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Methods of modification of the surface of PTFE nanoparticles with a purpose to increase their hydrophilic properties

The paper considers with three methods of modification of the surface of PTFE nanoparticles with a purpose to increase their hydrophilic properties: adsorption of esters of p-hydroxybenzoic acid; adsorption of branched fluorocarbon surfactant polymers containing perfluoroundecanoyoxy groups; and adsorption of fluorinated homopolymers and block copolymer. All three methods were analyzed in terms of their potential efficacy to provide a stable dispersion of sample of PTFE nanoparticles in polar solvents, and a preliminary conclusion that the method based on adsorption of fluorinated block copolymers containing blocks of pentafluorostyrene and acrylic acid seems to be most suitable for required purpose has been made.

Key words: nanoparticles, surface modification, adsorption, solvent, copolymer.

Introduction

Polytetrafluoroethylene (technical name fluorplastic4, F-4) is superior in the set of physicochemical and mechanical properties to all the known polymers. PTFE displays a high thermal stability, a high chemical resistance, a low friction coefficient, and a low surface energy. These properties, which are very important for some specific applications, together with the rubbing action, cause considerable disadvantages in applications in which adhesion-related problems are concerned. Since the materials with low surface energy can be used to prepare promising high-quality protective coatings, fluorocarbon in the molecular structure are characterized by several excellent properties. It is possible to use the polymers that contain fluorocarbon groups in the molecular structure to produce a surface to which some organisms could not adhere with tenacity, or from which the organisms could be removed easily. But the low surface energy of fluoropolymers and the difficulty in bonding them to the substrate make it necessary to utilize special adhesives or treatments in order to obtain the required adhesion to the substrate. Several techniques have been developed for modifying polymer surfaces to improve their dispersibility in solvent of paint and adhesion properties without altering their bulk properties.

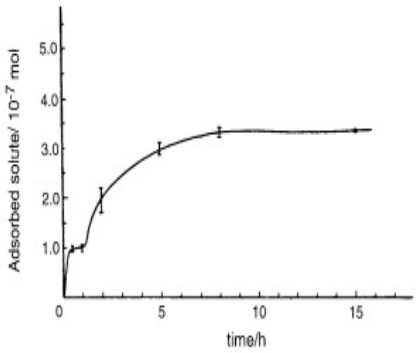
Analysis of the literature related to the surface treatment of PTFE with a purpose in increase polymer polarity which should provide the required increase in a dispersability of PTFE nanopowder shows the existence of several approaches. Most promising of them, in our opinion, are related to pure physical adsorption of one or several compounds on the surface of PTFE without chemical interaction of polymer chain with these compounds.

1. Physical adsorption of compounds on the surface of PTFE

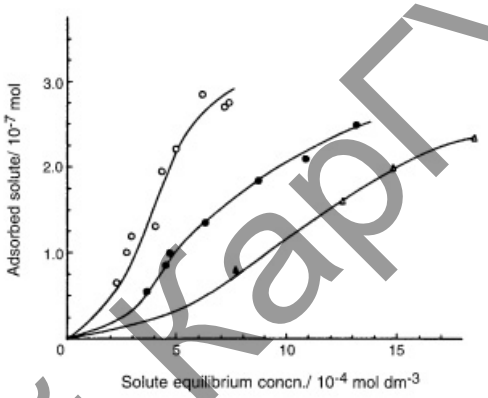
An important part of PTFE wide application arises from its stability and from being regarded as inert to adsorption [1]. Such properties can be attributed to the high stability of the C–F bond and to the display of both hydro- and oleophobicity by perfluorinated compounds [2, 3]. There have been, however, some reports

of sorption/adsorption on Teflon for compounds such as iron carbonyl, chloroform, acetic acid [4], ammonia [5] inorganic acids and bases [6], surfactants [7–11] and alkyl *p*-hydroxybenzoates [1]. In the case of amphiphilic molecules, contact angle measurements also revealed an increase in Teflon wettability due to the solute interaction with the polymer surface.

Adsorption of these relatively non-polar compounds, particularly *n*-propyl ester of *p*-hydroxybenzoic acid and several other esters on the surface of PTFE has been reported in paper [1]. The authors of paper [1] indicated that the most reproducible results were obtained when PTFE has been used not in form of powder, but in form of tubing. The time dependent extent of adsorption is shown in Fig. 1A for amyl ester of *p*-hydroxybenzoic acid (AEHBA).



A — Extent of solute removal as a function of contact time, for AEHBA in water at an initial concentration of 0.7 mM. Each point represents an average of, at least, two independent experiments



B — Adsorption isotherms for (Δ) propyl ester and (●) butyl ester of *p*-hydroxybenzoic acid and (o) AEHBA on the PTFE tubing, after 5 hours [1]

Figure 1

Figure 1A suggests that the process may be divided in two steps: the first, faster, occurring before 1 h of contact; and the second, slower, between 1 h and the plateau reached after 5 h. Keeping in mind that the size of the AEHBA molecule is 3.62A [12], and applying this data to the amount of solute removed at the first plateau of Fig. 1A, the area occupied by the solute molecules can be estimated as ca. 240 cm^2 which is close to the internal area provided by the tubing. On that account it is reasonable to suggest the picture of a flat solute adsorption onto the PTFE surface, leading to a monolayer, followed by a slower rearrangement. According to the data presented in Fig. 1A, the average area per solute molecule is reduced to a third after equilibration. Such a decrease might be caused by some solute clustering at the polymer surface or could be a reflection of some extent of solute penetration into the polymer.

