

Novel Electron Beam-Modified Surface-Coated Silica Fillers: Physical and Chemical Characteristics

SUDIP RAY, ANIL K. BHOWMICK

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

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ABSTRACT: A novel process of surface modification of silica fillers has been performed by coating with an acrylate monomer, trimethylol propane triacrylate (TMPTA) and with a silane coupling agent, triethoxy vinyl silane (TEVS), followed by electron beam irradiation of these coated fillers. The surface-modified fillers have been characterized by Fourier-Transform Infrared Analysis (FTIR), Electron Spectroscopy for Chemical Analysis (ESCA), Contact angle measurements by dynamic wicking method, Scanning Electron Microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), Transmission Electron Microscopy (TEM), Fractal studies, Thermogravimetric analysis (TGA), and X-ray diffraction (XRD) studies. Presence of the acrylate and the silane coupling agent on the modified fillers is confirmed from the above studies. The contact angle measurements suggest a significant improvement in hydrophobicity of the treated fillers, which is supported by water flotation test. After irradiation and acrylate treatment an increase in filler aggregation is observed, which is not as significant in the case of silanized silica filler. However, XRD studies demonstrate that the entire modification process does not alter the bulk properties of the fillers. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2255–2268, 2002

Key words: silicas; electron beam irradiation

INTRODUCTION

Conventional particulate polymer composites, often called filled polymers, are of significant commercial importance in industrial applications. Fillers have important roles in modifying the properties of various polymers. The effect of fillers on properties of a composite depends on their concentration and their particle size and shape, as well as on the interaction with the matrix. The theory of filler reinforcement of polymers predicts

the formation of a boundary layer of a matrix material on the surface of the filler.¹

Reinforcement of rubber by precipitated silica is adversely affected due to lack of strong polymer–filler bonding. To improve polymer–filler interaction, the use of surface coatings on the silica fillers has been known for many years.^{2–4} Recently, van Ooij et al.⁵ have reported plasma modification of silica, which changes the surface chemistry of the filler. The literature survey reveals that the surface coatings of the fillers can be done by either some coupling agents or coating the filler surface with some monomer followed by polymerization of the coated monomer. During the past 30 years or so, coupling agents for the surface treatment have been developed. These have, in general, two functions: (1) they react with filler or get adsorbed on it, and (2) they also have an affinity with the polymer.⁶

Correspondence to: A. K. Bhowmick (anilkb@rtc.iitkgp.ernet.in).

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An example of the use of silica with the coupling agents is given by Boonstra,⁷ which shows an improvement in tire tread wear brought about by its use.

In conventional technology, the reaction between silica and silane coupling agent takes place in the rubber–filler batch during compounding. This *in situ* modification requires a number of precautions regarding the mixing sequence and the mixing temperature, as well as a careful adjustment of mixing conditions for every silane containing compound. But in fillers pretreated with silane, the silane has already undergone a chemical reaction with the filler, which renders the above precautions superfluous. However, it has been found that no reaction takes place between filler and silane when the treatment is performed at room temperature, but such interactions will take place at elevated temperatures.^{8,9} So an attempt has been made to improve the interaction of silica and silane by irradiating the silane-coated filler via electron beam technique at room temperature instead of thermal treatment.

A great deal of effort has been made in the past to treat the surfaces of reinforcing silica fillers with different organic compounds to make the surface of the silica hydrophobic.¹⁰ Evidences like, surface coating of silica fillers followed by thermal treatment or plasma treated fillers are well known, but the electron beam modification of precoated silica fillers is a novel process. There is virtually no literature reference on this topic or no commercial process in which the surface of the fine powder particles is modified by this method. Although the effects of such treatments are not completely understood in terms of detailed mechanisms, such processes are generally believed to clean the surface effectively. Further, new chemical functionalities can be introduced, which may improve the interactions between the treated surface and other materials, resulting in improved wettability and adhesion.

The use of polyfunctional monomers, such as multifunctional acrylates and allylic reactive molecules, in blends with the base polymer, is very effective in achieving the crosslinking at a reduced radical dose level to meet the optimum properties without much deterioration of the base polymer.^{11,12} Bhowmick et al.¹³ carried out surface modification of ethylene propylene diene monomer (EPDM) rubber in the presence of an acrylate monomer, trimethylol propane triacrylate (TMPTA). The influence of electron beam ra-

diation on polymers was reported by several authors.^{14–17}

The effect of filler on the physico-mechanical properties of both natural and synthetic rubbers under the influence of γ -radiation is reported in the literature.¹⁸ Although there is extensive work on grafting and crosslinking of pure rubber, only a preliminary study has been carried out so far regarding the electron beam crosslinking of rubbers in the presence of fillers.¹⁹ Surface coating of silica fillers by different organic monomers has been studied but the use of an acrylate monomer, namely trimethylolpropane triacrylate, for the filler surface modification is entirely a new and novel approach.

In this present article, silica fillers are coated with an organosilane, TEVS (triethoxy vinyl silane) followed by irradiation of the coated filler via electron beam technique. In another part, silica fillers are coated with an acrylate monomer, TMPTA, and then polymerized by electron beam treatment. Characterization of the above surface-modified powders has been carried out by infrared (IR) spectroscopy, electron spectroscopy for chemical analysis (ESCA), contact angle measurements by dynamic wicking method, scanning electron microscopy (SEM), coupled with energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and X-ray analysis.

EXPERIMENTAL

Materials

The silica filler, VULKASIL S, specific surface area = 175 m²/g, determined by nitrogen adsorption method according to ISO 5794/1, Annex-D; pH = 6.4 and volatile matter = 5.8% was provided by Bayer A.G., Germany. The acrylate monomer, TMPTA (flash point > 100°C, boiling point > 100°C, specific gravity 1110 kg/m³) and the silane coupling agent, TEVS (b.p. 160–161°C) were supplied by UCB Chemicals, Belgium and Aldrich Chemical Company Inc., Germany, respectively. KBr and Acetone used were of chemically pure grade and obtained from E. Merck Ltd., Mumbai, India. For contact angle measurements, doubly distilled water and for TEM study spectroscopic grade methanol were used.

Preparation of Samples

Modification by Organosilane

The silica fillers were mixed with 3 wt % solution of TEVS in acetone in a polyethylene beaker un-

Table I Specification of the Electron Beam Accelerator

Energy range	0.5–2.0 MeV
Beam power over the whole energy range	20 kW
Beam energy spread	± 10%
Average current (E-1.5 MeV)	15 mA
Adjusting limits for current	0–30 mA
Accelerating voltage frequency	100–120 MHz
Duration	400–700 μ s
Repetition rate	2–50 Hz
Pulse rate:	
Maximum	900 mA
Minimum	400 mA
Power supply (PS) voltage	3 × 380/200 V
PS voltage frequency	50 Hz
Consumption of power (total)	150 kW

der constant stirring with a Teflon rod followed by removal of solvent via evaporation. The dry fillers were then ground into fine powders.

