

Surface Activation of Polytetrafluoroethylene by Bonding of Polymeric Silicic Acid

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SYNOPSIS

When porous polytetrafluoroethylene (PTFE) is treated in a silicon tetrahalide atmosphere and then hydrolysed by means of a water jet, it is possible to achieve surface activation of the PTFE with silicic acid. This results in the surface of the PTFE becoming completely wettable, particularly if SiCl_4 is used. This paper provides an account of the physical and chemical investigation into the surface of the activated system. Measurement of the contact angles (with water) and determination of the silanol groups provide evidence of the surface activity. ESCA experiments show that concentrations of silicic acid above 14% w/w result in almost complete coverage of the PTFE surface. Using the BET method to measure the specific surface area, it can be seen that this is not simply a result of adding the areas of the two components, PTFE and silicic acid. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The unusual properties resulting from the perfluorinated carbon chains in polytetrafluoroethylene (PTFE) lend it a significant role in the production of a diverse range of materials, for example, plastics, fibers, and foils.¹ Apart from its high thermal and chemical stability, PTFE also has a very low surface energy, which gives rise to a complete lack of adhesion with many substances. Although this surface property is beneficial to a large number of applications, it does raise problems in some areas of use (e.g., in composites with other polymeric materials and as a filtration medium for aqueous systems), because there is no guarantee of adhesion in composites and high pressure heads occur in filtration. It is therefore necessary, in many cases, to activate the inert PTFE surface. However, owing to the almost unlimited chemical and physical stability of PTFE, very few methods of activating the surface are known. Such methods largely involve the use of reducing agents (e.g., $\text{Na}^{2,3}$ or Li^4 in liquid ammonia, naphthalene-sodium in tetrahydrofuran,³ or benzoin dianion^{5,6}), the influence of corona discharge,⁷ and high-energy radiation.^{8,9}

These methods generally lead to changes in the chemical structure of PTFE. Although this does in fact bring about an alteration in the surface behaviour, it also means that the basic properties of PTFE are impaired because they depend on an intact primary structure. Another method of modifying the surface of PTFE is based on bonding it to polymeric silicic acid. In contrast to the above-mentioned methods, this causes no chemical alteration to the PTFE and thus ensures that it retains its characteristics of stability. In this method a porous PTFE film is first exposed to a silicon tetrahalide atmosphere; the aim of this is for the low molecular weight particles from the gaseous phase to penetrate the film. The jet of water that is then applied causes the absorbed silicon tetrahalide to be hydrolysed to silicic acid. The result of this modification process is a PTFE material with unchanged bulk properties and polymeric silicic acid firmly bonded to its (non-adhesive) surface.

According to the concept of solubility parameters, silicon tetrahalides should be relatively strongly absorbed by PTFE. Their use in activating the surface of PTFE is based on the fact that they readily undergo hydrolysis in the presence of water to give silicic acid. As early as 1959, Herr and Beck¹⁰ described the formation of oxide layers on PTFE surfaces after treatment with silicon tetrachloride and

subsequent hydrolysis; the use of silicon tetrafluoride was also described at a later stage.¹¹ ESCA was employed to provide evidence of such modification.¹²

This paper investigates this method of surface modification with silicic acid in greater detail, with SiBr_4 being used for the first time as well as SiF_4 and SiCl_4 . The aim is to improve the modification conditions so that the PTFE surface obtained is completely wettable. The methods of surface and physical chemistry applied in characterizing the activated PTFE/ SiO_2 system include determination of the silanol groups, determination of specific surface area, ESCA, and contact-angle measurement.

EXPERIMENTAL

PTFE Starting Material

Modification was carried out on microporous PTFE film, ZITEX G110, provided by the Norton Chemplast Company, Wayne, NJ. This is a melt-crystallized (according to DSC) stretched PTFE film with irregularly structured porous areas and the following physical characteristics: thickness of film, 0.25 mm; volume of pores, 40%; density, pycnometer method, 2.15 g/cm^3 ; contact angle (water), 152° ; specific surface area, N_2 adsorption in accordance with BET, $50 \text{ m}^2/\text{g}$; melting point, DSC, extrapolation to a heating rate of 0, 327°C ; degree of crystallinity, from the specific density^{13,14} 42.2%; M_n , latent heat of crystallization,¹⁵ $6.2 \times 10^5 \text{ g/mol}$. The data for density, degree of crystallization, molecular weight, and melting point were taken from the literature.¹⁶

Modification of PTFE With Silicic Acid

Apparatus

Modification is carried out in a closed apparatus (Fig. 1). This consists of two autoclaves, A and B (stainless-steel, wall thickness 0.3 mm, internal diameter 95 mm, height 240 mm, volume 1.7 L), with various inlet ports (stainless steel, 6 mm in diameter) fitted with appropriate stop valves. Autoclave A is used for both the treatment with SiX_4 and the hydrolysis. Autoclave B merely serves as a water reservoir.