Assuming the Einstein relation for molecular motion, and a diffusion coefficient around 10^{-8} cm^2 s^{-1}, the mean displacement of the solute molecules at 5 h would be near 0.02 cm. If a sorption process was occurring, one should expect much longer saturation times, as a reflection of larger mean displacements. Therefore, the authors [1] concluded that such a small displacement, together with a relatively short time for the attained saturation, suggests that the solute removal cannot be ascribed to a sorption process.

Figure 1B shows the isotherms for the adsorption process of three esters of *p*-hydroxybenzoic acid, obtained after 5 hours. These curves are upper-limited by the low solubility of the investigated compounds in water. For methyl and ethyl esters, the extent of adsorption was too small to be detected. The shape of the curves is consistent with the class of low affinity isotherms [13]. It might also suggest a cooperative nature for the process which could represent the solute reorientation on the polymer surface. The maximum amounts of removed solutes were small: 10, 5, and 3 %, for AEHBA, butyl ester and propyl ester of *p*-hydroxybenzoic acid, respectively[1].

Sorption processes are commonly observed in polymers and depend on the affinity between polymer and the solute. In the case of PTFE, it has been shown [14] that the swelling by organic solvents is related to their mutual affinity as described by the Hildebrand parameters, δ. Perfluorinated compounds have low d values, around 12–13 [15]. According to [1] the esters of *p*-hydroxybenzoic acid are somehow similar to 4-methyl and 4-octylresorcinol, which have δ values of 28.4 and 25.4 [15]. The results summarized in

Fig. 2B reveal that, besides the substantial difference in δ values, the solute–polymer interaction cannot be disregarded.

The preliminary observation of increased wettability of PTFE powder upon adsorption of the esters of *p*-hydroxybenzoic acid upon adsorption reported in paper [1] suggests that, although some extent of solute incorporation might occur, a significant amount solute molecules should remain on the polymer surface. These molecules, probably oriented with their polar moieties toward the aqueous solution and the apolar ones in contact with PTFE, would cause a decrease in the interfacial tension between the polymer and water. Therefore, besides the hydrophobic effect of the removal of apolar solutes from water, represented by the increase of solute removal along the homologous series, such interaction also conveys some contribution due to the decrease of the interfacial energy between PTFE and the polar liquid. Authors of paper [1] indicated that although similar observations have been already reported for surfactants, their results point out that solute–PTFE interaction should be taken into account even when considering smaller, but still apolar molecules.

2. Adsorption of polar fluoropolymers, containing perfluoroundecanoyloxy groups on the surface of PTFE

This interesting type of the treatment of PTFE firstly has been investigated in papers [16–18]. The purpose of these studies consisted of making the PTFE surface more suitable for biomedical applications, like ability of modification with bioactive molecules. It was emphasized [16] that fluorinated copolymers containing side-chains of perfluoroundecanoyloxy groups can play the role of surfactant. Their adsorption can provide a well-defined surface modification that is nondestructive to the PTFE surface and easier to perform than high-energy reactions such as plasma or chemical etching using alkyl lithium or benzoin dianion.

One concern, as with any approach to surface modification that involves noncovalent interactions, is the adhesion stability of the surfactant on the solid substrate. Adhesion stability can be improved by increasing the molecular weight of the surfactant, such as moving from classical molecular diblock surfactant structure [19] to polymeric systems, decreasing the entropy of the surfactant by adopting a branch or comblike structure, or by increasing hydrophobic–hydrophilic balance [20,21].

According to [16], these options are also consistent with the results from Fleer's self-consistent-field theory of polymer adsorption [22–24]. Some preliminary work [25, 26] has been performed on hydrophobic polymers like polyethylene and nonionic dextran surfactant polymers which demonstrated effective surface assembly at a solid/aqueous interface and useful interfacial properties, such as suppression of protein adsorption, which are highly beneficial for blood-contacting medical devices [27]. The polymer surfactants were composed of poly(vinylamine) with pendant dextran and alkanoyl groups. When adsorbed on a hydrophobic surface such as polyethylene, the alkanoyl side chains adhere to the hydrophobic substrate, while the dextran side chains are oriented into the aqueous environment to provide a biocompatible oligosaccharide interface.

However, it was shown that the existing surfactant polymers with hydrocarbon side chains readily adsorb on PTFE but do not show stable adhesion [16]. This observation suggests that favorable enthalpic, as well as entropic, changes may be important for achieving stable surfactant–PTFE adhesion. Accordingly, the authors [16–18] have designed surfactant polymers with fluorocarbon side chains, which would be expected to favor adsorption and strong adhesion on PTFE under aqueous solutions. They are more hydrophobic and have a larger molecular cross section than hydrocarbons [28, 29].

