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Master thesis report
Crosslinked fluoropolymers
Tvärbundna fluoropolymerer

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Abstract

Fluoropolymers, and especially PTFE, have impressive properties in terms of chemical, electric or thermal inertness. However, this inertness gives to this material low mechanical properties. This major drawback comes from the low intermolecular affinity of PTFE. Several attempts to crosslink this material have been made since the 1970's in order to transform PTFE into a strong material. These processes can be surface treatments or bulk treatments. This report intends to present these various ways to create a crosslinked fluoropolymer and then to explore the plasma modification of PTFE and FEP.

Several surface properties of these materials are studied, including adhesion and contact angle of limonene, a terpenic liquid. Several hypotheses are made in order to explain the behaviour of plasma-modified fluoropolymers. These assumptions are then tested via close observation of the polymer surfaces using visual inspection and scanning electron microscopy.

The major parameters of the plasma process are studied in order to determine their respective effects on the studied properties. This leads to very impressive and complex effects that are described in the sections 3 and 4 for respectively the macroscopic behaviour of the modified fluoropolymers and the microscopic observations of the surfaces.

These experiments seem to imply that plasma modification of fluoropolymers has an effect on

1. the hydrophility of the chains

2. the surface roughness

3. and can also lead to chain scission if the treatment energy is too high.

These effects has also been observed with crosslinking techniques. An increased surface roughness is also observed during plasma sputtering of fluoropolymers, which is the creation of a fluoropolymer surface under low pressure of a fluorinated gas, like tetrafluoroethylene. The last one is reported to occur for bulk crosslinking made by irradiation.

Sammanfattningen

Fluorpolymerer, och särskilt PTFE, har imponerande egenskaper vad gäller kemisk-, värme- och elektrisktålighet. Emellertid får denna tålighet på bekostnad av materialens dåliga mekaniska egenskaper. Detta beror på fluoropolymerers svaga intermolekylara krafter. Försok att tvärbunda PTFE gjordes från och med 1970-talet och den första att förstå att det var möjligt att tvärbunda PTFE var Tutiya år 1972. Dessa försök gjordes för att ge PTFE bättre mekaniska egenskaper. Dessa processer kan modifiera hela materialet eller bara ytan. Denna rapport presenterar olika tvärbundningprocesser och fokuserar speciellt på plasma modifierade PTFE och FEP.

Olika ytors egenskaper studeras. Egenskaperna är vidhäftning och kontaktvinkeln mellan materialet och limonen, en terpen. Några hypoteser presenteras för att förklara de modifierade fluorpolymerernas uppträdanden. Dessa antagande testas genom både visuall examinering och svep elektron mikroskopi.

Plasmas största parametrarna studerades så respektive inflytanden på studerande egenskaperna bestämdes. Effeketerna beskrivs i 3:e och 4:e delarna. Den 3:e delen beskriver makroskopiska och den 4:e mikroskopiska egenskaper.

Plasma modifierade fluorpolymerer blir mer hydrofila och får en grovre yta och kan vidkänna kedjenedbrytning. Dessa effekter kan också observeras för olika tekniker. Till exempel erhålls en grovre yta med plasma sputtering. Kedjenedbrytning erhålls vid gamma strålning.

1 Introduction

Polytetrafluoroethylene (PTFE) has superior properties in a large broad of properties. These properties include high chemical, heat resistance or high electric insulation. Indeed, these properties belongs, being more or less developed, to all the fluoropolymers (FPs). Their high chemical resistance comes from the low affinity of PTFE molecules to any kind of chemical reaction. This low affinity leads to a major drawback, which is the quite low mechanical resistance of this material. Another major drawback of PTFE is its low radiation resistance.

Indeed, as early as the 1950s [CHA 60], it has been understood that high-energy radiation with dosage as low as some kGy can lead to severe damages to its useful properties. Since it has a very high sensitivity to radiations, PTFE has been considered as the typical radiation degradative polymer. Therefore, no way was seen to transform PTFE into a radiation-resistant and a mechanically stronger polymer.