The PTFE film to be modified (extracted with ethyl acetate in a soxhlet apparatus for 3 h and dried at 60°C for 1 h, and at room temperature in a vacuum for 24 h) is fixed to the water sprinkler attachment as follows. When SiF_4 and SiBr_4 are used, the circular sample (70-mm diameter) is suspended in a horizontal position on the flat sprinkler attachment

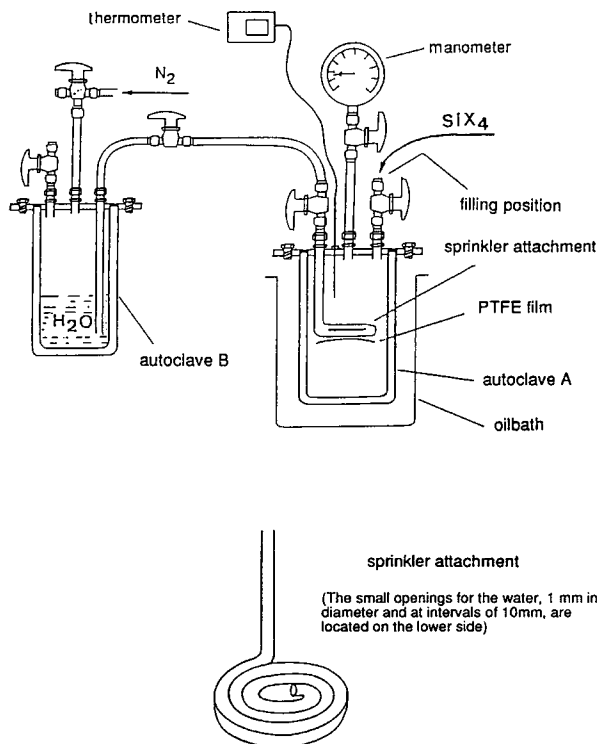


Figure 1 Apparatus used for the modification.

by means of Kevlar threads at two opposite sites on the sample. When SiCl_4 is used, the circular sample (70-mm diameter) is suspended flush against a Teflon sieve (Teflon film of thickness 0.5 mm and diameter 85 mm) by means of Kevlar threads attached to two opposite sides of the sample (5 mm apart and 2 mm in diameter). The Teflon sieve with the suspended sample is then fixed in a horizontal position to the sprinkler attachment by means of metal clips (Fig. 2). [When small volumes of water are used, the sample is first stretched between two PVDF rings (70 mm in diameter) and then suspended from the Teflon sieve at 4 positions.]

Method of Surface Modification

The water sprinkler with the attached sample is screwed into autoclave A. After the lid, which is fitted with a 0.5-mm Teflon seal, has been fastened autoclave A is evacuated. The appropriate quantity of SiX_4 is then pipetted into the evacuated autoclave through a length of tubing attached to the inlet port. SiF_4 is fed in from a cylinder. The autoclave is then heated to 150°C (SiF_4 and SiBr_4) or 110°C (SiCl_4) within a period of 30 min and maintained at this temperature for 60 min. The reaction vessel is then rapidly cooled to 100°C (SiBr_4), 65°C (SiCl_4), or 40°C (SiF_4). Nitrogen at a pressure of 12 bar then

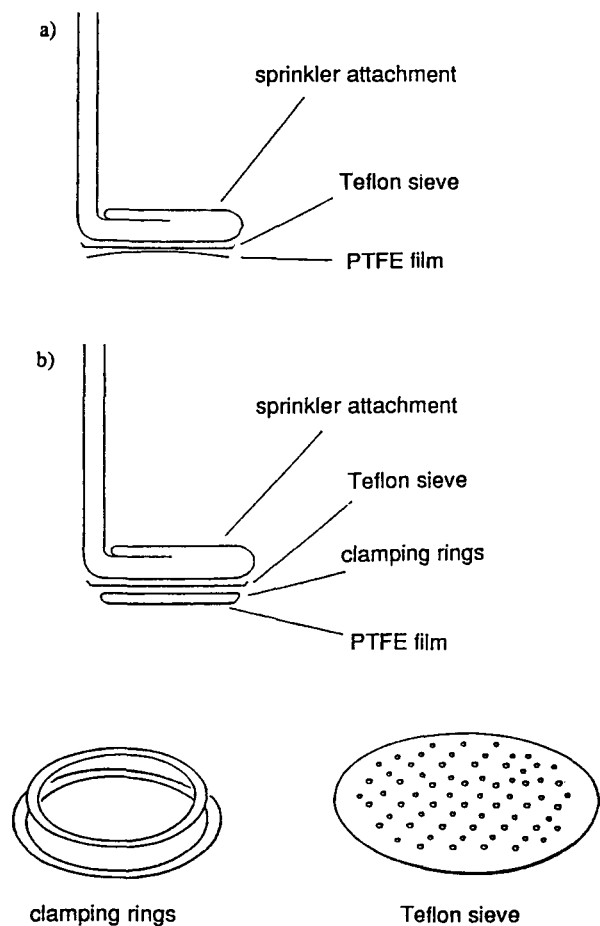


Figure 2 Arrangement of the sample on the water sprinkler when SiCl_4 is used. (a) without clamping rings, (b) with clamping rings.

forces water from autoclave B against the film in autoclave A. At the end of the reaction the mixture of gases is fed into a solution of dilute sodium hydroxide via a tube attached to one of the ports on autoclave A. The autoclave is then opened and the sample is taken out. Silicic acid adhering to the surface of the sample is removed by scrubbing the sample thoroughly in warm water. (Any remaining silicic acid is later removed by thoroughly rubbing the film after it has been dried.) In the next stage, the film is treated in water at 80°C for 20 min. After a preliminary drying process, the sample is dried overnight in a vacuum (10 Torr). The dried sample is then used to determine the increase in weight.