Modification by Acrylate Monomer

Similar to the above, the powder fillers were mixed with 3 wt % solution of TMPTA in acetone in a glass beaker under constant stirring with a glass rod and then the solvent was removed by evaporation technique, followed by grinding of dry fillers to obtain the surface coated fine powders.

Irradiation of the Samples

The treated fillers were irradiated in air in an electron beam accelerator (Model ILU-6) at Bhabha Atomic Research Center, Mumbai, India. All the samples were irradiated at a dose of 100 kGray. Specifications of the electron beam accelerator are reported in Table I. To study the effect of silane coupling agent and acrylate monomer on the fillers, silica powders were also electron beam irradiated without performing the silane or acrylate modification. The formulations of the various surface treated fillers are presented in Table II.

CHARACTERIZATION AND PROPERTIES OF MODIFIED FILLERS

FTIR Study

The surface chemistry of the powdered fillers was characterized by Fourier-Transform Infrared

Spectrophotometer (FTIR), NICOLET, NEXUS™ with DRIFTS (Diffuse Reflectance) attachment operated in the absorption mode, in the wave number range of 4000–400 cm^{-1} by mixing with KBr powder. The concentration of the samples in the KBr was held constant to 0.7% (w/w) after a series of trial runs. The spectra were obtained using a resolution of 4 cm^{-1} and averaged over 100 scans. A background spectrum obtained with uncoated KBr powders was subtracted from the acquired spectra in all cases. A standard software (Omnic ESP, version 5.1) was used for data acquisition and analysis.

ESCA/XPS Study

Electron Spectroscopy for Chemical Analysis (ESCA) of silica fillers was taken using a VG Scientific ESCA lab MK II Spectrophotometer employing an exciting radiation of 1253.6 eV. The samples were in the form of thin pellet and mounted with double sided adhesive tape onto the probe tip. The spectra reported here were recorded with the MgK_{α} anode operated at a voltage of 15 kV and a current of 20 mA. The survey spectra were obtained with pass energy of 50 eV and the narrow scans were acquired at 0.5 and 0.1 eV stepwise. The working pressure in the instrument was 1×10^{-9} Torr, and the photoelectron take off angle was 180° with respect to the pellet surface. C(1s), O(1s), and Si(2p3/2) spectra were deconvoluted with the help of a standard Gaussian programme using Origin 5.0 software. The atomic concentration C_i of an element i can be calculated by using the peak areas in the following equation:²⁰

$$C_i = \frac{A_i/S_i}{\sum_j A_j/S_j} \quad (1)$$

Table II Formulation of the Various Surface Treated Silica Fillers

Sample Designation	VULKASIL S (g)	TMPTA (g)	TEVS (g)	Radiation Dose (kGray)
V	100	—	—	—
V10	100	—	—	100
VM103	100	3	—	100
VV103	100	—	3	100

where, m is the number of elements in the sample and A_i and S_i are the peak area and the sensitivity factor (or photoionization cross-section values) for element i , respectively.

Contact Angle Measurement

A dynamic wicking meter was used to measure the contact angle of the powders. The powder fillers of 0.07 g was tapped 200 times and filled in the graduated capillary tube (2 mm inner diameter, 50 mm long), of which one end was sealed with nylon mesh (pore size 20 μm). The tube was placed vertically, and the nylon mesh-sealed end of the tube was contacted with a liquid in the beaker. As the surface of the nylon mesh touched the liquid surface, the liquid penetrated up into the column of the powders by the capillary action. The principle of the dynamic wicking meter as well as the specific experimental procedures has been described in details by Inagaki et al.²¹ In the determination of the dynamic wicking property, the weight of the penetrating liquid into the column was measured using an electric balance as a function of time after the liquid contact.

The contact angle of liquid on the surface of the powders was calculated from the following equations:

$$\cos\theta = S_p \times \frac{\rho_p}{\rho_L^2} \times \frac{1 - \epsilon}{\epsilon^3} \times \frac{2\eta}{\gamma_L} \times \frac{1}{t} \times \frac{W^2}{S} \quad (2)$$

and

$$\epsilon = 1 - \frac{W_p}{hS\rho_p} \quad (3)$$

where θ is the contact angle of the liquid; S_p is the surface area of the powders per unit weight; ρ_p is the density of the powders; ρ_L is the density of the liquid; ϵ is the porosity of the powder column; η is the viscosity of the liquid; γ_L is the surface energy of the liquid; t is the time after the liquid contact; W is the weight of the penetrating liquid; and S is the cross-section of the cylindrical tube, respectively.

The porosity of the powder column, ϵ , was estimated from eq. (3), where W_p is the weight of the powders tapped in the column, h is the height of the powder in the column, S is the cross-section of the cylindrical column, and ρ_p is the density of the powders, respectively.

SEM/EDX Study

Scanning electron microscopy (SEM), coupled with energy dispersive X-ray analysis (EDX), was performed on both untreated and treated fillers in a JEOL-JSM 5800, scanning microscope operating at an accelerating voltage of 25 kV and equipped with Linux X-ray analyzer. The powders were fixed on the sample holder by a double-sided adhesive tape, then gold coated. Secondary electron images were recorded using 5-keV acceleration voltage. Regional average EDX spectroscopy was obtained at the same time.

TEM Study

Transmission electron micrographs (TEM) were obtained with an Hitachi H-600 model using an acceleration voltage of 100 kV and a resolution of 4.5 Å. For the TEM study, a 0.1 wt % of the powder samples in methanol was made and sonicated for 1 h.

Fractal Study

TEM measurements were used to evaluate the "line fractal" characteristic of the aggregates. The principle of the method used is the so-called "perimeter-area" relationship.²² This method is based on the fact that for a standard Euclidean object the ratio, Λ , of the perimeter (P) of the object over the square root of its area (A) is independent of the characteristic size of the object. Mandelbrot proposed that by using the ratio of the perimeter to the power $1/D$ to the square root of the area, the fractal dimension D of the boundary can be calculated as,

$$\Lambda_D = P^{1/D}/\sqrt{A} \quad (4)$$

The logarithmic form of that expression,

$$\log \Lambda_D = (1/D)\log P - (1/2)\log A \quad (5)$$

$$\log P = D/2 \log A + D \log \Lambda_D \quad (6)$$

indicates that by plotting $\log P$ vs. $\log A$ a straight line should be obtained, from which slope ($D/2$) and thus the fractal dimension, D can be calculated.