The decay of the properties of PTFE was assigned to the radiation induced chain scission occurring that leads to a lowering of molecular weight. This loss of molecular weight wasn't overrun by a crosslinking the new-formed radicals could have started. However, Tutiya [TUT 72] observed, for a high temperature (over melt temperature) that irradiated PTFE has an abnormal behaviour but concluded to a change of morphology due to chain scission. Since then, these abnormal behaviours slowly grow up and the possibility of radiation crosslink PTFE started to be a subject of discussion. In 1993, Oshima *et al.* and Sun *et al.* (respectively [OSH 95] and [SUN 94]) separately gathered enough information and evidences in order to conclude to the feasibility of radiation crosslinking of PTFE and to determine some very interesting properties of this material.

A point needs to be said on this feasibility. Even if it is feasible, PTFE still undergoes chain scission under irradiation. Therefore, irradiating a sample of PTFE leads to a better material under the condition that crosslinking is faster than chain scission. This condition is obtained if, according to the authors previously cited, PTFE is treated at a temperature over its melt temperature, around 600K, and not over 673 K. The process window is therefore narrow and it gets even narrower if one considers the fact that the interest of crosslinking depends on the dose of radiations.

However, since these early works that demonstrated the feasibility of crosslink PTFE with a radiation treatment, other works has been done that demonstrated the possibility to make a crosslink FP *via* plasma processing. New works seem to demonstrate that a more "classical" chemical way to have FP crosslink is feasible.

The following sections aim at presenting the different ways to fulfil the goal of crosslinking FPs. All present known ways and yet prospective ways are studied and some remarks are expressed on the different articles already studied.

1.1 Chemical crosslinking

It is well known that treating a polymer *via* plasma can make its surface crosslink or can lead also to insert reactive moieties onto its surface, for more details, see section 1.3 page 7. These moieties can be, for example, radicals made of the polymer, or, if the plasma contains some reactive species, the corresponding radicals (e.g. $OO*$) or some chemical functions, like carboxylic acids. Using this
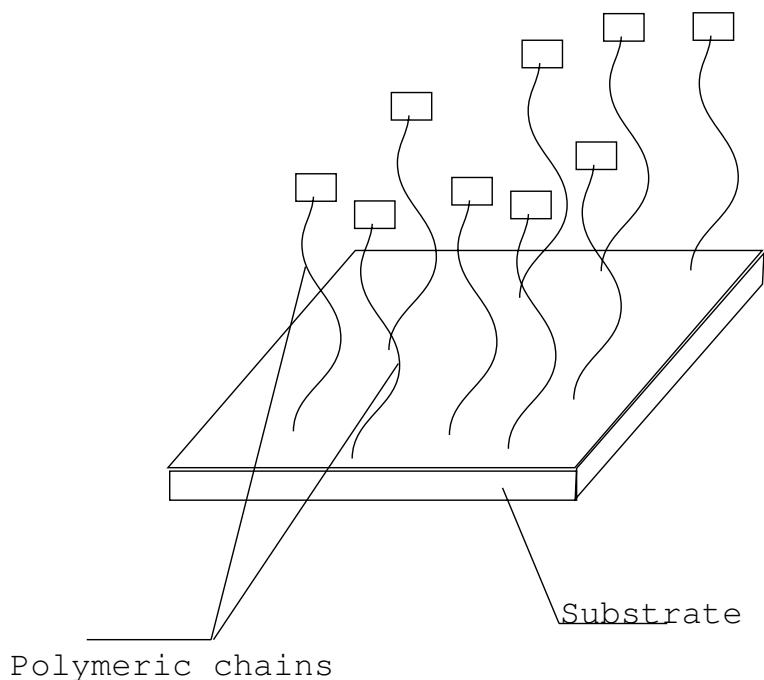
Figure 1: Product obtained by "graft-copolymerisation" on an inert solid

technique, as in [HED 98] or [YUQ 99], one can prepare a mechanically strong crosslinked polymer in order to, on a second step make a FP graft copolymerise on it.