Investigative Methods

Determination of Silanol Groups

The silanol groups were in principle determined according to the thionyl chloride method.^{17,18}

Approximately 1.2 g of the dried (10 min, 90°C) samples of small sections cut from the modified PTFE films and silicic acid powder are each placed in a specimen tube (2 cm in diameter, 5 cm in height). The specimen tubes are then transferred to a 250-mL single-necked round-bottomed flask and centred so that they are unable to move. Thionyl chloride is then added in sufficient quantity to cover the pieces of modified film or, in the case of silicic acid, to give a moist mass. (If large quantities of thionyl chloride are used with silicic acid, violent bumping occurs on heating.) The apparatus is then heated under reflux on an oil bath at 85°C for 12 h. Here it is important to make sure that the thionyl chloride returning from the reflux condenser is distributed more or less equally among the specimen tubes. After this, a stillhead is fitted to the flask and excess thionyl chloride is distilled off while excluding moisture. Residues of thionyl chloride and any other reaction products are removed by heating at 190°C under high vacuum (20 h at 0.2 Torr and 10 h at 0.025 Torr). Following this, the flask is filled with dry N_2 . The specimen tubes are taken out and the samples are weighed immediately. Six hundred milligrams of the cut modified films and 300 mg of silicic acid are each weighed into a 100-mL conical flask with the ground-glass joint, to which, respectively, 30 and 60 mL of 10% sodium hydroxide solution are added immediately. The contents are then stirred, first for 10 min at 60°C and then for 40 min at ambient temperature, before acidification with H_2SO_4 and the addition of 2 mL of methanol. The solutions then undergo potentiometric titration with 0.01 and 0.02 N silver nitrate solution, for the modified films and silicic acid, respectively (Apparatus: Mehrohm 686 Titroprocessor with 665 Dosimat). Indicator electrode: Ag rod; reference electrode: standard calomel electrode.

ESCA Readings

The analysis was performed on a VG ESCA LAB V electron spectrometer. X-rays: A 1 K (1486.6 eV); reference: Au $4f_{7/2}$: 83.8 eV.

Determination of Specific Surface Area

The readings were taken on a computer-controlled Sorptomatic 1900. Prior to the measurements, the samples (10×10 mm strips of film or silicic acid powder) were dried at 100°C for 1.5 h, weighed immediately afterwards, and then dried again under vacuum (0.2 mbar) at 160°C .

Contact-Angle Measurements

Contact-angle measurements (with water) were recorded with a G1 measuring apparatus supplied by Krüss of Hamburg.

RESULTS

Determination of Optimum Modification Conditions

The two stages in the process (treatment with SiX_4 and hydrolysis), which have to be carried out consecutively, are performed in a 1.7-L autoclave fitted with a number of ports. PTFE film attached to a sprinkler device inside the autoclave is first exposed to an atmosphere of silicon tetrahalide of specified concentration. A certain period of heat treatment is followed by a short cooling process. Hydrolysis of the silicon tetrahalide is instigated by a jet of water directed onto the film through a sprinkler attachment (pressurized by a stream of N_2 at 12 bar).

It is important in the hydrolysis that the water jet hit the film relatively quickly to forestall desorption of the silicon tetrahalide by the PTFE. This desorption is favoured by the abrupt pressure drop in the autoclave due to reaction of the gas with the incoming water. On the other hand, a strong jet of water directed at the film will wash away any newly formed low-molecular-weight water-soluble silicic acid molecules. The process therefore benefits from the water striking the film as soon as possible, without it washing away the newly formed silicic acid. These requirements were found to be conveniently met by a sprinkler attachment made from a tube coiled in the horizontal plane, with small openings on the lower side.

Different silicon tetrahalides were used for the modification: silicon tetrafluoride, silicon tetrachloride, and, in a number of cases, silicon tetrabromide. Modification was accomplished with all the silicon tetrahalides used, albeit with varying degrees of success: whereas silicon tetrafluoride was only able to bring about an increase in weight of up to approximately 1.5%, conditions were found that resulted in weight increases of up to 20% for silicon tetrachloride. A comparison of the resulting modification was made between all three silicon tetrahalides at very low concentrations (0.045 mol/L). Silicon tetrabromide was found to give a higher increase in weight than either SiCl_4 and SiF_4 . The large volume of water absorbed by the silicic acid produced in the modified films gives them a transparent quality.

An investigation of the parameters for the modification demonstrated that neither the temperature nor the duration of the treatment have any significant influence on the increase in weight or consequently the silicic acid content.

In contrast to this, the hydrolysis conditions greatly affect the proportion of silicic acid in the product, which is particularly apparent in the case of SiCl_4 . The volume of water used in hydrolysis and hence the molar ratio of $\text{H}_2\text{O} : \text{SiCl}_4$ plays a particularly significant role. According to the equation for the reaction, the complete hydrolysis of each mole of SiCl_4 requires 4 moles of water. However, as can be seen from Figure 3, this volume of water only produces a slight increase in weight. It is only when an excess of water is used that a rapid increase in the silicic acid content occurs. A maximum increase in weight (c. 17%) is achieved when the molar ratio of $\text{H}_2\text{O} : \text{SiCl}_4$ is in the range of approximately