The TEM photographs of the silica fillers were digitized, and the image analysis was performed using a standard image analysis software.

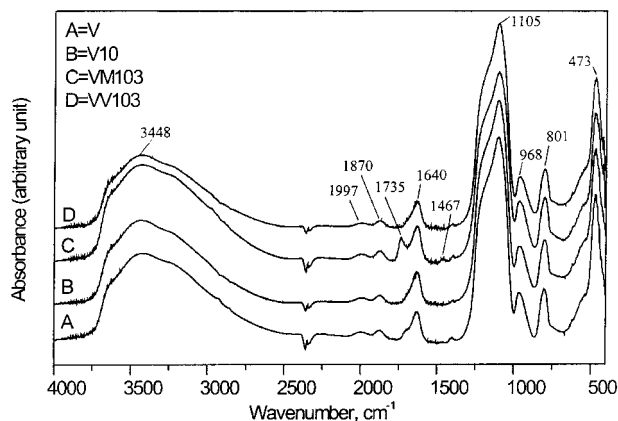


Figure 1 Plot of the FTIR spectra of silica fillers.

Thermo Gravimetric Analysis (TGA)

Thermogravimetric analysis was performed on a thermal analyser (DT-40) SHIMADZU from ambient temperature to 1000°C at a programmed heating rate of 20°C/min in an air atmosphere.

X-ray Study

X-ray diffraction profiles were recorded in a Philips X-Ray Diffractometer (Type PW 1710), Holland using CoK_α radiation in the angular range from 10–50° (2θ) at an operating voltage of 40 kV and a current of 20 mA with a wavelength of 1.7902 Å. For data acquisition and analysis, Origin 5.0 software was used.

RESULTS AND DISCUSSION

FTIR Study

Vibrational spectroscopy has been used extensively for the understanding of the surface chemistry of many materials including silica.^{23,24} The full FTIR spectra of both untreated and treated silica fillers in the region 4000–400 cm^{-1} are presented in Figure 1. The peak positions and their assignments are given in Table III. They agree well with the values given in the literature.²⁵ The region above 3000 cm^{-1} wave number contains information about the silanols, which, however, is overlapped with those of the large water band. The weak broad features between 2000–1800 cm^{-1} are due to overtones and combination modes of bulk SiO_2 vibrations.²⁶ The peaks in the region 1640–1620 cm^{-1} are due to O—H stretching vibrations of the adsorbed water. Fig-

Table III Assignments of Bands in IR Spectra of Silica Fillers

Frequency (cm^{-1})	Assignment
3404–3448	O—H stretching of Si—OH group, and water of crystallization
2000–1800	Overtones and combination modes of bulk SiO_2 vibration
1735 ^a	C=O stretching, saturated aliphatic esters
1640–1620	O—H stretching vibration
1467 ^a	—CH ₂ —scissoring; CH ₃ asymmetric (bending) deformation
1102–1105	Si—O—Si stretching
963–968	Symmetric Si—O—Si stretching
801	Symmetric Si—O—Si stretching
468–473	Symmetric Si—O—Si stretching

^a Only for VM103.

ure 1 shows no significant changes after irradiating the silica filler. However, on modification with TMPTA, new peaks at 1735 cm^{-1} , due to C=O stretching vibration for saturated aliphatic esters and at 1467 cm^{-1} due to —CH₂— scissoring and CH₃ asymmetric bending deformation are observed, which confirm the presence of acrylate in

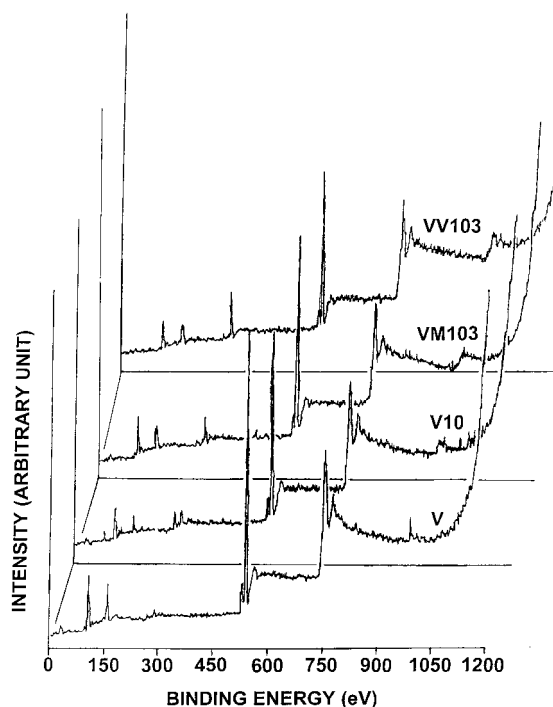


Figure 2 XPS wide scan spectra of silica fillers.

Table IV Results of XPS Analysis for Silica Fillers

Sample	Element	Peak Position (eV)	Peak Area		Atomic ^a Conc	O/C (%)	O/Si (%)	Si/C (%)
			Total (eV/ms)	Relative Area (%)				
V	Si(2p _{3/2})	103.3	14.21	96.5	48.1	9.0	1.0	9.3
		105.8		3.5				
	O(1s)	532.6	68.43	92.0				
		534.4		8.0				
		284.5		2.65				
V10	Si(2p _{3/2})	103.2	5.58	99.9	35.8	3.6	1.4	2.6
		105.1		0.1				
	O(1s)	532.1	38.99	93.4				
		534.0		6.6				
		284.5		3.77				
VM103	Si(2p _{3/2})	103.7	8.07	99.9	37.7	2.0	1.1	1.8
		108.0		0.1				
	O(1s)	533.0	44.33	98.5				
		535.8		1.5				
		284.5		7.74				
VV103	Si(2p _{3/2})	103.4	5.08	93.0	34.3	1.3	1.1	1.2
		105.1		7.0				
	O(1s)	532.9	27.32	99.6				
		533.3		0.4				
		284.5		7.44				
		286.7		15.4				

^a Where photoionization cross-section for Si(2p_{3/2}) = 0.573, O(1s) = 2.85, C(1s) = 1.00.

VM103. The peak at 1102 cm⁻¹ is due to Si—O—Si stretching vibration. In the case of VV103, there is a shifting of the above peak by +3 cm⁻¹, which is probably due to the interaction of the silane coupling agent on the silica surface.