Furthermore, the method developed by Devaux *et al.* [DVX 02] can lead to think it is possible to "graft-copolymerise" any polymer, e.g. PTFE, on any surface or material, not only a polymer one. This method creates some counter radicals at the surface on an inert solid and then have them react with styrene in order to create chains of polystyrene (PS). PS chains form a "brush" over the surface of the material, see figure 1 page 5.

One can imagine using this technique with any FP in order to create a smooth, chemically inert surface on the material. The substrate will give to the composite its mechanical properties. Moreover, on the opposite of what can be seen sometimes with Teflon© linings, the lining should be able to support high shear since each molecule is chemically bonded to the substrate.

It should be underlined that this operation, *i.e.* grafting a FP to another material by this method had not yet been realised according to the information available to the author at the date of writing.

1.2 Irradiation crosslinking

1.2.1 Overall presentation

More than 30 years ago, Tutiya in 1972 observed a response in terms of mechanical properties to an irradiation of PTFE at high temperatures but he didn't talk of crosslinking at this time. Indeed, PTFE was considered as a degradative

polymer for irradiation and no crosslinking was ever believed as possible for PTFE *via* irradiation. Studies existed at that time in order to try to improve the resistance of PTFE to irradiation. Indeed, PTFE shows only a poor resistance against radiations. Crosslinking of PTFE has been first reported as a possibility by Sun *et al.* [SUN94]. Results were soon found to be astonishing, since this treatment improved both mechanical and radiation resistances of the material. From this time numerous articles have been written on the subject, especially originating from the Japan Atomic Energy Research Institute (e.g. [OSH 95], [OSH 97] or [KAT 99]). These studies covered a broad array of fields linked to this new polymer, the radiation crosslinked PTFE (RX-PTFE). An interesting and main difference between irradiation and other ways to crosslink PTFE is that irradiation is not just a surface treatment. One can treat a bulk material whereas plasma is only able to create a film with a thickness around 1 mm (see section 1.3 on page 7) and chemistry needs a copolymer to graft on the PTFE chains (see section 1.1 on page 4). The thickness of the crosslinked PTFE will then be only one molecule long.

This crosslinking has been successfully experimented with, as a source of energy, either a γ-ray source, like ^{60}Co, or an electron beam (EB). All the studies were based, except the first ones, which deal with the possibility of this crosslinking ([SUN 94] and [OSH 95]), on a protocol involving a melt PTFE for crosslinking. As stated above, RX-PTFE was incidentally discovered while researchers tried to improve its resistance against radiation. It is therefore logical that studies were pursued on the radiation resistance of RX-PTFE. It soon appeared [OSH 97] that radiation made radicals were quite time and temperature-stable in both PTFE and RX-PTFE in vacuum. This may be explained *via* the stabilising effect of the highly electronegative fluoride atoms of the matrix on the radicals.

1.2.2 Differences between EB and γ-ray crosslinking

Both EB and γ-ray crosslinking allow preparing RX-PTFE but the protocols used by authors are different in terms of energy doses and time of processing. Therefore, a question is whether these differences leads to noticeable differences in terms of the properties of the final material or these differences are here to overcome the differences in terms of sensitivity of the PTFE to the two different energy sources. Not a lot of data can be gathered for trying to determine an answer to this question, but, if one compares precisely the different data from [OSH 95], it seems that, under a comparable treatment in terms of temperature and dose, a γ-ray treated PTFE will have an elongation at break about 50% higher than the one of an EB treated PTFE. On the other hand, an EB treated PTFE will have a tensile strength about twice as high as the γ-ray treated PTFE's one. These results come from two points of comparison for each property that is a dose of 5 kGy and an irradiation temperature of whether 340¡C or room temperature.