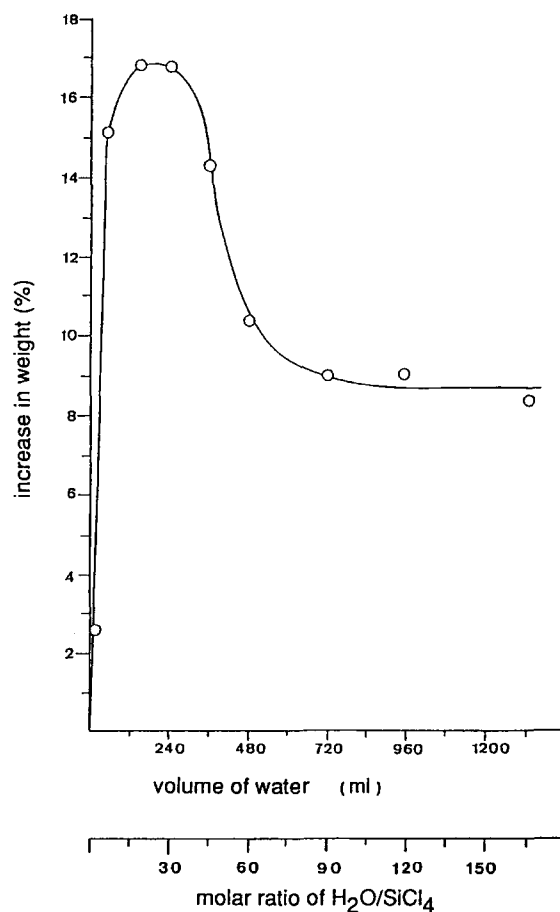


Figure 3 Increase in weight as a function of the volume of water used and the molar ratio of $\text{H}_2\text{O} : \text{SiCl}_4$ (quantity of SiCl_4 used: 0.44 mol, corresponding to a concentration of SiCl_4 : 0.26 mol/L).

10–40. It is here that the highest yields of silicic acid adhering to the surface were recorded. A further excess of water produces a relatively sharp decline in the weight increase, levelling off beyond a molar ratio of about 70 (a molar excess of water of approximately 17.5, taking into account the stoichiometric hydrolysis) at a value of about 8%. This decrease is obviously a result of the newly formed, low-molecular-weight, and thus relatively soluble, silicic acid being removed by the constant stream of water.

The dependence of the proportion of silicic acid on the SiCl_4 concentration used varies according to the volume of water employed. As can be seen from Figure 4, if the SiCl_4 concentration used is halved from 0.26 to 0.13 g/mol, the proportion of silicic acid is also halved when 240 mL of water is used. In contrast to this, there is only a slight fall in the proportion of silicic acid when a large excess of water, and consequently an extremely high molar ratio of $\text{H}_2\text{O} : \text{SiCl}_4$ is used.

At low SiCl_4 concentrations, the resulting proportion of silicic acid is practically independent of the volume of water. This is obviously due to the fact that the volumes of water used still represent an extremely large molar excess.

The increases in weight achieved depend to a large degree on the type of PTFE film used. For example, proportions of silicic acid above 70% could be detected when other microporous, ultra-thin PTFE

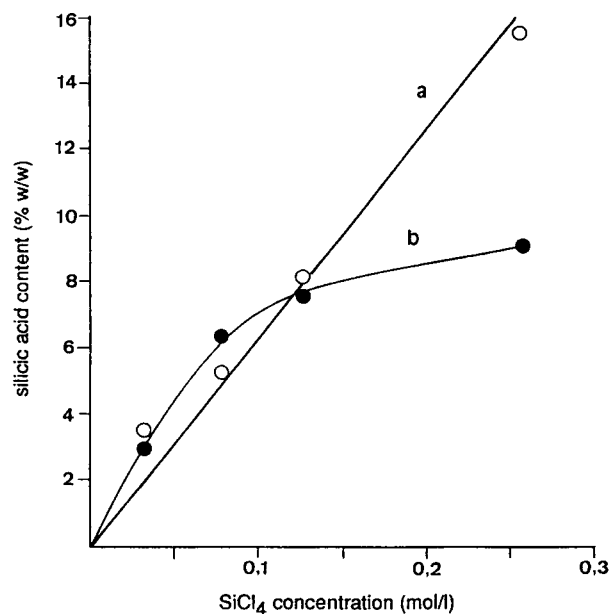


Figure 4 Proportion of silicic acid obtained as a function of SiCl_4 concentration used; volume of water used (a) 240 mL and (b) 960 mL.

membranes were used (film thickness $< 100 \mu\text{m}$, GORE-Tex).

The modification was seen to result in a good degree of permanence for all the samples, as shown by experiments with hot water in a soxhlet extractor. In these tests, no significant weight loss was detected after 30 h of treatment.

Properties of Modified PTFE Films

The (sub)microscopic properties and the resulting macroscopic properties of the activated PTFE (PTFE/SiO_2) surface are investigated by means of various analytical techniques. Information concerning the concentration and distribution of the silanol groups located on the surface is of particular interest, as is the influence of the silicic acid content upon the density of the surface layer. From this characterization of the microstructure it is then possible to interpret the macroscopic properties of the surface that occur, for example, the wettability. Wettability, as a measure of the surface energy, can be determined by measuring the contact angle.

Determination of Silanol Groups

Quantitative determination of the silanol groups on the PTFE/SiO_2 surface was performed with the aid of the thionyl chloride method. The underlying principle of this method^{17,18} is that reaction with thionyl chloride results in substitution of the silicon-bonded hydroxyl group by chlorine (analogous to the method of preparing acid chlorides). (Chlorination of the silicic acid surface can also be brought about by direct reaction with chlorine gas or treatment with sulphuryl chloride.¹⁹) After the distillation of excess thionyl chloride, any remaining traces of the unreacted compound are removed by heating the reaction products in a high-vacuum at 190°C . However, this does not always succeed completely if finely porous silicic acids are involved.¹⁷ The chlorine content can then be determined potentiometrically by means of a precipitation titration with silver nitrate and then related back to the quantity of silanol groups.