Photoelectron Spectroscopy (XPS) Study

The chemical compositions of the modified surfaces are difficult to analyze by internal reflection IR spectroscopy because of its deep penetration (~ 10 μm); consequently, chemical changes in a thin surface layer are missed. On the other hand, ESCA is a surface chemical analysis technique that typically examines the top 7 nm of a solid material and is considered as an excellent quantitative tool, elucidating the presence of all elements (excluding H and He) in concentration greater than 0.1 to 0.2 mol % in the near surface region of the material. Survey scans from 0–1200 eV are obtained to determine the elements

present at or near the surface of the powder fillers. XPS wide scan spectra of both untreated and treated silica fillers are shown in Figure 2. The individual peak positions, peak area, the atomic concentration, and the atomic ratios for silica fillers are summarized in Table IV. The binding energy scale of all spectra are corrected such that the peak maximum of the C(1s) spectrum was located at 284.5 eV.

Silicon Spectra

From the XPS wide scan spectra (Fig. 2), the peaks due to Si(2s), Si(2p_{1/2}), and Si(2p_{3/2}) for both untreated and treated silica fillers are identified at around 152, 100, and 103 eV respectively. Among these, the Si(2p_{3/2}) peak is found to be the most intense one, which on deconvolution gives rise to the presence of satellite peak at around 105 eV (Fig. 3). An increase in the relative area of this peak by 3.5% is observed (Table IV) in the

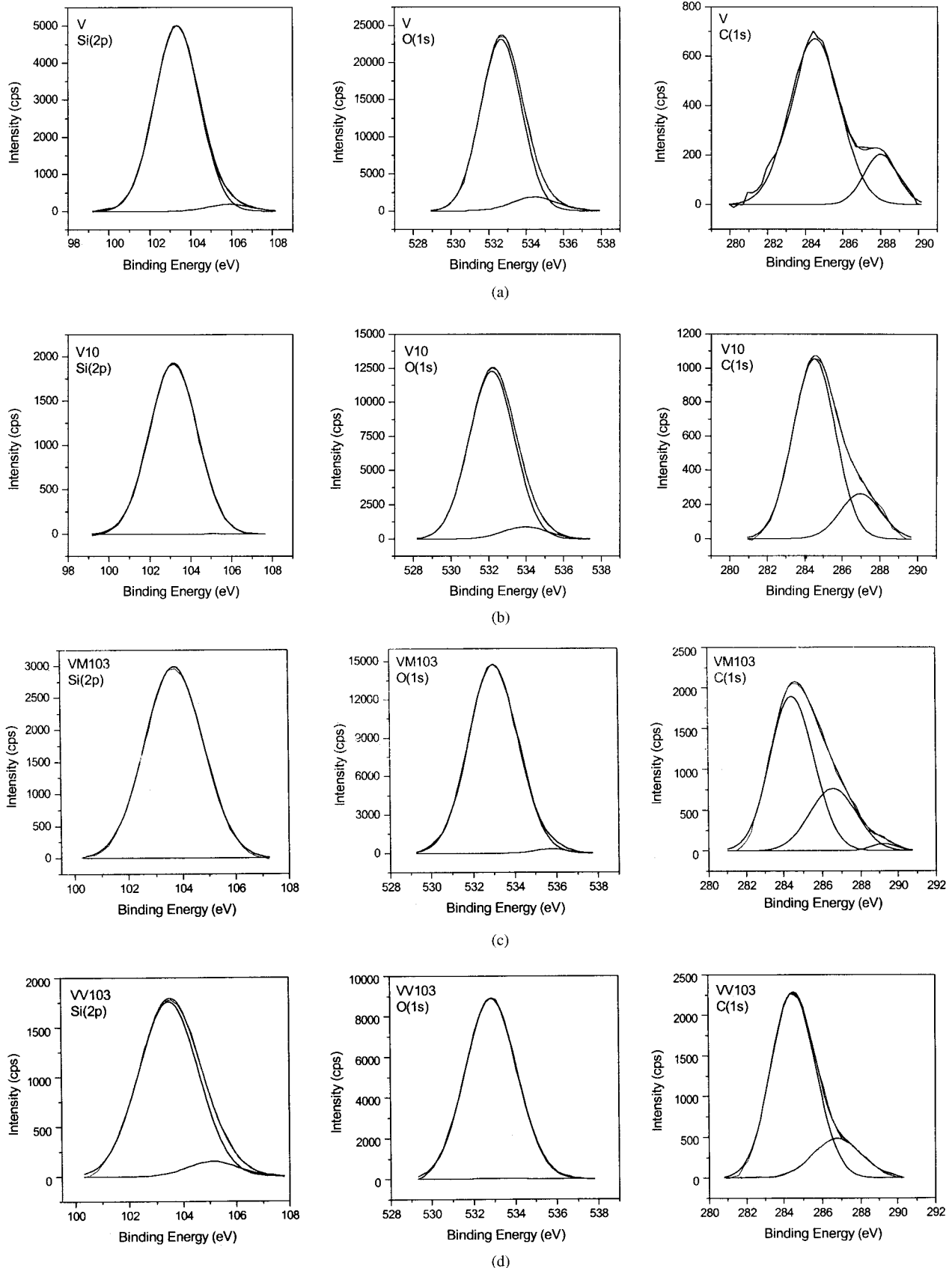


Figure 3 XPS deconvoluted spectra of (a) V, (b) V10, (c) VM103, (d) VV103.

case of VV103, compared to the control silica filler. The silane treatment of the silica filler is likely to form additional Si—O linkages on the filler surface, which in turn, probably increases the relative area of this satellite peak. However the above satellite peak almost disappears in the cases of V10 and VM103.

Oxygen Spectra

The peak binding energies due to O(1s) for the silica samples are observed in the 532–533 eV region as obtained from Figure 3 and Table IV. A very weak peak due to O(2s) is also observed at around 25 eV in the wide scan spectra. The O(1s) peak of the acrylate and silane-treated fillers are shifted to slightly higher binding energies (533.0 and 532.9 eV, respectively) than that of the silica control sample V (532.6 eV), which probably elucidates the surface modification of these fillers. A sharp rise in the oxygen atomic concentration and the O/Si ratio are observed in the case of V10 (Table IV), suggesting surface oxidation due to irradiation process. However, no such change in the O/Si ratio is there in the case of acrylate and silane-treated filler, which indicates that here the modification process dominates over the oxidation process.