For instance, fluorocarbon surfactant polymers that adhere to PTFE surface under aqueous conditions and provide a stable oligosaccharide interface suitable for biomedical applications have been described [16]. The polymers, consisting of a poly(vinylamine) backbone with dextran and fluorocarbon side chains, were characterized by FT-IR, NMR, and XPS, with surface activity demonstrated by significant reductions in water surface tension at the air–water interface, and by XPS after modification and exposure to dynamic flow conditions over the shear stress range of 0–20 dyn/cm^2.

The general strategy for the synthesis is based on poly(vinylamine) (PVAm) chemistry. PVAm was obtained by method [25] from basic hydrolysis of poly(*N*-vinylformamide) (PNVF), which was prepared by free radical polymerization of *N*-vinylformamide in DMF with AIBN as the initiator. The molecular weight of PVAm (M_n ~ 35 000, M_w/M_n ~ 1.3) was deduced from that of PNVF assuming 100 % hydrolysis and no loss in the purification process. PVAm can be easily modified with a variety of functional groups, such as carboxylic acid, lactone, isocyanate, or aldehyde. Dextran molecules were attached to PVAm by reacting the amino groups with dextran lactone. Fluorocarbon branches were attached to the backbone by reacting the amino groups with perfluorocarbon succinimide.

Graft polymers with either hydrophobic fluorocarbon branches or hydrophilic dextran branches were synthesized, as well the complete fluorocarbon surfactant polymer. PVAm-FC11 was prepared by reacting the amine groups of PVAm with *N*-(perfluoroundecanoyloxyl)succinimide in methanol. The reaction of succinimide with amine is selective, so that hydroxyl groups on dextran do not need protection.

Unlike the synthesis of analogous hydrocarbon surfactant polymers, fluorocarbon surfactants cannot be synthesized by reacting PVAm with dextran lactone and succinimide simultaneously. Since the fluorosuccinimide reacts much faster with PVAm than does dextran lactone, the resulting PVAm-FC11 would precipitate, thus preventing further attachment of the hydrophilic dextran.

According to paper [16], while the dextran content is a constant for each surfactant polymer, the fluorocarbon branch density, determined by XPS analysis, increases from 15 to 45 mol % of reacted amines in the polymer backbone (Table 1). The structural information (x, y, and z) determined using XPS itself is in excellent agreement (±2 mol %) with the data in Table 1 obtained using the combination of NMR and XPS. In addition, there are many unreacted amine groups along the polymer backbone. This is attributed to steric inhibition effects of the attached bulky dextran molecules. However, any remaining unreacted amine groups can be capped by reaction with smaller molecules such as glucolactone or acetic succinimide, as was demonstrated in a paper [25].

Table 1

Fluorocarbon Surfactant Composition [16]

	PVAm(Dex:FC11) dextran:perfluoroundecanoyl ratio		
Composition	1:0.5	1:1	1:2
Mol wt[a](M_n)			
PVAm	35000	35000	35000
Surfactant	370000	397000	504000
Composition (mol %)			
Dextran[b]	22	22	22
Perfluoroundecanoyl[c]	15	21	45
Amine	63	57	33
Groups per surfactant			
Dextran	179	179	179
Perfluoroundecanoyl	122	171	366
Amine	512	464	269

Notes: [a] Based on GPC/light scattering of poly(*N*-vinylformamide) (Mw/Mn = 1.3). [b]Based on NMR data. [c]Based on XPS data.

The surface-active properties of fluorocarbon surfactants at the air/water interface were obtained from surface tension measurements. The surface tension data were plotted against the logarithm of concentration, as shown in Fig. 2. Surfactant efficiency, defined as $\log(1/C)_\pi = 20$, where C is the bulk concentration in mol/L, measures the surfactant concentration needed to lower water surface tension by 20 dyn/cm. The efficiency for surfactants 1:0.5, 1:1, and 1:2 is estimated to be around 4.7, 4.8, and 5.2, respectively, as determined from the data in Fig. 2. The increased content of fluorocarbon branches in surfactant 1:2 provides a greater thermodynamic driving force for surfactant assembly at the air/water interface and thus is more efficient in reducing water surface tension. In terms of effectiveness, defined by the minimum surface tension, all three polymers are very similar up to the solubility limit. This suggests similar fluorocarbon coverage at the interface, since effectiveness depends on the van der Waals attractions of the hydrophobic groups in the surfactants [30]. No critical micelle phenomenon for all three surfactants was observed over the measured concentration range. This result is consistent with previous observations for hydrocarbon surfactant polymers [25].

The authors of paper [16] investigated the surface adsorption and adhesion on PTFE. In the presence of a solid surface, surfactants in water can minimize interfacial energy by forming micelles, assembling at air–water interface, and by adsorbing at the solid/water interface. XPS analysis (Fig. 3) shows surfactant adsorption on PTFE obtained under different shear stress conditions. For comparisons between each surfactant, the N_{1s} atomic percent is normalized against the value obtained for the respective bulk polymer. For surfactant polymer PVAm(Dex: FC11) with branch ratios ranging from 1:0.5 to 1:2, the nitrogen percentage at 0 dyn/cm^2 increases monotonically from 40 % to 90 %, indicating increasing amount of adsorbed surfactant.

This follows the same order as the results obtained for surface activity at the air/water interface. These finding also are consistent with theoretical considerations, which show adsorption increases with increased hydrophobic content [22–24]. Electrostatic interaction is not a significant factor in controlling surfactant adsorption, since zeta potentials for all three surfactants measured in PBS solution are close to 0 mV.