The investigations include films modified by various methods with different silicic acid contents. In addition, silicic acid prepared under the modification conditions was also tested, as was pure PTFE film as a control.

The results of the silanol group determinations are compiled in Table I, together with the degree of water absorption. The latter was determined by weighing the dried sample (40 min, 40°C) before

Table I Concentration of Silanol Groups and Degree of Water Absorption

Modified Films		
Proportion of Silicic Acid (% by wt)	Concentration of Silanol Groups (mmol OH/100 g Film)	Degree of Water Absorption (g H ₂ O/g Film)
15 ^a	6.0	0.16
9 ^a	6.4	0.15
1 ^b	0.2	< 0.02

Silicic Acids Prepared Under Modification Conditions

Details of Silicic Acid Preparation	Concentration of Silanol Groups (mmol OH/100 g)
0.44 mol SiCl ₄ , 240 mL H ₂ O	175
0.44 mol SiCl ₄ , 960 mL H ₂ O	240
0.44 mol SiF ₄ , 960 mL H ₂ O	8

^a From SiCl₄.^b From SiF₄.

immersing it in water for 1 min. The sample was then taken out, pressed between two filter papers for 2 s and weighed again.

Modified Films. The silanol group concentration of the films modified with SiF₄ was very low (approximately 0.2 mmol OH/100 g film). This is probably a consequence of the action of the HF generated during hydrolysis on the hydroxyl groups of the surface-bonded silicic acid. As a result condensation occurs between neighbouring silanol groups, and hence there is an overall loss of silanol groups. HF is credited with a catalytic effect in the condensation of silicic acid.²⁰

In contrast, the samples modified with SiCl₄ exhibited much higher concentrations of silanol groups. Here it can be seen that samples with very different silicic acid contents (15 and 9% w/w) have practically identical quantities of silanol groups. This indicates that there is a great variety in the silanol group concentrations of the silicic acids in these samples, with the 9% w/w sample having a much greater concentration of silanol groups in relation to the silicic acid content. As the samples were prepared with different volumes of water in the hydrolysis of SiCl₄, the differences observed in the silanol group concentrations must be a consequence of the prevailing hydrolysis conditions. A large vol-

ume of water means, on the one hand, that the heat generated during hydrolysis is absorbed and, at the same time, that a lower concentration of monosilicic acid is produced. Under such conditions (low temperature, large excess of water), the position of the hydrolysis equilibrium will be shifted in the direction of noncondensed silanol groups. The result is a higher concentration of silanol groups. The findings of the silanol group determination correlate well with those of the water absorption test (Table I).

Silicic Acid Prepared Under Modification Conditions. The silicic acids produced from SiF₄ only have a very low content of silanol groups (similar to the modified films) and thus have a relatively strongly hydrophobic character. Macroscopically, this hydrophobic character can be recognized by the fact that this silicic acid floats on the surface of the water in the autoclave.

In contrast to this, the silicic acids produced from SiCl₄ are observed to have a much higher concentration of silanol groups. Here it can be seen that the silicic acid produced with a large volume of water has a higher concentration of silanol groups. This corresponds with the finding that the use of a very large excess of water during the modification of PTFE leads to a higher silanol group content in relation to the silicic acid component. The reason for these differences in the concentration of the silanol groups, as already mentioned above, is probably the shift in the condensation equilibrium when different volumes of water are used in the hydrolysis.

Determination of Specific Surface Area

The specific surface area was measured according to the BET method, by recording the N₂ adsorption isotherms at low temperature.

Modified Films. A specific surface area of 50–55 m²/g was recorded for the unmodified films. It was to be expected that the modified films would have a higher specific surface area due to the silicic acid content. However, in-depth investigations revealed that this is often not the case. The reason for this is probably due to the fact that the bonding of polymeric silicic acid has changed the accessibility of the PTFE surface for the N₂ molecules to be adsorbed. As previous investigations with scanning electron microscopy show,²¹ the modification produces a significant change in the surface structure, particularly if the proportion of silicic acid is high. Consequently, the specific surface area to be determined is not simply made up by adding the surface

areas of the PTFE and silicic acid portion. This in turn means that there is no straightforward explanation for the derivation of the specific surface areas obtained for the modified films.

As can be seen from the adsorption isotherms (Fig. 5), the modified films first adsorb N₂, without there being any significant effect on the adsorption pressure (the curve does not start at 0). This fact is obviously due to the ability of the silicic acid to incorporate N₂ molecules into the inner zones of its pore structure. Surface adsorption does not occur until the capacity of the pore structure has been largely exhausted. This is taken into account in the measuring technique by starting the actual measurements once the relative pressure has reached a value of approximately 0.05.

Silicic Acids Prepared Under the Modification Conditions. The values obtained for the specific surface area are much larger for the samples prepared with SiCl₄ than for those with SiF₄ (see Table II).