Carbon Spectra

To quantify the results, the C(1s) peaks of all the samples have been curve fitted. The deconvoluted spectrum of the V and V10 for C(1s) in Figure 3 show the presence of satellite peak near the 287 to 288 eV region, indicative of carbon linked to oxygen groups, which are probably due to the presence of carbon impurity in these fillers. In

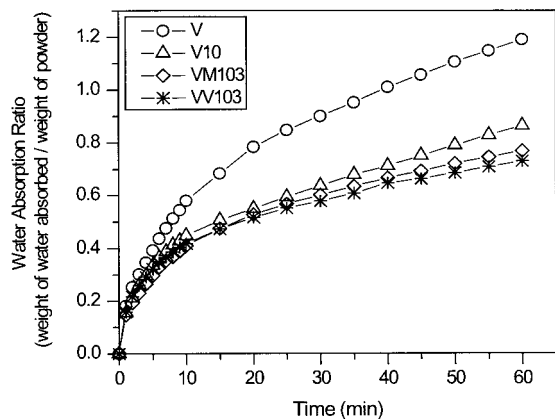


Figure 4 Plot of water absorption of silica fillers.

Table V Results of Contact Angle Measurements

Sample	Cos θ	Contact Angle, θ (Degree)
V	1.00	0°
V10	0.85	32°
VM103	0.61	52°
VV103	0.53	58°

this comparative study the control silica and the irradiated silica, i.e., V and V10 are also acetone treated, which may lead to the presence of carbon impurity in these fillers. According to Briggs and Seah,²⁷ oxygen attached to carbon atoms induces shifts to higher binding energies by 1.5 eV per the C—O bond. Thus, on modification of the silica surface with TMPTA (Fig. 3), the peaks in addition to 284.5 eV, i.e., at 286.6 eV (a shift of +2.1) and 289.3 eV (a shift of + 4.8) may be ascribed to the C—O and O—C=O groups, respectively, which clearly indicates the presence of acrylate on the surface of the filler in VM103. However, in the case of silanized silica, VV103 (Fig. 3), the carbon satellite peak at 286.7 eV is observed due to the presence of the C—O group in the organosilane compound. From Table IV it is found that the carbon content increases sharply when modified with TMPTA and TEVS. The decrease in O/C and Si/C ratios confirms the presence of the acrylate and the silane in VM103 and in VV103, respectively. Thus, the ESCA results are in good agreement with FTIR results.

Contact Angle Measurements

Deionized water adsorption curves of silica fillers before and after modification with the acrylate and the silane coupling agent are shown in Figure 4. Table V shows the water contact angle measured for the silica fillers before and after treatment. The silica fillers are hydrophilic in nature, and have a high specific surface area (175 m²/g). The objective of the surface modification was to increase the hydrophobicity of the silica powders, so that they would become more compatible with polymers such as rubbers. From Table V it is found that the water contact angle for the untreated silica is 0°. After surface modification with the acrylate and the silane coupling agent, the contact angle increases to 52 and 58°, respectively, indicating noticeable improvement in the

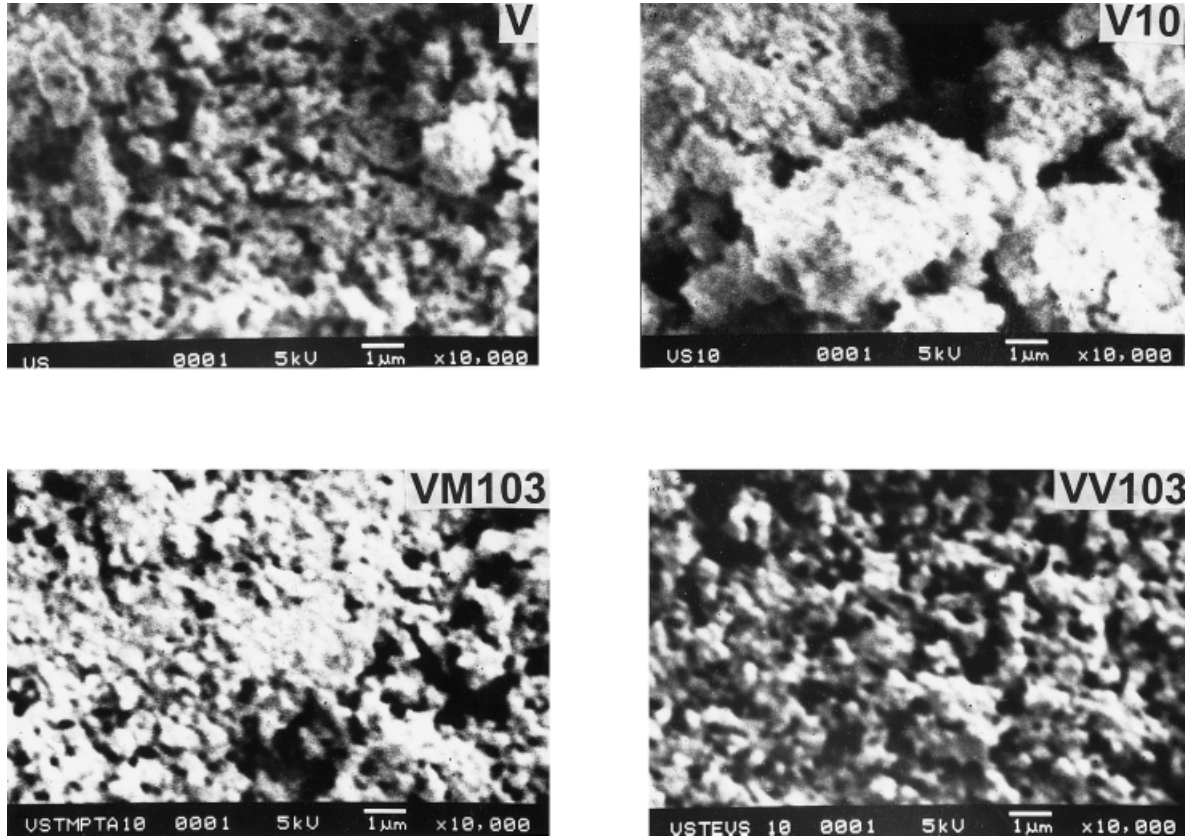


Figure 5 SEM photographs of silica fillers.