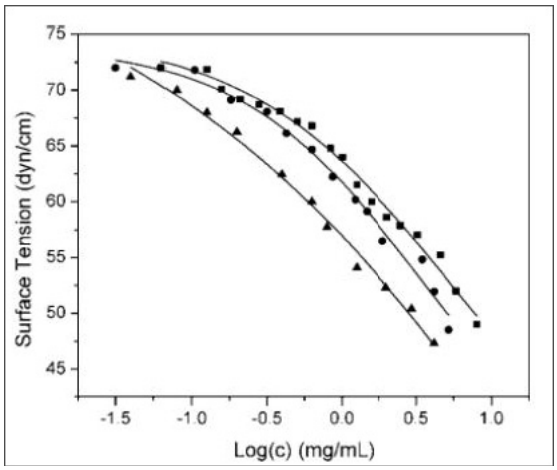


Figure 2. Surface tension of fluorocarbon surfactant polymers in aqueous solutions. The dextran to fluorocarbon branch ratio in PVAm(Dex:FC11) is held constant at three different values: 1:0.5 (■); 1:1 (•); 1:2 (▲) [16]

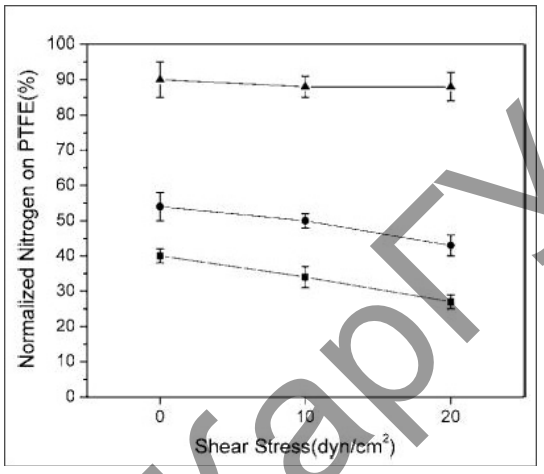


Figure 3. Normalized nitrogen percentage on PTFE as a function of shear stress experienced by the surfactant polymer. The dextran to fluorocarbon branch ratio in PVAm(Dex: FC11) is held constant at three different values: 1:0.5 (■), 1:1 (•), and 1:2 (▲) [16]

The adhesion of surfactants on PTFE was investigated by exposing surface adsorbed surfactant to different applied shear stress for 1 h. For the surfactant with a dextran:fluorocarbon branch ratio of 1:2, there is no significant change in the amount of adsorbed surfactant polymer after exposure to shear stress ranging from 0 to 20 dyn/cm^2. This indicates that the adsorption was not kinetically reversible on the time scale of the measurements. In contrast, the amount of adsorbed surfactant decreases by 32 % and 20 % for surfactants with branch ratios of 1:0.5 and 1:1, respectively, over the same shear stress range. The results obtained under applied shear stress suggest that increasing the fluorocarbon branch density correlates with increasing surfactant adhesion on PTFE. Consequently, the fluorocarbon branch density appears to be an important factor in controlling surfactant polymer adsorption and adhesion on PTFE.

The stability of adsorbed comblike polymer surfactants on solid polymer substrates will depend on many factors, including polymer backbone molecular weight, the length and ratios of the hydrophobic and hydrophilic branches, and surfactant–surfactant and surfactant–substrate intermolecular interactions. The chemical similarity between the fluorocarbon branches and the PTFE is designed to improve the thermodynamic compatibility between the surfactant and the substrate compared with the hydrocarbon branches used previously. The fluorocarbon branch also possesses a symmetric cylindrical shape, which should match the geometry of surface fluorocarbon chains in PTFE and increase adhesive intermolecular contact [16].

We would like to point out that the synthesis of fluorinated copolymers containing side-chains of perfluoroundecanoyloxy groups described in [16] is rather complicated multistep procedure which can potentially limit its practical application. With this respect the approach investigated in PhD study [31] related to adsorption of less complex fluorinated homopolymers and, especially, block copolymers on the surface of PTFE (which will be considered in next section) could be more suitable for modification of PTFE nanoparticles with a purpose of improving their ability to be dispersed in polar media.

3. Adsorption of fluorinated homopolymers and block copolymers on the surface of PTFE

Adsorption of fluorinated homopolymers, such as poly(pentafluorostyrene) (PFS), poly(tetrafluoropropylmethacrylate) (PTFPMA) and poly(tetrafluoropropyl acrylate) (PTFPA) (Fig. 4) on the surface of PTFE films has been investigated [31]. Table 2 summarizes data related to molecular weight of investigated polymers and amount of fluorine atoms on the polymer chain which was calculated from the molecular mass of polymer and structure of repeating units.

