

Surface activation of non-porous perfluorinated polymers by deposition of silica

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A method to enhance the surface energy of non-porous films of three different types of perfluorinated polymer [polytetrafluoroethylene with and without a perfluorinated modifier and poly(tetrafluoroethylene-*co*-hexafluoropropylene)] is described. The surface was activated by the deposition of silica, produced *in situ* from SiCl₄ and water, without any chemical degradation or modification of the polymer bulk. By adding perfluorohexane and 1,1,1,3,3,3-hexafluoroisopropanol as auxiliaries to the SiCl₄ and water in the gas phase respectively, extended silica layers with spherical morphologies could be generated, which were permanently fixed to the films. By use of low voltage scanning electron microscopy (LVSEM) it was shown that the adhesion of the silica to the fluoropolymers is due to its mechanical anchoring, ultimately resulting from the diffusion of SiCl₄ and water into the polymer surface. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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Introduction

Perfluorinated polymers like Polytetrafluoroethylene (PTFE), Poly(tetrafluoroethylene-*co*-hexafluoropropylene) (Fluoroethylenpropylene, FEP) and Poly(tetrafluoroethylene-*co*-perfluoroalkylvinylether) have a remarkable chemical inertness, good thermal stability and a very low surface energy¹. Therefore, these materials are often used for working with aggressive chemicals at high temperatures², as high performance lubricants or on stain-resistant textiles³. But in some cases the low surface energy is a problem, as it is not possible to adhere perfluorinated polymers to other materials. To overcome this drawback, i.e. to increase the surface energy and to prepare the polymers for adhesion, different methods have been developed. The most common technique is the reduction of the surface with sodium in liquid ammonia or with other strong reducing agents⁴. Plasma⁵, laser⁶ and electron beams⁷ are also used for surface modification. A disadvantage of these techniques is that they could cause chemical modification or even degradation of the polymer surface. The method of depositing hydrophilic silica on porous PTFE-surfaces was developed some time ago⁸. This method consists of treatment with SiCl₄ followed by a kinetically controlled hydrolysis with water, thus avoiding the degradation of PTFE. This results in a hydrophilic PTFE surface with silica anchored to the porous areas leaving the non-porous areas uncovered⁹. In this paper an improvement of this method to create extended silica covered areas also on non-porous perfluorinated materials is described. In addition, the surface appearance of the silica is characterized and a proposal for the mechanism of anchoring is presented.

Experimental

Three different non-porous perfluorinated polymer films with a thickness of 100 μm (manufactured by Dyneon GmbH, Gendorf, Germany) were used and are characterized in *Table 1*.

The following procedure was used for the treatment of the surfaces. First the films were washed three times with ethyl acetate. After drying in an oven at 110°C they were mechanically fixed in a stainless steel frame without further support (available polymer area 2 × 3 cm). The samples prepared in this manner were placed in an autoclave and treated with gaseous SiCl₄ at temperatures between 90 and 130°C, for between 1 and 48 h. The corresponding pressures were between 220 kPa at 90°C and 300 kPa at 130°C. Under these conditions water vapour, produced in a second autoclave at pressures between 500 and 800 kPa, was blown through a pipeline directly against the films under its own pressure. The autoclave and the treatment procedure is described elsewhere in more detail¹⁰. To cause better mixing and wetting of the different components with each other and with the films, 30% (per volume) Perfluorohexane was added to the SiCl₄ and 50% (per volume) 1,1,1,3,3,3-Hexafluoroisopropanol to the water-phase (by using these wetting and mixing auxiliaries a more homogeneous surface modification could be achieved). After opening the autoclave, the films were rinsed with 50 ml of dist. water. To remove any silica not permanently fixed to the films, they were brushed for 30 s under wet conditions and for a further 30 s after drying for 24 h at room temperature with an electrically driven brush emitting ultrasonic waves ('Sonicare' Model TX1, manufacturer Optiva Corp., Seattle).

The thermal properties of the polymer films were measured using a Mettler DSC 30 with a heating rate of 10°C min⁻¹.

Contact angle measurements were made with a Krüss G 40 using water as the liquid. For every value five measurements were taken and a confidence interval of 95% was calculated.