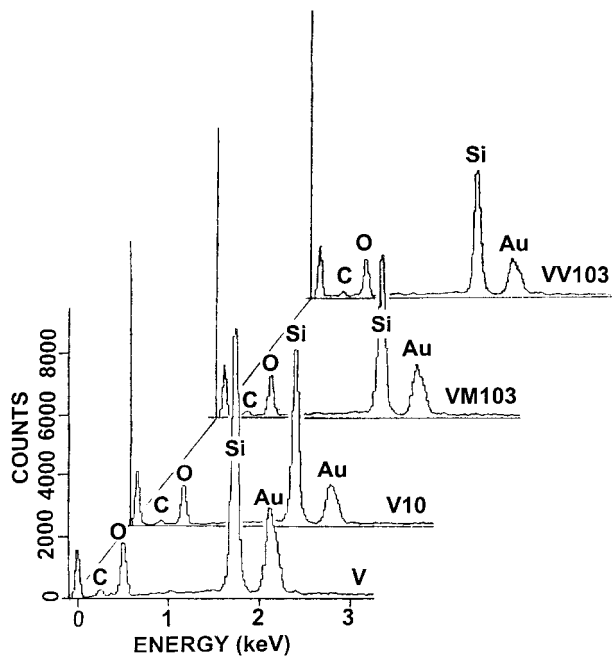


Figure 6 EDX spectra of silica fillers.

hydrophobicity of the silica filler. To check the hydrophobicity, the powder fillers are allowed to disperse in water. Before treatment, the particles are very hydrophilic in nature, and sink in water immediately. After treatment, a portion of the sample floats on water. That effect is also fairly stable, demonstrating that the hydrophobicity is permanent. From ESCA and EDX (discussed later) studies it is inferred that the carbon content on the filler surface increases after modification. The above improvement in the hydrophobicity may be due to the increase in hydrocarbon

Table VI Results of EDX Study for Silica Fillers

Sample	Atomic Concentration (%)			O/C (%)	O/Si (%)	Si/C (%)
	Carbon	Oxygen	Silicon			
V	2.4	16.2	81.4	6.7	0.2	33.9
V10	2.7	18.2	79.1	6.7	0.2	29.3
VM103	3.3	19.8	76.9	6.0	0.2	23.3
VV103	4.0	22.9	73.1	5.7	0.3	18.3

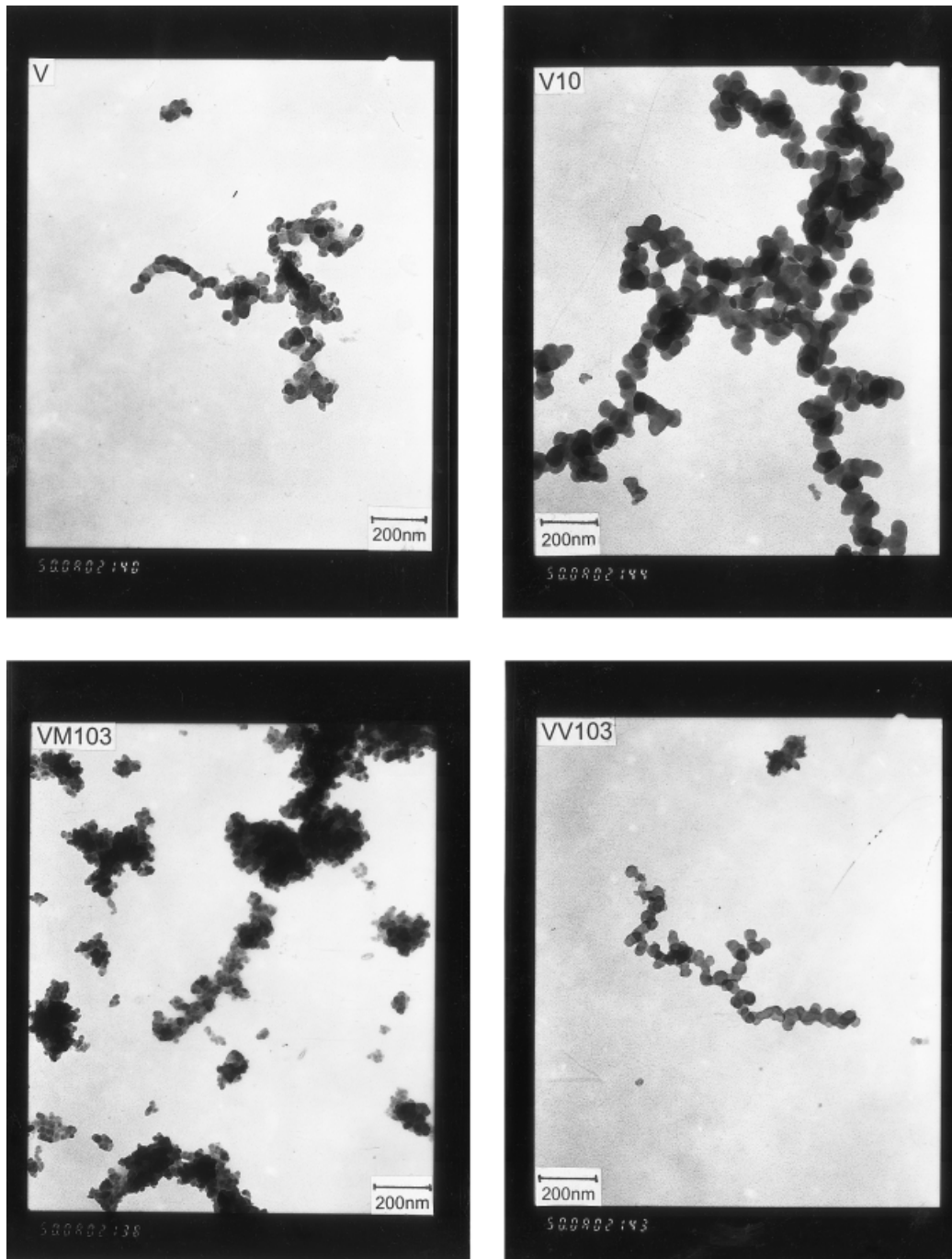


Figure 7 TEM photographs of silica fillers.

content on the filler surface after modification. Another interesting thing is that in these series of silica fillers the contact angle of VV103 is the maximum one, and the result is in good agreement with the ESCA and EDX analyses, where the carbon content is found to be maximum with the silanized silica.

Electron Microscopy

The SEM images of both untreated and treated silica fillers are shown in Figure 5. Difference between the SEM images of the irradiated and TMPTA-treated and untreated fillers are noticeable. Visually, it is observed that after modifica-

tion with TMPTA, packing density increases. The vinyl silane-treated surface has apparently similar morphology as that of the control one. The acrylate and silane films are so thin that even at higher magnification they are not detected.

Typical EDX spectra of each sample are shown in Figure 6. The atomic concentration of the individual elements and their ratios based on the respective peak heights are presented in Table VI. There is no significant change in the case of V10 compared to the pristine silica. However, an increase in the carbon concentration and decrease in O/C and Si/C ratios are observed when the silica filler is treated with the acrylate and silane coupling agent indicating their presence in VM103 and VV103, respectively. This also confirms that the film is actually there, although it is too thin to be observed clearly on the SEM images.