If these values can be interpolated, one shall say that EB-treated PTFE seems to be more crosslinked than the γ-ray one for a same energy under the same temperature. The reason why this phenomenon happens seems unobvious. One may think it is due to a better efficiency of the electron beam, *via* a "pool" effect, *i.e.* an electron can break away a bonding by bouncing on it and then break another one.

1.3 Plasma crosslinking

1.3.1 Overall presentation

Plasma crosslinking of FPs can be done *via* two main ways.

1. Either a virgin, without any FPs, surface is bombarded with a plasma containing fluoromonomers. This method is known as plasma polymerisation. A description of the process can be found in [BIE 00]. This method, also known as sputtering can be done with bombarding a target with plasma made of a noble gas (Ar, He) and monomers or with plasma made of pure monomers. In the latter, also known as self-sputtering, argon will be used only at the beginning of the deposition in order to initiate the discharge.

2. Either a block of FPs is bombarded with a noble gas. One talks there of plasma crosslinking. This bombing, that can be done using ionic gas or only activated species, leads to a crosslinking of the surface of the polymer. If one uses a non-ionic gas, the method is then called the CASING effect, or Crosslinking *via* Activated Species of INert Gases as described in [YAS 01]. An overview of this method is the subject of the subsection 1.3.2 page 7.

Since plasma crosslinking used relatively heavy particles (noble gases, mainly Ar and eventually another atmospheric gas), the depth of penetration, and then the depth where crosslinking occurs, is quite low. This treatment leads only to a surface modification of the material. On the other hand, plasma polymerisation leads no more to a bulk crosslinked FPs. Indeed, this process is quite slow and needs an electronic field to be created. Since polymers do not lead electricity, the thickness of the created film is limited by the power of the electric field. For both kind of plasma processing, a thickness of some thousands of Å(tenths of μm) seems to be the limit.

Plasma treatment of any polymer, including FPs, can lead, if the atmosphere is partly composed of reactive gases, to the formation of reactive moieties that can be used for further treatment *via* chemical reactions, as described in section 1.1 on page 4. These moieties can be radicals or chemical functions. As an example, one can talk of the effect of a plasma made with O_2. This will lead to either the creation of peroxide radicals (OO^o) or creation of oxygen-containing functions directly on the carbon backbone of the polymer. Since fluorine atoms are very electronegative, radicals can be stabilised in plasma treated FP and they may survive until they are in contact with species more reactive than the FP backbone, e.g. atmospheric gases or liquids.

1.3.2 The CASING effect

The CASING effect, or Crosslinking *via* Activated Species of INert Gases, is made using noble gases (He, Ar...). Many researchers have indicated that this phenomenon can stabilise the surface layer of polymers against ageing by forming a cohesive skin, and, if used with a non-inert atmosphere, create polar groups that may improve wettability and reactivity. Yasuda *et al.* [YAS 01] showed that this effect appeared for thermoplastic olefins and especially for polypropylene, a typical degrading-type polymer in the radiation chemistry of polymers. Therefore, even if it cannot be surely anticipated, the same CASING effect may happen for other radiation degrading polymers, like PTFE. The main problem,

which is also encountered in γ-ray crosslinking of PTFE (see the section 1.2 on page 5 on radiation crosslinking), will be the degradation of the polymer resulting in a loss of efficiency, or an opposite effect, on the properties of the polymer. Another characteristic of this method, in the case of PTFE, will be the persistence of radicals after the treatment. The radicals will be stabilised by the fluorine atoms until they can react with non-inert species, especially O_2 or N_2 from the atmosphere. However, even if a CASING treated PTFE is still quite reactive to its environment, one may think that a post-treatment leading to a stabilisation of PTFE is possible. One may, for example, self sputter tetrafluoroethylene monomer (TFE) on it in order, either to entrap the radicals properly inside the matrix, far from reactive species, either to make the radicals react one with another. This method should then be compared to the graft copolymerisation by plasma, *i.e.* the "peroxide method" [HED 98], see the section 1.1 on page 4 on chemical crosslinking.