Clearly the silicic acids prepared with SiCl₄ have different specific surface areas depending on the synthesis conditions. The specific surface area of a silicic acid prepared with a large excess of water is approximately 20% higher than one produced with a small excess. The silanol group densities calculated for the SiCl₄ samples lie between 2 and 2.5 OH/m². As five silicon atoms occupy an area of roughly 1

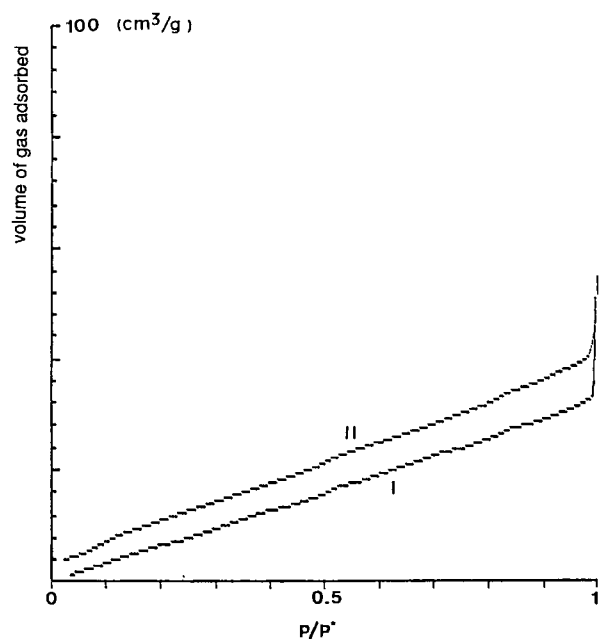


Figure 5 BET isotherms of unmodified (I) and modified (II) films (modified with 0.44 mol SiCl₄, 240 mL H₂O).

Table II Specific Surface Areas and Silanol Group Densities for Synthesized Silicic Acids

Details of Silicic Acid Preparation	Specific Surface Area (m ² /g)	Silanol Group Density (OH/nm ²)
0.44 mol SiCl ₄ , 240 mL H ₂ O	530	2.1
0.44 mol SiCl ₄ , 960 mL H ₂ O	640	2.4
0.44 mol SiF ₄ , 960 mL H ₂ O	140	0.4

nm², the figure obtained corresponds to approximately half of the maximum attainable.

As expected, the silicic acids prepared from SiF₄ gave a very low density of silanol groups of about 0.4 OH/nm². This corresponds to a very sparse covering (< 10%) of the surface and can be explained by the action of the HF generated on the surface (*cf.* above).

ESCA Study

Table III presents the results for the surface coating of PTFE films (prepared with SiCl₄) with silicic acid. The materials examined are the same samples as were used in the determination of the silanol groups and the specific surface area. Figure 6 shows a typical ESCA spectrum.

As expected, the unmodified PTFE used as a control merely exhibits peaks for carbon and fluorine in the ratio of 1 : 2 (binding energies for the C_{1s} electrons: 290.2 eV and for the F_{1s} electrons: 689.8 eV).

By comparison, in addition to the F and C peaks, the modified PTFE samples also exhibit signals for O_{1s} electrons at 533.6 eV, and Si_{2p} electrons at 103.6 eV, which can be attributed to the silicic acid (O : Si ratio, 3 : 1). There are, however, considerable differences in the quantitative composition of the surface, depending on the silicic acid content. For instance, a sample with a low silicic acid content (9% w/w) shows intense signals emanating from the PTFE, whereas the intensity of these lines in a sample with a high silicic acid content (15% w/w) is negligibly small. This means that the latter sample has an almost complete silicic acid layer on the surface of the PTFE. As ESCA yields information to a depth of approximately 10 nm, and PTFE signals could still be detected for this sample, the thickness of the silicic acid layer is probably less than 10 nm.

Table III ESCA Data Obtained for PTFE and PTFE/SiO₂

Sample	BE (eV)	Assignment	$b_{1/2}$ (eV)	I	Composition (Atom %)
PTFE	689.8	F	2.3	274	66
	292.0	C (—CF ₂ —)	1.9	13527	33
PTFE/SiO ₂ 9% w/w	689.9	F	2.4	8342	27.9
	292.0	C (—CF ₂ —)	2.3	3845	12.0
	285	C (contam.)	1.9	1281	4.0
	533.6	O	2.5	12297	41.0
	103.6	Si	2.2	4058	13.6
15% w/w	690.3	F	—	222	2.3
	285.7	C (contam.)	2.9	563	6.4
	533.3	O	1.9	6060	68.7
	103.8	Si	> 1.2	2000	22.0

Prepared with 0.44 mol SiCl₄ and BE, 960 mL H₂O (9% w/w SiO₂), $b_{1/2}$ 240 mL H₂O (15% w/w SiO₂).

BE, binding energy, $b_{1/2}$, half-width value ($b_{1/2}$ due to apparatus = 1.2 eV); I, corrected intensity; obtained by dividing the experimentally determined intensity (count rate) by the atomic sensitivity factor (ASF, ASF values: C_{1s} = 1, O_{1s} = 2.5, Si_{2p} = 1.1, F_{1s} = 4.5); The ASF values for C, O, and Si were taken from the literature²² and converted for the spectrometer employed.²³ The value for F was obtained from the F : C ratio, using pure PTFE as the reference.

Sample charge: PTFE: 6.1 V; PTFE/SiO₂ (9%): 4.2 V; PTFE/SiO₂ (15%): 4.9 V.

As indicated by the values obtained for the corrected intensity, the degree of surface coating for the sample with a high silicic acid content has a value of approximately 40%.

Furthermore, the modified samples exhibit a much lower degree of charging in comparison to the pure PTFE, which indicates reduced insulating properties.

The spectra of the modified films also have a carbon peak of low intensity that because of its position, must be unfluorinated. This clearly can be attributed to traces of contamination that are a result of the adsorption capacity of silicic acid.

