42	1.34	5.8	43.3	7.5
25–650 °C at 4 ° min^{-1} and 2 h at 650 °C	0.40	<0.30	5.5	9.7	1.8

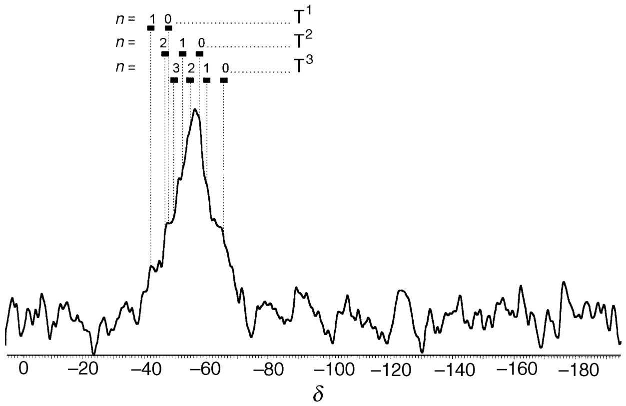
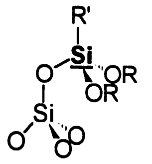
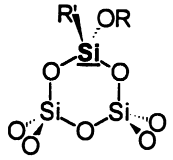


Fig. 3 ^{29}Si CP MAS NMR spectrum of γ-MPS-modified C alumina. T^1: SiR′(OR)$_2$(OSi≡)$_{1-n}$(OAl=)$_n$; T^2: SiR′(OR)(OSi≡)$_{2-n}$(OAl=)$_n$; T^3: SiR′(OSi≡)$_{3-n}$(OAl=)$_n$, where R=H or CH$_3$, R′=(CH$_2$)$_3$OCOC(CH$_3$)=CH$_2$.

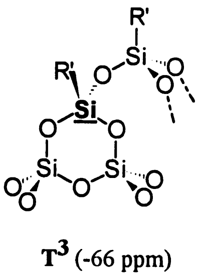
various ^{29}Si chemical shifts have been previously observed corresponding to the following structures:[7,8]



T^1 (-48 ppm)



T^2 (-58 ppm)



T^3 (-66 ppm)

where R=H or methyl groups and R′=(CH$_2$)$_3$OCOC(CH$_3$)=CH$_2$. If Al atoms are substituted for vicinal Si atoms, such ^{29}Si signals would be shifted 5–6 ppm per Al atom toward the lower field, as demonstrated in previous studies on phyllosilicates.[29]

Chemical shifts have been calculated for such T^1, T^2 and T^3 ^{29}Si environments and reported on the NMR spectrum of Fig. 3. The major absorption signal at δ *ca.* −56 is most likely a combination of several poorly resolved peaks. The left portion of this peak (between δ −40 and −56) is assigned to the bonding of γ-MPS onto Al$_2$O$_3$ surface with the establishment of one or two Si—O—Al bonds. The right portion of the signal (between δ −56 and −66) is assigned to the formation of multibridged grafted Si atoms, consisting of essentially Si—O—Si bonds assembled in multilayers or aggregates. The formation of 'polysiloxane' multilayer films has already been proposed by other authors.[5]

These results confirm that covalent Al—O—Si bonds are established. Such a demonstration was not possible in previous studies dealing with the grafting of γ-MPS onto porous silica (despite the better resolution of the ^{29}Si NMR spectra) because the ^{29}Si signals for silane molecules grafted onto the surface of SiO$_2$ could not be distinguished from those arising from the grafting onto a γ-MPS additional layer.[7,8]

The M—O—Si chemical bonding is the primary force holding the molecule at the surface. Hydrogen bonding (*via* carbonyl group) as indicated by FTIR spectroscopy data plays only a minor role. The number of 'polysiloxane' additional layers is probably limited by the steric hindrance around γ-methacryloylpropyl groups. This explains why regardless of the excess γ-MPS added the amount of the grafted material is constant (see Table 2).

Additional experiments conducted on γ-MPS modified VP ZrO$_2$ powders, using primarily X-ray photoelectron spectroscopy (XPS), are detailed in another paper; they confirm the covalent bonding of γ-MPS onto the powder surface and the presence of more or less thick domains of silane surface resulting in interlinkage between γ-MPS molecules.[30]

Conclusion

Grafting of 3-(trimethoxysilyl)propyl methacrylate onto the surface of Al$_2$O$_3$, ZrO$_2$ and TiO$_2$ powders is shown to occur. A large excess of the silane reagent is not necessary as the grafted amounts appear to be limited by steric factors and not silane availability. Surface densities of grafted γ-MPS are generally between 4 and 7 μmol m^{-2} with even higher values for ZrO$_2$. ^{29}Si CP MAS NMR spectroscopy suggests that powder surfaces consist of multilayers of silane and establishes the existence of M—O—Si bonds. Attempts are currently underway to study the copolymerisation of these hybrid 'macromonomers' with (meth)acrylic monomers and to characterise the mechanical properties of such materials.

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