1.3.3 Other interesting effects of plasma treatment on FPs

Plasma sputtering of FPs has several interesting effects, including crosslinking, but it is not the same. These effects are described in several articles, e.g. [ZHA 02]. First of all, the fluorine ratio, *i.e.* the ratio between the amounts of fluorine atoms and the carbon atoms is function of the power used for sputtering. More precisely, this ratio decreases while the power increases. A more precise study of this ratio, involving the study of the populations of the different carbon groups (e.g. CF_xH_y) shows that double bindings are created with the crosslinking points. These properties lead to a surface that should be easier to wet than classical FPs. In fact, the surface contact angle of a water drop is comparable with the ones observed for pristine FPs. This is due to an increased roughness of the surface that counterbalances the loss of hydrophobicity due to the lower fluorine ratio.

1.3.4 Prospects for some other use of plasma techniques

As stated over, plasma processing is a surface technique. But, it may seem that it is not a very important limitation for its use with FPs. Indeed, FPs are characterised by a low to very low surface energy. Therefore, they will tend to, when mixed with other polymers, to separate from the blend and migrate to the surface. So, a homogenous blend of a classical polymer and a FP will tend to have a layered structure, with the FP leaving the core to concentrate on the surface. So plasma treating that kind of blend will lead to a product made of an outer layer of crosslinked FP followed by uncrosslinked FP and then the core, made of the classical polymer. A comparison of the effect of plasma crosslinking on different FPs under different atmospheres (Ar, N_2, O_2, air...) and their properties after crosslinking can be interesting to study.

1.4 Different reactions occurring during the process

If one talks about the process that leads to crosslinking Teflon©, the chemical way to crosslink it looks very like a classical graft-polymerisation, *i.e.* a three-step process, which the first one is the crosslinking of the first polymer, then the activation of its surface and lastly the graft polymerisation of a FP on it.
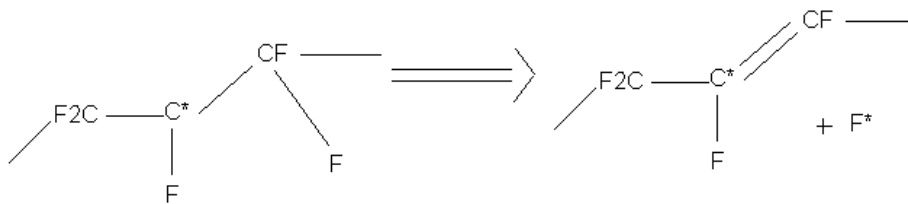
Figure 2: Transformation of a fluorinated radical into an unsaturated polymer

The "physical" ways to crosslink it, *i.e.* either the plasma or the irradiation processes, are in two steps. First, external energy, coming from plasma, radiation or electrons, break some single bonds to create radicals. These bonds can be C-C or C-F bonds. Only the breakage of a C-F bond creates a radical that is sure to recombine into a crosslinking point. Another reaction may occur. If one consider an activated chain (-CF2-C*F-CF2-), it may react according to the figure 2 on page 9

It should be noted that this reaction is more effective if a hydrogen atom is near the radical than a fluorine atom. This parallel reaction leads to a loss of fluorine and an improvement of the reactivity of the polymer chain. Indeed, this will lead to a double bonding that can be used later for *e.g.* oxidation. This increase of reactivity can be either an advantage or a drawback. If one wants to graft other molecules to the polymer, these double bonding will be of great aid since they will be like "doors" to let reactions occur. But if one wants to use the FP as an inert lining, then these double bonding can allow the lining to degrade under the action of its environment.