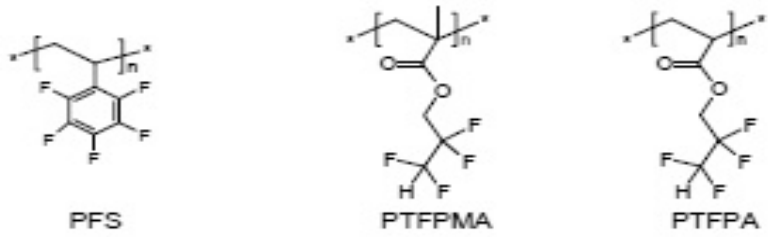


Figure 4. Chemical structure of fluorinated homopolymers used for modification of PTFE surface [31]

This study was carried out by soaking the PTFE films in 1mg/ml polymer solution in one of four solvents: dichloromethane (DCM), fluorobenzene (FB) and methylethyl ketone (MEK) and dimethylformamide (DMF) for about 16 hrs then washing three times with the same solvent used for soaking and then dried. The films were analyzed by X-ray photoelectron spectroscopy (XPS) and contact angle measurements.

Table 2

Molecular weight of investigated polymers and amount of fluorine atoms on the polymer chain [31]

Sample	Polymer	M_n	n	PDI	No. F[a]
4B	PFS	27417	140	1.06	700
4C	PTFPMA	38951	193	1.13	773
4D	PTFPA	39959	213	1.06	853

Note. *a* — Number of fluorines on the polymer chain was calculated from the M_n and structure of repeating units.

According to the XPS survey spectra, the untreated PTFE (sample 4A, it is not shown in Table 2) and PFS-absorbed (sample 4B, Table 2) show only presence of F and C, whereas a small amount of O was observed on the PTFPMA- and PTFPA-adsorbed PTFE films (samples 4C and 4D, respectively). This is in agreement with the chemical structures. The atomic concentrations of all samples are summarized in Table 3. The theoretical values of the F/C ratios of PTFE, PFS, PTFPMA and PTFPA are 2, 0.63, 0.57 and 0.67, respectively. Therefore adsorption of these polymers should decrease the F/C ratios. The untreated PTFE showed an F/C ratio of 2.2 which is slightly higher than the theoretical.

Adsorption of PFS reduced the F/C ratios to 1.2–1.5, depending on the solvent used. In the case of PTFPMA and PTFPA, the presence of O can also be used to identify polymer adsorption. Both polymers showed the appearance of O (1.1–1.3 %) when adsorbed in DCM with a concomitant reduction in F/C ratios to 1.2–1.3. When FB was used, there was also some O (0.7–0.8 %) seen as well as a reduction in the F/C ratios (1.5–1.6). But these changes were smaller than those obtained in DCM. In case of MEK, there was no O, and the F/C ratios were high (1.7–1.8).

The high resolution C1s XPS spectra were found to be useful for identifying the polymer adsorption. Figure 5 shows the high resolution C1s XPS spectra of untreated and PFS adsorbed PTFE films [31].

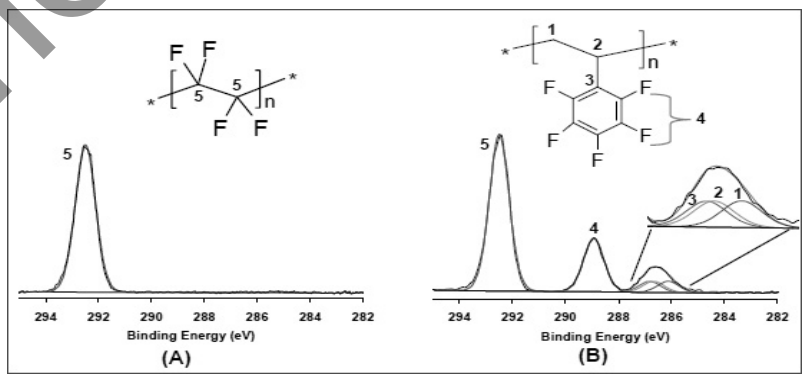


Figure 5. C1s narrow scans of PTFE films (A) untreated (sample 4A) and (B) PFS adsorbed (sample $4B_3$)

The peak at 292.5 eV corresponds to the $C–F_2$ from PTFE. Untreated PTFE showed trace amounts of aliphatic carbons (0.7 %) at 285.3 eV, indicating the presence of a small hydrocarbon impurity. The C1s

spectrum of the PFS adsorbed PTFE surface can be curve-fitted using five peak components with binding energies at about 286.1, 286.7, 286.8, 288.9, and 292.5 eV. These are attributed to C*–H (peak 1), C*–C_6H_5 (peak 2), C*–CF (aromatic, peak 3), C*–F (aromatic, peak 4) and C*–F_2 (PTFE, peak 5) species, respectively [32, 33].

Three types of fluorinated homopolymers were tested for adsorption onto PTFE in different solvents (DCM, FB and MEK). PFS showed the greatest adsorption onto PTFE in all solvents. From XPS, the highest PFS adsorption was found when MEK was used as the solvent. For PTFPMA and PTFPA, some adsorption was observed only when DCM was used. Since these polymers had higher amounts of fluorine atoms in each polymer chain (773 and 853, respectively) compared to PFS (700), this would appear to indicate that the structure of the repeating unit affect the adsorption.

According to [31], there are two factors that need to be considered regarding the solvent: swelling of PTFE and solubility of the polymer (which affects both adsorption and desorption). Since the same solvent was used for adsorption and washing, a good solvent for polymer enhances the desorption during washing. A good swilling solvent for PTFE allows the fluoropolymers to entangle and anchor well. However, it is also possible that this solvent will remove adsorbed polymers in the washing step.