The TEM study further corroborates the findings from the SEM studies. It reveals the presence of very irregular aggregates of silica parti-

Table VII Results of Fractal Study for Silica Fillers

Sample	V	V10	VM103	VV103
Linear fractal dimension	1.15	1.19	1.32	1.18

cles, consisting of a branched chain-like structure. The representative transmission electron micrographs of these branched aggregates of the silica particles are presented in Figure 7. In the cases of V, V10, and VV103, the aggregates are again composed of firmly fused nodular subunits and the particle size is in the range of 20–40 nm. However, in VM103, instead of individual silicon chains highly irregular agglomeration is observed. The appearance of very light dark shade probably elucidates the presence of acrylate layer in VM103.

To study the morphology of the aggregates quantitatively the TEM photographs have been digitized and the individual aggregate size is measured for each sample. The data obtained consists of sets of perimeter and area values of the aggregates. From these data, linear fractal dimension, D , is calculated using eq. (6). Figure 8 shows the logarithmic plots of area–perimeter relationship of both untreated and treated silica filler aggregates. The fractal values of the silica samples are presented in Table VII. It is found that after irradiation the D value increases by 0.04 from 1.15 as obtained for V, which on treatment with acrylate further increases by 0.17. A slight increase in the D value by 0.03 is also observed in the case of VV103 compared to pristine silica. The increase in D value after irradiation is the indicative of particle aggregation, which is found to be the maximum one in the case of acrylate treated silica. The results are also in

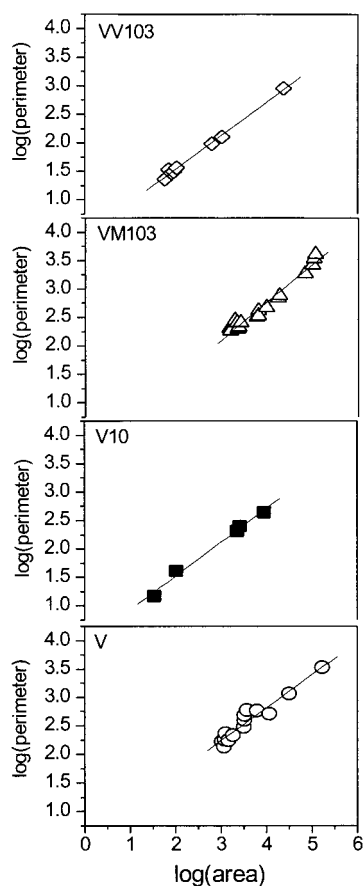


Figure 8 Logarithmic plots of area–perimeter relationship of the silica filler aggregates.

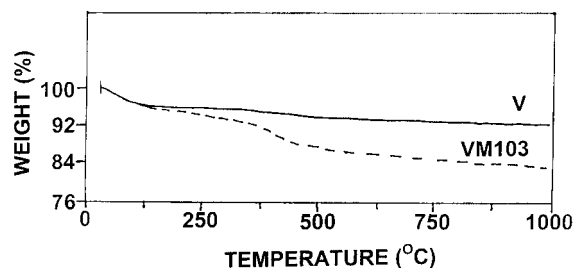


Figure 9 TGA thermograms of untreated silica and acrylate-treated silica fillers.

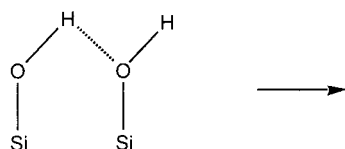
Table VIII Results of Thermogravimetric Analysis of Silica Fillers

Sample Designation	Initial Temperature (T_1), °C	Intermediate Temperature (T_F), °C	Weight Loss between ($T_1 - T_F$), (%)	Total Weight Loss (%)
V	25	150	4.0	8.0
	150	675	3.9	
	675	995	0.1	
VM103	25	200	5.5	16.2
	200	315	1.9	
	315	535	6.1	
	535	997	2.7	

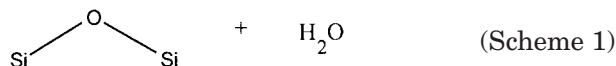
correspondence with the observations from SEM and TEM photographs.

Thermogravimetric Analysis

The thermal stability of the untreated silica and the acrylate treated silica is displayed in Figure 9. The results of the thermogravimetric analysis (TGA) as obtained from Table VIII show that



untreated silica loses $\sim 8\%$ of its weight in two stages while heating up to 675°C . Beyond that, there is no significant loss in weight. The initial weight loss of $\sim 4\%$ between 25°C to 150°C is due to the expulsion of the loosely bound water molecules. The hydrogen bonded hydroxyls start to condense to liberate water when silica is heated above 150°C ,²⁸ the reaction being,



In the case of acrylate-modified silica, the entire weight loss process can be divided into four stages. In the temperature range between 25 to 200°C , an initial weight loss of $\sim 5.5\%$ is observed, which is due to the adsorbed water molecules on the silica surface. In the second stage, a weight loss of $\sim 2\%$ is incurred in the temperature range between 200 – 315°C , which may be due to the onset of the condensation of hydrogen bonded silanol groups followed by removal of water and the decomposition of the acrylate monomer. Between 315 – 535°C a significant weight loss of $\sim 6\%$ is observed, which may be due to the removal of rest of the water via condensation of silanol groups and the degradation of the polyacrylates. In the last stage, between 535 – 998°C loss in weight of $\sim 2.7\%$ is probably due to the degradation of highly crosslinked polyacrylates. The above considerable loss in weight in the last two stages indicates that a good amount of polymerization reaction takes place on the acrylate modified silica surface. It is observed that the acrylate

treatment followed by electron beam irradiation causes additional $\sim 8.2\%$ weight loss in silica, which clearly implies the presence of acrylate on the treated filler.

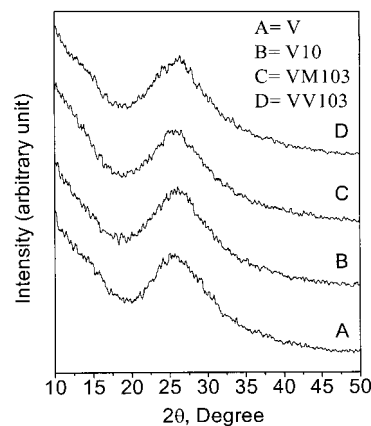


Figure 10 X-ray diffraction patterns of silica fillers using CoK_α radiation source.