As stated already, if the environment in which FP is crosslinked is able to react, *i.e.*it is not made of pure noble gas or is void, then some heteroatomic radicals can be created. The best and most common example is the reaction between a carbon radical and a molecule of O_2. This will give birth to a peroxide radical (COO¡) that may react easily with everything that may encounter the material in its future life.

2 Protocols

2.1 Adhesion tests, ASTM D 3165, modified by Korrosion Institutet

2.1.1 Introduction

Performing these tests is to determine the adhesion properties of the plasma-modified surfaces. Indeed, as stated before, plasma modification will lead to an entrapment of radicals and creation of double bindings in parallel of crosslinking points. Therefore, the surface will be more eager to react with another one, *i.e.* to bind these two surfaces together. The method used is the one described in the American standard **ASTM D 3165** modified by S. RÖMHILD at Korrosion Institutet. The modified FP is bonded to a polymer and then a shear is applied. The shear to break is measured as the function of $\tau(u)$, where τ is the shear and u the displacement. This series of experiments gives interesting results that can be compared to contact angle results. Depending on the gas used, the mechanism of plasma reaction can change. This will depend on the ability of the gas to perform chemical reactions with the substrate. For example, argon, a noble gas, cannot react chemically. Thus, it will only punch out some fluoride atoms and create radicals. This is the "pool" effect since the gas molecule act as a pool ball that put away the other atom. Hydrogen can use not only this mechanism but can also replace a carbon fluoride link by a carbon hydrogen link. This will be more eager to react with the glue and so make the bond polymer-resin stronger. Oxygen and nitrogen can create radicals and peroxides and nitrides groups that can react further, since they are quite fragile.

2.1.2 Protocol

The protocol to perform this experiment can be separated in 3 steps.

1. The first one is to prepare the surfaces one wants to test. In our case, it consists in treating both surfaces with a given treatment. This treatment should be defined precisely, *i.e.* with dose, power effect, gas... known. The surface should be precisely known and superior to $50 * 25 \ mm^2$. The most convenient way to be sure to have two surfaces as equivalent as possible is to treat them at the same time in the same reactor. So the dose and energy received by the surfaces are the same.

2. Then, these two surfaces, which are *de facto* completely equivalent, are glued together with a vinylester polymer on a square of more or less $25 * 25 \ mm^2$, see figure 3. This sandwich is put to cure, first 24h at open air, then 24h more at $80°C$ and then 12h at open air.

3. At last, these samples are tested in an Instron machine and the failure force recorded. Then, the actual glue surface is measured after the failure. This allows to precisely know this surface. This surface can indeed evolve while it cures. The main reason is that the resin is first liquid and so, can flow, even if some care is taken to avoid this. Knowing the surface of the glue and the failure force allow to know the failure stress which is plotted.

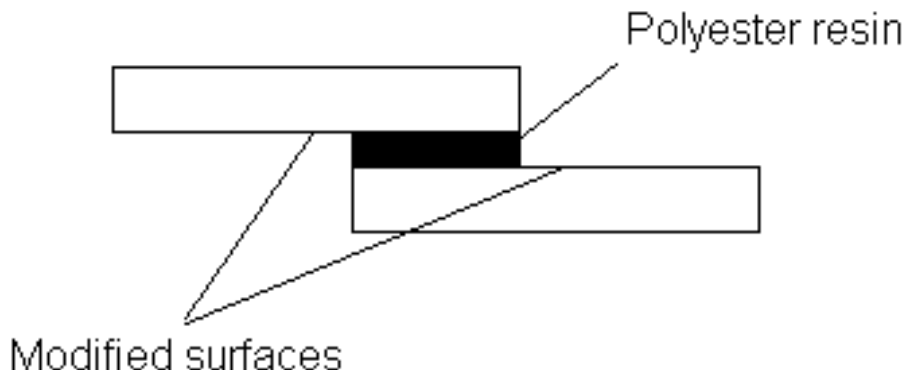Lastly, it should be noticed that all the experiments are doubled.