Determination of Contact Angle

Measurements of contact angles were taken in order to assess the improvement in the degree of wettability resulting from the alterations in the microstructure of the surface. The results given are the average of at least 15 readings taken for each sample. There were, however, often considerable deviations between measurements taken on different areas of the film (see statistical data in Table IV). This indicates that distribution of the silicic acid, and hence the silanol groups, on the film was not uniform. The results are summarized in Table IV.

Unmodified Films. In the unmodified (untreated or only thermally treated films), the contact angle was measured as approximately 152°. This value considerably exceeds the figure of 109° that is given for

PTFE in the literature.⁷ This is obviously a result of the highly contoured surface of the PTFE films used; this surface roughening of the hydrophobic PTFE means that a larger area will be in contact with the water droplet, which is energetically unfavourable.²⁴ This is compensated for by greater contraction of the water droplet, which in turn is reflected by an increase in the contact angle. This is confirmed by comparative measurements of the contact angle on two PTFE samples, a microporous PTFE membrane and a smooth nonporous PTFE film. A contact angle of 145° was observed for the microporous PTFE sample whereas a value of 114° was recorded for the smooth PTFE film, which agrees well with the theoretical value of 109°.

Modified Films. The investigation first considered films that had been modified with very small quantities (0.045 mol/L) of the different silicon tetrahalides (see Table IV). Only those samples that had been modified with SiBr₄ showed noticeably smaller contact angles (down to *c.* 100°), and thus significantly improved wettability. This can be attributed to the higher silicic acid content of these samples, and hence a higher concentration of silanol groups. In addition, samples were also examined that had been modified with higher concentrations (0.128 and 0.256 mol/L of SiF₄ and SiCl₄ (Table IV). Where SiF₄ had been used as the modifying agent, the contact angle of the films was only reduced to approximately 100°. In contrast, the samples modified with

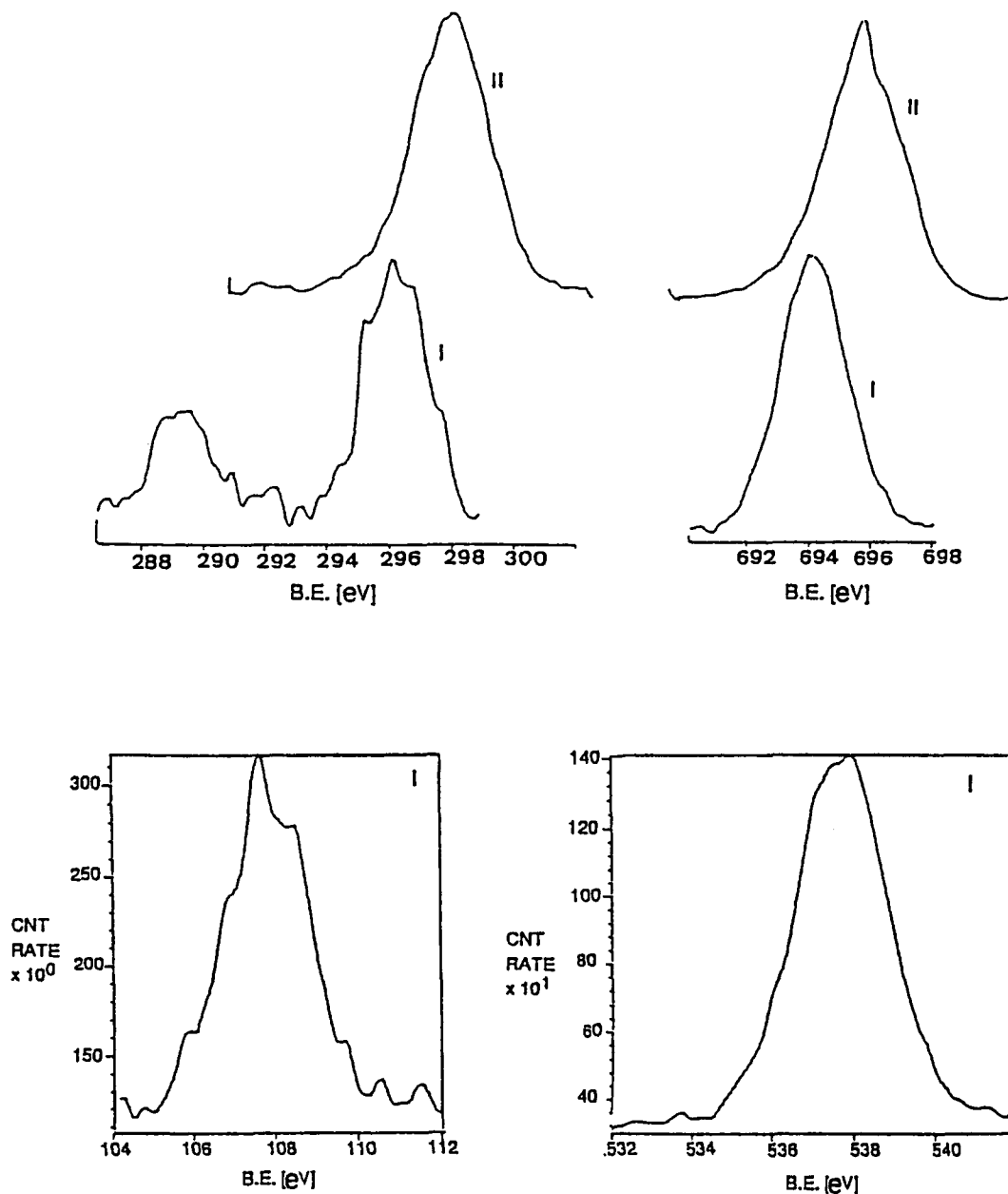


Figure 6 ESCA spectra; top: C_{1s} and F_{1s} ; bottom: O_{1s} and Si_{2p} . I: SiO_2 -modified film (9% w/w) (SiCl_4); II: unmodified PTFE film.