In paper [34] the swelling of PTFE film in different solvents has been investigated. The sorbed liquid was found to be 0.35 % for DCM, 0.15 % for methanol, and 0.23 % for benzene. Thus DCM was the best solvent. From this trend, it can be predicted that PTFE swelling is higher in DCM than in MEK. It is also possible that FB is a better swelling agent than benzene.

It was found that although both DCM and fluorobenzene swell PTFE, the results may indicate that interaction between the fluorinated solvent (i.e. FB) and the polymers (PTFPMA and PTFPA) are so strong, they prevent adsorption onto the PTFE [31, 33]. There was no adsorption of these polymers when MEK was used as the solvent, this is in agreement with the prediction that MEK is a low-swelling solvent for PTFE.

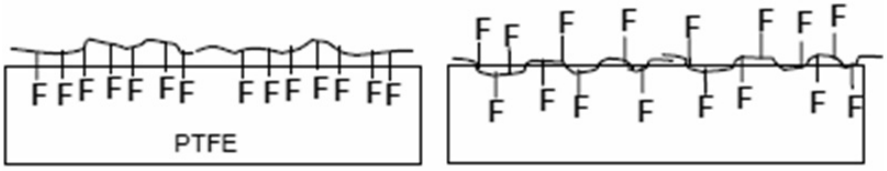
The contact angle measurements of sample 4C1 (PTFPMA adsorbed PTFE in DCM) was carried out. The advancing and receding angles were found to be 97 +/–3° and 91 +/–4°, respectively that were slightly lower than those of PTFE (~110°) (shown in Table 3).

Table 3

Advancing and receding water contact angles of polymer-adsorbed PTFE films [31]

Sample	Adsorbed Polymers	Deposition Solvent	Advancing Angle (°)	Receding Angle (°)	Hysteresis (°)
4A[a]	–	–	109 ± 6	111 ± 6	
$4C_1$	PTFPMA	DCM	97 ± 3	91 ± 4	6 ± 5
4F	P(FS_{101}-b-tBA_{237})	MEK	88 ± 2	86 ± 5	2 ± 5
4G	P(FS_{101}-b-tBA_{141})	MEK	98 ± 3	90 ± 6	8 ± 7
4H	P(FS_{101}-b-AA_{237})	DMF	91 ± 6	31 ± 3	60 ± 7
$4I_1$	P(FS_{101}-b-AA_{141})	DMF	88 ± 5	28 ± 3	60 ± 6
$4I_2$	P(FS_{101}-b-AA_{141})	MEK	101 ± 4	49 ± 3	52 ± 5

The author of study [31] compared the contact angle of PTFPMA-adsorbed PTFE with contacted angle of poly (*tert*-butyl acrylate), P*t*BA. If only the fluorine atoms of the PTFPMA were adsorbed into the PTFE chains (Fig. 6A), the contact angle of this surface would be expected to be close to that of P*t*BA (88°), assuming uniform polymer coverage since XPS showed that the total atomic C% from the adsorbed polymer is over 10 %. The fact that the contact angle obtained was higher Θ_{adv}= 97°), could indicate that the whole PTFPMA chain is in fact entangled (Fig. 6B).



A B

Figure 6. Schematic representation of fluoropolymer adsorption onto PTFE by (A) fluorine adsorption and (B) chain entanglement

In the case of PFS, the highest adsorption was observed when MEK was used. According to paper [35], the solubility of linear PFS can be dissolved in FB, MEK and DCM up to concentration 0.417, 0.143, and 0.009 g per gram of solvent at room temperature. This support the suggestion that in FB, PFS is well solvated and in a stretched conformation, whereas in DCM, the chains are more coiled. In MEK, although the chains are possibly only slightly coiled, the swelling of the PTFE film is less, therefore more chains are packed on the surface, compared to those adsorbed from DCM (Fig. 7).

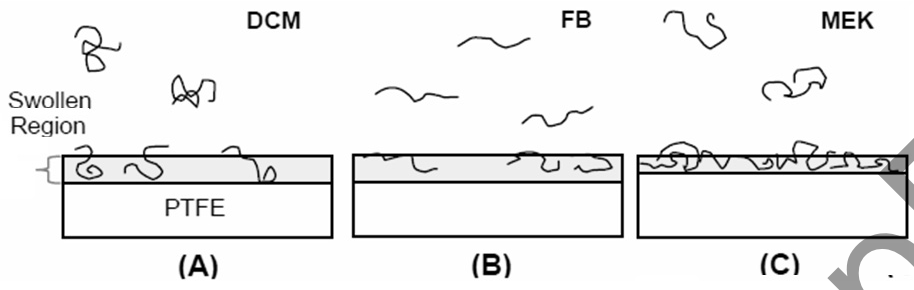


Figure 7. Possible adsorption behavior of PFS onto PTFE from different solvents

According to [31], the most important interactions for fluoropolymer adsorptions are hydrophobic and fluorine-fluorine interactions. PFS was the most hydrophobic polymer studied and it showed the best adsorption. It is also possible that in PFS, fluorine atoms are easier to polarize due to the presence of the aromatic ring when in close contact with the PTFE. Therefore, the fluorine-fluorine interaction between PFS and PTFE becomes stronger than for the other polymers. Since PTFPMA and PTFPA contain carbonyl groups (i.e. they are more hydrophilic), some repulsion between these polymers and hyghly hydrophobic PTFE may occur. This results in competition with the fluorine-fluorine interactions.