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Table 1 Characteristics of the polymeric samples

	TF 1750 ^a	TFM 1700 ^a	FEP 6107 ^a
Materials ^b	Tetrafluoroethylene homopolymer	Tetrafluoroethylene polymer with less than 1% perfluorinated modifier	Poly(tetrafluoro-ethylene-co-hexafluoropropylene)
Void content ^b (%)	0.75	0.26	< 0.1
Density ^b (g cm ⁻³)	2.160	2.165	not available
Melting point ^c (°C)	330	329	258
Melting enthalpy ^c (J g ⁻¹)	47	51	24
Water contact angle before treatment ^d (°)	102.7 ± 4.7	100.4 ± 1.0	99.5 ± 5.1
Water contact angle ^d after treatment (°)	32.5 ± 3.1	32.5 ± 2.5	37.4 ± 6.5
Crystallinity ^b (%)	approx. 60	approx. 60	not available

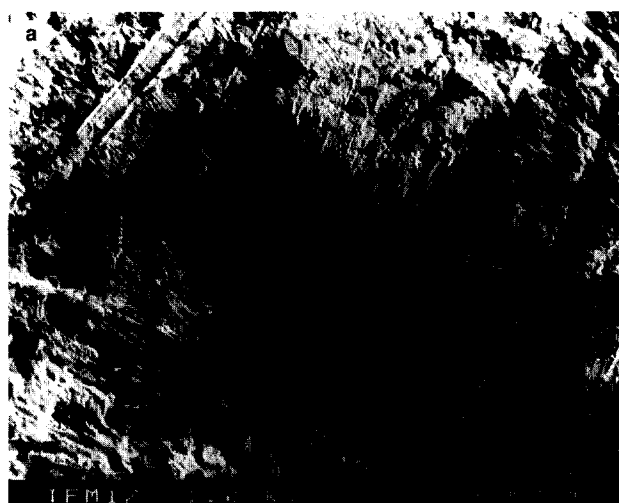
^aGerman trade name, Dyneon GmbH, Gendorf, Germany^bInformation from the manufacturer^cInformation by d.s.c.^dAverage value from five measurements; 95% confidence interval

Figure 1 (a) Untreated polymer surface (TFM), representative for all three polymer types, modified in this work. (b) A survey of a silica covered polymer surface (TFM). All samples, shown as micrographs, were treated at 125°C for 40 h. The pressure of the water vapour was 800 kPa. The treatment conditions are as described in the experiment part

Slices of the treated films were, without additional conductive coating, directly fixed with carbonized glue on specimen holders. To observe the surface morphology a Hitachi S-4500 low voltage scanning electron microscope (LVSEM) was used at an accelerating voltage of 1 kV and a

working distance of 7 mm. For further details of LVSEM applications on polymers a survey is given in ref. ¹¹.

Results and discussion

In *Figure 1a* a perfluorinated polymer film (representative for the films made from the three different perfluorinated polymers), prior to modification is shown. The surfaces of the TF and the TFM films have a rough structure with irregular flat ditches formed during the peeling of the films from a polymer block. The FEP film was manufactured thermoplastically, this means extrusion and calendering, but the surface looks very similar to those of the TF and TFM films. There are no visible pores on any of the films (see *Table 1* in which the abbreviations are also explained).

On this surface (*Figure 1b*) a layer of silica has been deposited by the following sequence of reactions, which are well known from the literature¹².



SiCl_4 was chosen because of its good wetting properties on perfluorinated polymers and its solubility parameter which is in the range of the perfluorinated polymers [$\delta(\text{SiCl}_4)$: 15.1 (J cm⁻³)^{1/2}; $\delta(\text{PTFE})$: 12.7 (J cm⁻³)^{1/2}]¹³. The other perfluoropolymers should have similar solubility parameters to that of PTFE. From these values the diffusion of SiCl_4 into the perfluorinated polymers is to be expected. Water can also diffuse into the perfluorinated polymers. For the diffusion of water into FEP a permeability of $12.8 \times 10^{-13} \text{ cm}^3 \text{ cm} (\text{cm}^2 \text{ s Pa})^{-1}$ at 25°C is given in the literature. For PFA the value at 23°C is $13.4 \times 10^{-13} \text{ cm}^3 \text{ cm} (\text{cm}^2 \text{ s Pa})^{-1}$ ¹⁴. For pure PTFE there is no value given, but it should be in the same region as FEP and PFA. Values for the diffusion of SiCl_4 into perfluorinated polymers are not given in the literature. The parameters given demonstrate that diffusion of SiCl_4 and water into perfluorinated polymers is possible and probable. In order to obtain a tightly anchored silica layer on the polymer surface only the experimental conditions must be optimized.

The chosen temperature for the treatment of the three films was 125°C, since at lower or higher temperatures the silica layer becomes macroscopically inhomogeneous and anchors poorly to the polymers as was shown by treating the surface with the electrically driven brush emitting ultrasonic waves. The α -transition temperature of the fluoropolymers is 125°C¹⁵ (TF, TFM) and this behaviour might be due to a change in the diffusion properties of SiCl_4 , water and the



Figure 2 A large crater with its bottom covered with small silica spheres (TF) which grow from the remaining SiCl_4 and water after the crater has been formed

fluorinated wetting and mixing auxiliaries. At higher or lower temperatures, there are often areas where the silica does not adhere well and is easily removed with the electric brush.