SiCl_4 (with a silicic acid content $> 7\%$) exhibited complete wettability of the surface (contact angle $< 10^\circ$). Here the water droplets were rapidly absorbed by the dry sample, resulting in the surface of the film becoming transparent.

DISCUSSION

In principle, all of the three silicon tetrahalides employed, SiF_4 , SiCl_4 , and SiBr_4 , are capable of acti-

vating the surface of PTFE with silicic acid. The decisive factors in the resulting degree of modification are both the content and nature of the silicic acid (silanol group concentration, size of the specific surface area). Although SiF_4 results in a low silicic acid content and therefore a limited modification effect, it is possible to obtain extremely highly modified PTFE films using SiCl_4 (and SiBr_4 too). The conditions for the apparatus and the chemical reaction devised for this investigation made it possible to achieve silicic acid contents in the PTFE films

Table IV Determination of Contact Angle (With Water)

	Contact Angle (°) $\bar{x} \pm SD q^a$
Unmodified films	
PTFE film (microporous)	152 ± 4 ± 2.3
PTFE membrane (microporous)	146
PTFE film (nonporous)	114 ± 7 ± 5.8
Modified using different SiX ₄	
SiF ₄ (SiO ₂ : < 0.2% w/w)	133 ± 7 ± 4.4
SiCl ₄ (SiO ₂ : < 0.5% w/w)	119 ± 12 ± 7.6
SiBr ₄ (SiO ₂ : < 3.5% w/w)	100 ± 9 ± 4.5
With different SiO ₂ contents (% w/w)	
Prepared from SiF ₄	
0.5	117 ± 14 ± 8
1.0	101 ± 16 ± 7
Prepared from SiCl ₄	
6.5	60 ± 15 ± 9
9.0 ^b	< 10 or complete spreading
15.0 ^b	< 10 or complete spreading

^a 95% confidence interval.

^b In these samples the drop of water placed on the surface was absorbed by the film, causing transparency.

used (film thickness: 0.25 mm) of up to 20% w/w with 0.44 mol SiCl₄. It was thus still possible to carry out the reaction at very mild temperatures (< 100°C), which is especially important in avoiding temperature-induced changes in the film, such as shrinkage due to the presence of frozen-in strain. The highest yield of surface-bonded silicic acid is achieved when a two- to eightfold molar excess of water is used for the hydrolysis of SiCl₄. If a still greater quantity of water is used, although the equilibrium of the condensation reaction is shifted in favour of silicic acid with a large number of silanol groups, it also produces a reduction in the silicic acid content.

Because the different SiX₄ would be expected to interact with the PTFE in a comparatively similar manner during the first part of the treatment, the variation in the extent of the modification must be primarily a result of the different processes in the hydrolysis. In the cases of SiCl₄ and SiBr₄, hydrolysis proceeds according to the same principle, whereas the hydrolytic decomposition of SiF₄ follows a different path. This is due to the fact that the HF generated can react with both the remaining SiF₄ and the newly formed SiO₂. The reaction with SiF₄, which acts as a Lewis acid, leads to the formation of hexafluorosilicic acid, H₂SiF₆, which can only ex-

ist in aqueous solution. Hence a portion of the SiF₄ employed is not converted to silicic acid. In addition to this, HF has a hydrophobic effect on the silicic acid surface.²⁵ HF is in fact attributed with a strong catalytic function in the silicic acid condensation.²⁰ Due to the character of their surface, the single particles of silicic acid that are generated under these conditions exhibit different coagulation behaviour, which in turn affects the nature of the silicic acid generated.

As has been shown by investigations using scanning electron microscopy coupled with X-ray microanalysis,²¹ the PTFE films used here consist of insular smooth areas surrounded by cavernous regions that represent the pore structure. Large portions of the silicic acid particles (in the case of SiCl₄) and rather peculiar sponge-like silicic acid structures (in the case of SiF₄) were observed around the edges of the pores owing to the modification, with the smooth areas remaining practically free of silicic acid up to an SiO₂ content of 7% w/w. As the ESCA investigations showed, at silicic acid concentrations higher than 14% w/w the surface coverage is almost complete. It is therefore to be expected that the silicic acid extends to cover the smooth areas at very high concentrations. And in fact macroscopically there is a noticeable stiffening of these samples, which obviously results from the formation of an almost continuous layer of silicic acid. Determination of the specific surface area by the BET method revealed that the values obtained for the modified samples are not simply the sum of the PTFE and silicic acid components. Microscopic examination of the silicic acid on the modified films, at least below silicic acid concentrations of 7% w/w, shows that there are two areas of different and irregular distribution, which differ not only in terms of their structure but also their polarity. As a result, there are two distinct patterns of wettability in the microscopic range, so that the macroscopically determined contact angle represents an average of these differences. Because the use of SiCl₄ produces a dense silicic acid coverage and a high concentration of silanol groups, the samples that were modified with this reagent exhibit complete wettability of the surface (contact angle < 10°). On the other hand, the sparse surface coverage and extremely low concentration of silanol groups obtained with SiF₄ give only a minor improvement in the wettability of the surface. The pronounced wetting capacity of the films modified with SiCl₄ can be observed at the macroscopic level by the fact that dried samples immediately become transparent when immersed in water due to the enormous uptake of water.

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