Block copolymers are known to exhibit similar behavior as surfactants. The adsorption of block copolymers onro substrates, including polymers, have been widely investigated [36]. The driving force for adsorption is dependent on the nature of the system. Surface micellisation and micelle adsorption of block copolymers onto hydrophilic and hydrophobic surfaces have been well studied [37]. Greater rates of adsorption for micellar solutions over non-micellar solution have been observed.

The micellisation of block copolymer of polystyrene and polyacrylic acid, P(S-b-AA) in DMF, which is a good solvent for both chains, and toluene, which is only good for PAA has been investigated [38]. It was found that the number-average hydrodynamic diameters (D_H) of P(S_{153}-b-AA_{175}) and P(S_{153}-b-AA_{234}) in DMF were 6.2 and 6.3 nm, respectively, whereas in toluene, they were 42.5 and 44.5.

In study [31] it was shown that the D_H of the P(FS-b-AA) block copolymers in DMF and MEK were between 21–30, indicating formation of some kind of aggregates. DMF is a good solvent only for the PAA segments, whereas MEK is good only for PFS segments. Therefore, it could be predicted that inverse-structures of aggregates in DMF and MEK occur with the outer layer PAA segments in DMF, and PFS segments in MEK.

Both P(FS-b-AA)-attached films prepared in DMF showed advancing angles of ~90° (Table 3). This suggests that the aggregates with PAA segments as the outer layer possibly reorganized when adsorbed and dried onto PTFE exposing the PFS segments on the surface in order to reduce surface tension (Fig. 8 and 9) [31].

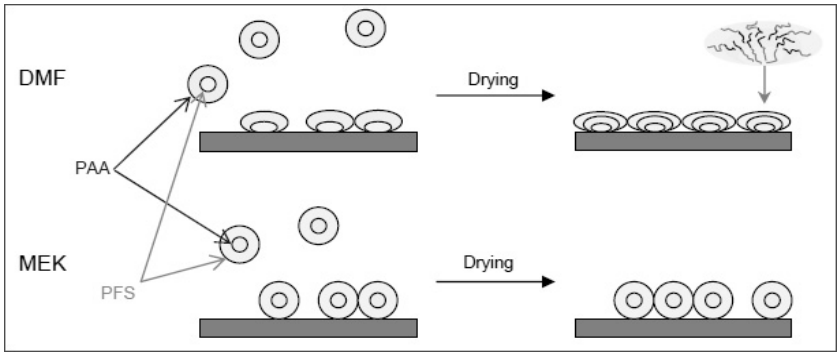


Figure 8. Aggregate adsorption onto PTFE surfaces in different solvents

Receding angles of these surfaces were ~30°, indicating some reorganization of the polymer chains during the contact angle measurements (Table 3). After soaking these samples in water, the advancing angles reduced to 73° (~17° decrease). This also suggests the existence of flexible polymer chains on the PTFE surfaces [31].

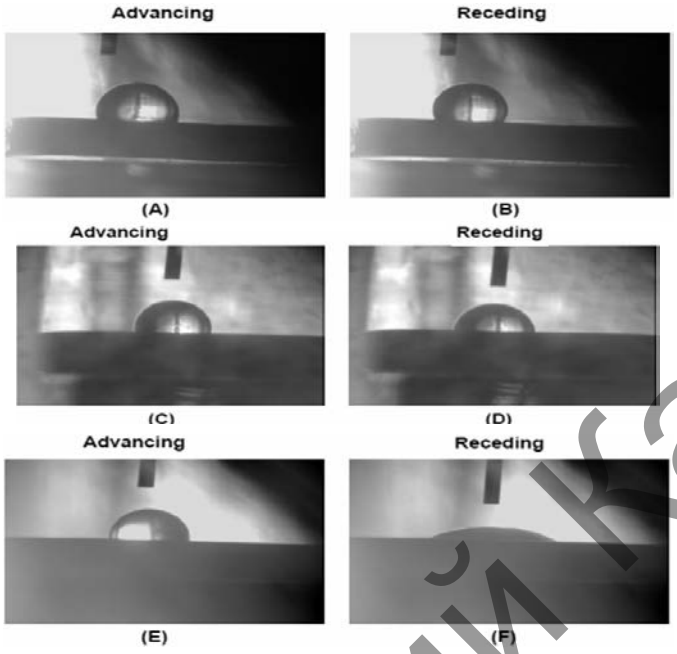


Figure 9. Water droplet profiles on the surfaces of untreated PTFE (Sample 4A, Table 2) (A) advancing and (B) receding. $P(FS_{101}\text{-b-}tBA_{141})$ adsorbed PTFE (sample 4G) (C) advancing and (D) receding, and $P(FS_{101}\text{-b-}AA_{141})$ adsorbed PTFE (Sample $4I_1$) (E) advancing and (F) receding [31]

Copolymer $P(FS_{101}\text{-b-}AA_{141})$ adsorbed onto PTFE in MEK showed the highest advancing angle (101°). In MEK, aggregates with PFS segments in the outer layer possibly adsorbed onto PTFE without structural change. The receding angle was 50°, and did not change after soaking in water, which indicates that full rearrangement occurs during the contact angle measurement.