Differential scanning calorimetry (d.s.c.) measurements of the modified polymer films show the same thermograms as for the untreated films. Neither new peaks, nor shifting or broadening of the polymer peaks could be observed. This shows, that the polymer remains unchanged, because in the case of defluorination and polymer degradation the melting peak should become significantly broader.

The deposition of silica alters the surface properties and morphology totally. There are extended silica covered hydrophilic areas. The contact angles of water (shown in *Table 1*) for the silica covered polymers are distinctively lower than for the untreated polymers in each of the three samples. The hydrophilicity of the three silica covered polymer samples is similar.

The appearance of the silica covered areas is completely different from that of the untreated polymer surfaces. After the modification the surface is made up of characteristic spherical structures, each with a size of between 1 and 5 μm , which are more or less integrated into a layer (*Figure 1b*). For illustrating each result presented in this section only one of the three treated perfluorinated films is shown, although the results apply to the films on all three polymers.

This spherical surface morphology is typical for the solidification of silica and depends neither on the substrate nor on the method in which the silica layer is obtained. It has been shown in the literature, that silica, which has been precipitated by the treatment of alkali metal silicates with sulfuric acid in a neutral or alkaline medium, also contains spherical structures¹⁶.

By using similar experimental conditions to those described here, spheres of silica of the same size as on fluoropolymer substrates are also formed on glass surfaces, indicating that the substrate does not cause any significant change in the silica morphology.

The surfaces of the silica deposited films show characteristic features. Craters (*Figure 2*) are presumably formed by gaseous HCl which is produced by the hydrolysis reaction (equation (1)) during the modification of the polymer films. Even after the polymer surface has been completely covered with a silica layer, the hydrolysis



Figure 3 (a) A crack with a thin silica layer at its base (FEP) indicating, that the crack has been formed during the hydrolysis in the autoclave. (b) Cracked surface formed during sample preparation used for estimating the thickness of the silica layer (TFM). (c) Fibrils pulled out of the polymer surface (TFM) indicating adhesion between the silica and the perfluorinated polymer

reaction still occurs in the polymer. As a result there is gaseous HCl between the polymer and the silica layer. The HCl breaks through the silica layer forming craters. After the eruption a thin layer consisting of smaller spherical

silica particles (smaller than 1 μm in diameter) builds up on the bottoms of the craters from the remaining SiCl_4 and water.

There are also two different types of cracks on the surface. Type I (Figure 3a) could be formed during the condensation of the silica, when silica particles grow on and within the surface of the polymer causing an expansion of the polymer sample. The brittle silica layer cannot expand with the flexible polymer, and the resulting strain causes cracking. The cracks arise during the treatment in the autoclave, because the thin silica layer on the floor of the crack and its round edges can only be the result of growing silica from the remaining SiCl_4 and water after the cracking of the surface.

On Figure 3b the second type of crack is visible. The silica layer, which is more brittle than the polymer, can form the type II crack during the handling of the films after the surface treatment. On the bottom of these cracks the polymer surface shows a well aligned fibrillar morphology (fibrils vertical to the crack) unlike the untreated polymer (Figure 1a). The same fibrillar morphology is shown in Figure 3c, but these fibrils have even been pulled out of the polymer surface by a silica sheet, which was not only cracked but also lifted off the polymer mechanically. These fibrils demonstrate an anchoring of the silica to the polymer. The relationship between fibrillation and the adhesion of materials on PTFE during delamination, is extensively discussed in ref. 17. In a subsequent publication the formation of a mixed layer of SiO_2 and fluoropolymer will be demonstrated by a combination of light microscopy, LVSEM and EDX-analysis (energy-dispersive X-ray analysis) of cross-sectioned films. From the micrographs, shown in Figure 3a-c, the thickness of the silica layer can only be estimated, this is best shown with micrograph Figure 3b. The corresponding picture was taken at an angle of 40° . Since the layer is not even but contains spherical structures, its thickness cannot be exactly determined, but only estimated to be between 1 and 1.2 μm .

In a previous study silica was deposited on porous PTFE films in order to hydrophilize them^{9,10}, using in principle the same approach as in this study. But instead of water vapour, liquid water was sprayed, under the relatively high pressure of 1100 kPa, over a short distance onto the polymer to hydrolyse the SiCl_4 in the earlier work. The advantage of using water vapour is the better mixing of the reaction partners, SiCl_4 and water, in a homogeneous reaction. This should lead to a faster reaction, thus not allowing the SiCl_4 to diffuse out of the polymer before it is hydrolysed,

condensed and fixed in the polymer. As a result not only porous PTFE-areas, as in the previous study, but also non-porous areas and even different non-porous perfluorinated polymer films can be permanently covered with silica.

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