Table IX Results of X-ray Diffraction for Silica Fillers

Parameter	Sample			
	V	V10	VM103	VV103
2θ (degree)	25.3	25.9	26.5	25.7
d_{111} (Å)	4.09	3.99	3.91	4.03
I (cps)	252	249	271	265

XRD Study

Figure 10 displays the XRD pattern of V, V10, VM103, and VV103, respectively, between 10 to 50° using a CoK_α radiation source. The precipitated silica used here is having β -cristobalite, face-centered cubic structure with $a_o = 7.13$ Å. It shows only one broad peak at the interplaner spacing value, $d = 4.087$ Å corresponding to the plane (111).²⁹ The 2θ , d , and I values of the silica fillers are presented in Table IX. The broad peak in silica is due to its amorphous nature. Little or no change is observed in the d -values, which indicates that intercalation process does not take place and the bulk properties of the fillers remain unaffected after the treatments. Due to the hydrophilic nature of silica, it contains some loosely bound water. A slight decrease in the d -values after irradiation may be due to the desorption of this water. Overall, it is observed from the X-ray studies that the electron beam irradiation and the treatment of acrylate and silane coupling agent cause little or no effect on the bulk properties of the silica fillers.

CONCLUSIONS

In the present study, silica powders are surface coated with an acrylate monomer, TMPTA, and then irradiated by electron beam technique. A vinyl silane coupling agent, TEVS, has also been tried. From the characterization studies of these surface-treated fillers the following points can be concluded:

1. From the FTIR spectra the presence of acrylate in VM103 is confirmed from the appearance of the new peaks at 1735 cm^{-1} and at 1467 cm^{-1} due to C=O stretching vibration for saturated aliphatic esters and due to $-\text{CH}_2-$ scissoring and CH_3 asym-

metric bending deformation. Although new peaks are not observed in the case of VV103 but the shifting of Si—O—Si peak indicates the silane modification in it.

2. The increase in carbon concentration and the decrease in O/C and Si/C ratios as revealed from the ESCA studies both for TMPTA and TEVS-modified silica fillers indicate their presence in the respective fillers. The increase in carbon content is also observed in the EDX studies, which supports the ESCA results and confirms the presence of TMPTA and TEVS in the modified fillers.
3. A noticeable increase in filler aggregation due to irradiation and the acrylate treatment is observed from the SEM and TEM photographs, which is also in agreement with the linear fractal values.
4. The presence of acrylate and its polymerization process due to electron beam treatment is evident from TGA studies.
5. A significant change in the surface properties of the silica fillers is observed from the contact angle measurements. An increase in contact angle in TMPTA and TEVS-modified silica indicates the improvement in hydrophobicity of these fillers.
6. However, the X-ray studies show that there is little or no change in the interplaner spacing values, which indicates that even after the entire surface modification process, the bulk properties of the powders remain unaffected.

Thus, from these characterization studies it can be stated that the surface coating with an acrylate monomer and vinyl silane coupling agent in silica fillers, followed by electron beam irradiation, causes significant changes in surface properties of the fillers without affecting their bulk properties.

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REFERENCES

1. Petrovic, Z. S.; Javni, I.; Waddon, A.; Banhegyi, G. *J Appl Polym Sci* 2000, 76, 133.

2. Wagner, M. P. *Rubber Chem Technol* 1976, 49, 703.
3. Wolf, S.; Görl, U.; Wang, M. J.; Wolf, W. *Eur Rubber J* 1994, 176, 16.
4. Iler, R. K. *The Chemistry of Silica*; John Wiley & Sons: New York, 1979, p. 570.
5. van Ooij, W. J.; Zhang, N.; Guo, S.; Luo, S. Paper presented at Functional Fillers and Fibers for Plastics '98, Beijing, P.R. China 1998, June 15–17.
6. Morrell, S. H. *Plastics Rubber Process Appl* 1981, 1, 179.
7. Boonstra, B. B. *Polymer* 1979, 20, 691.
8. Kornmann, X.; Berglund, L. A.; Sterte, Giannelis, E. P. *J. Polym Eng Sci* 1998, 38, 1351.
9. Görl, U.; Panenka, R. Paper presented at a meeting of the Deutsche Kautschuk-Gesellschaft (DKG) in Wurzburg, Germany, November 1992, and the International Rubber Conference in Beijing, P.R. China, October 1992.
10. Burns, G. T.; Deng, Q.; Hahn, J. R.; Krivak, T. G.; Okel, T. A.; Reese, C. C. U.S. Pat. 6,184,408 (February 6, 2001) (Assigned to Dow Corning Corporation, Midland, MI).
11. Dworjanyn, P. A.; Garnett, J. L.; Khan, M. A.; Maojun, X.; Reig, M. G.; Nho, C.Y. *Radiat Phys Chem* 1994, 42, 31.
12. McGinnise, V. D. *Crosslinking with Radiation*, Encyclopedia of Polymer Science and Technology; Wiley: New York, 1986, p. 421, vol. 4.
13. SenMajumder, P.; Bhowmick, A. K. *J Adhesion Sci Technol* 1997, 11, 1321.
14. Netsinghe, L. P.; Gilbert, M. *Polymer* 1988, 29, 1935.
15. Banik, I.; Bhowmick, A. K.; Tikku, V. K.; Majali, A. B.; Deshpande, R. S. *Radiat Phys Chem* 1998, 51, 195.
16. Haddadi-asl, V.; Burford, R. P.; Garnett, J. L. *Radiation Phys Chem* 1994, 44, 385; 1995, 45, 191.
17. Tikku, V. K.; Biswas, G.; Deshpande, R. S.; Majali, A. B.; Chaki, T. K.; Bhowmick, A. K. *Radiat Phys Chem* 1995, 45, 829.
18. Bohm, G. G. A.; Tveekrem, J. O. *Rubber Chem Technol* 1982, 55, 575.
19. Banik, I.; Bhowmick, A.K. *J Appl Polym Sci* 2000, 76, 2016.
20. Chi-Ming, C. *Polymer Surface Modification and Characterization*; Hanser Publishers: Munich, 1993, p. 118.
21. Inagaki, N.; Tasaka, S.; Abe, H. *J Appl Polym Sci* 1992, 46, 595.
22. Gerspacher, M.; O'Farrell, C. P. *Elastomerics* 1991, 123, 15.
23. Hair, M. L. *Infrared Spectroscopy in Surface Chemistry*; Dekker: New York, 1967, p. 79.
24. Farmer, V. C. *The Infrared Spectra of Minerals*; Mineralogical Society: London, 1994, p. 365.
25. Socrates, G. *Infrared Characteristics Group Frequencies*; Wiley-Interscience: New York, 1980.
26. Morrow, B. A.; Molapo, D. T. Paper presented in Silica '98, Mulhouse, France, 1998.
27. Briggs, D.; Seah, M. P. *Practical Surface Analysis, Volume I Auger and X-ray Photoelectron Spectroscopy*; John Wiley & Sons: New York, 1995, p. 444.
28. Morrow, B. A. *Stud Surface Sci Catal* 1990, 57A, A161.
29. *Selected Powder Diffraction Data for Metals & Alloys-Data Book*; JCPDS: Swarthmore, PA, 1978, p. 911, 1st ed., vol II.