Hydrophilicity/hydrophobicity of the PFS containing amphiphilic block copolymers adsorbed PTFE is found to be reversibly tuneable depending on the environment (e.g. water vs air). The author of study [31] pointed out that since the carboxylic acid groups of these chains are free, it is suited for further modification of these group (neutralization with metal, for example).

4. Synthesis of fluorinated block copolymers and possibility of scaling up

According to [31] the best way to synthesize fluorinated block copolymers includes using the Reversible Addition Fragmentation Chain Transfer (RAFT). It is a radical polymerization which uses a thiocarbonylthio compound added which acts as a highly efficient RAFT agent [39]. This transfer of the S=C(Z)S-moiety between the active and dormant chains maintains the living characteristics of the polymerization.

The synthesis of PEPDTA can be performed following published procedure [40, 41]. Benzyl chloride (20 g) was added dropwise to a mixture of magnesium turnings (3.75 g) in dry diethyl ether (100 ml). Following the vigorous initial reaction, the solution was refluxed for 3 h to ensure complete reaction. The mixture was then chilled and carbon disulfide (12.0 g) was added dropwise over 30 min, and then the mixture stirred at 0 °C for the following 2 h. The mixture was then poured onto ice-water (300 ml) and the aqueous portion collected following three washes with diethyl ether. A final layer of diethyl ether was added, and the mixture acidified using 30 % aqueous HCl. Phenyldithioacetic acid (~ 7 g) was collected *via* rotary evaporation of the ether. The acid was then reacted with styrene (9.0 g), with a small amount of acid catalyst (toluene-*p*-sulfonic acid) in chloroform (10 g). The product was then precipitated in cold methanol and recrystallised from methanol as fine yellow crystals (3.2 g).

The homopolymerization of pentafluorostyrene (FS) was carried out in presens of PEPDTA and 1,1'-azobis(cyclohexanecarbonitrile) (ABCHC) at temperature 80°C and concentration of PEPDTA 28 mM and 56 mM. In both cases the ratio of concentration [PEPDTA]: [ABCHC] was equal to 10:1.

It was found [32] that most consistent results have been obtained when ethyl acetate has been used as the solvent for block copolymerization. GPC chromatograms of P(FS-b-*t*BA) obtained from polymers synthesized in ethyl acetate showed an unimodal distribution as well as the presence of RAFT end-groups over the whole PFS distribution.

Conclusions

Three methods of modification of the surface of PTFE nanoparticles with a purpose to increase their hydrophilic properties have been described:

a) Adsorption of esters of *p*-hydroxybenzoic acid;

b) Adsorption of branched fluorocarbon surfactant polymers containing perfluoroundecanoyloxy groups;

c) Adsorption of fluorinated homopolymers and block copolymers.

The basics of all three approaches have been described and their potential advantages and disadvantages in terms of feasibility for creation of stable dispersions of PTFE nanoparticles in polar liquid media have been considered.

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Сутарқыштығын көтермелеу мақсатымен политетрафторэтилен (ПТЭФ) нанобөлшек бетінің түрөзгертушілік әдістері

Политетрафторэтилен (ПТФЭ) нанобөлшек гидрофилді қасиеттерін көтермелеу мақсатында оның бетінің түрөзгертушілігінің үш әдісі қарастырылған: *n*-гидроксибензойлық қышқыл эфирінің адсорбциясы; беттік-белсенді перфтордекан окситоптарын, фтор гомополимерді қамтылған айыр фторкөміртегі полимердің адсорбциясы және блок-қосполимерлер адсорбциясы. Барлық үш әдіс, оның әлеуетті тиімділігіне қарамастан, сараланған болатын, ПТФЭ ерігіш өрістерінде тұрақты нанобөлшектік дисперсиясымен қамтамасыз етуге пентафторстирол блоктарын құрайтын блок-қосполимерлер адсорбциясында негізделген әдіс және акрилдық қышқылдары осы мақсаттар үшін лайықты болып көрінетіндігі жайлы қорытынды жасалған.

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Методы модификации поверхности ПТФЭ наночастиц с целью повышения их гидрофильности

С целью повышения гидрофильных свойств наночастиц ПТФЭ рассмотрены три метода модификации их поверхности: адсорбция эфира *n*-гидроксибензойной кислоты; адсорбция разветвленных фторуглеродных полимеров, содержащих поверхностно-активные перфтордеканоксигруппы, а также адсорбция фторсодержащих гомополимеров и блок-сополимеров. Все три метода были проанализированы с точки зрения их потенциальной эффективности, чтобы обеспечить стабильную дисперсию наночастиц ПТФЭ в полярных растворителях. Авторами сделан предварительный вывод о том, что метод, основанный на адсорбции фторсодержащих блок-сополимеров, содержащих блоки пентафторстирола и акриловой кислоты, представляется наиболее подходящим для данных целей.