Figure 3: Composition of a sample ready for adhesion test

This failure stress depends of course of the treatment the polymer received but also of many other factors, example given, the resin used, the virgin polymer or the curing process. The parameters that are tested in this series of experiment are:

1. The specific dose received by the polymer, measured in J per square mm ($J.mm^{-2}$)

2. The gas used. 4 gases are used, hydrogen, oxygen, nitrogen and argon.

3. The substrate. Two substrates are used, PTFE and FEP. Since the chemical compositions of these substrates are different, their susceptibility to plasma treatment should be different.

The main parameters that are left constant are the power rate, the gas flow during the process, the resin used, or the time between the process and the final test. Between these two moments, 5h were spent in order to prepare all samples and to go to the test laboratory. The results are presented in the section 3.1 on page 16

2.2 Contact angle

Contact angle measurements give an idea of the wettability of a substrate by a given fluid. Here, plasma treating a fluoropolymer, by creating double bonds and eventually oxygen or nitrogen-containing functions, should make this polymer more hydrophilic. In order to measure directly the evolution of the hydrophility of the substrate, the fluid used will be a hydrophobic compound, limonene. Thus, the higher the contact angle, the more hydrophilic the substrate. Of course, one can easily compare this experiment with adhesion tests. Both deal with the relative attractiveness between a substrate and another material, in one case a liquid and in another one an adhesive. For practical reasons, measuring the contact angle won't be made using a goniometer but the method of sessile drops described in [DAH 80]. This method will be first generalised in the coming

sections before being used. Then, the following protocol will be applied and the results presented in the section 3.2 on page 20.

2.2.1 Method of sessile drops

Dahlgren *et al.* hypothesized in their article [DAH 80] that a drop of known volume V has a shape that can be approximated by a truncated sphere. Calling a the apparent radius of the sphere and θ the contact angle of the drop onto the substrate, they demonstrated that:

$$V = \frac{\pi a^3}{6}(3tan(\theta/2) + (tan(\theta/2))^3) \tag{1}$$

This equation allowed, *via* measuring a and V, to calculate θ with the help of any computer with a calculation software installed.

The major hypotheses in their theory are the following:

- The volume V is small enough so the gravity doesn't play an important role and the drop is as close as possible of a sphere

- The drop is deposited accurately enough so the apparent surface is a circle or it is close enough to a circle so the error can be neglected.

These two sources of error make the drop looking like a truncated ellipsoid instead of a truncated sphere. Of course, the latter is a particular case of the former. Under the hypothesis of a truncated ellipsoid, and with the symbols corresponding to those in figure 4 on page 13, the volume of a truncated ellipsoid between z = h and z = c is, according to [MathCentral]:

$$V = \int_{-q}^{q} \int_{-p}^{p} [C\sqrt{1 - (\frac{x}{A})^2 - (\frac{y}{B})^2} - h]dxdy \tag{2}$$

$$p = B\sqrt{1 - (\frac{x}{A})^2 - (\frac{h}{C})^2}$$
$$q = A\sqrt{1 - (\frac{h}{C})^2}$$

After calculation, this gives:

$$V = \frac{4}{3}\pi ABC(\frac{1 - h'^3}{2}) \tag{3}$$

$$h' = h/C$$

Since we are dealing with an ellipsoid, on the points (a, 0, c-h) and (0, b, c-h) that are on this ellipsoid one has:

$$A = a/\sqrt{1 - (1 - h')^2}$$
$$B = b/\sqrt{1 - (1 - h')^2}$$

since this ellipsoid is defined as all the points (x,y,z) satisfying $(x/A)^2 + (y/B)^2 + (z/C)^2 = 1$

These equations, used with equation 3 give:

$$C^3 - 2h\Gamma C + h^2(\Gamma - h) = 0$$
$$\Gamma = \frac{3V}{2\pi ab}$$
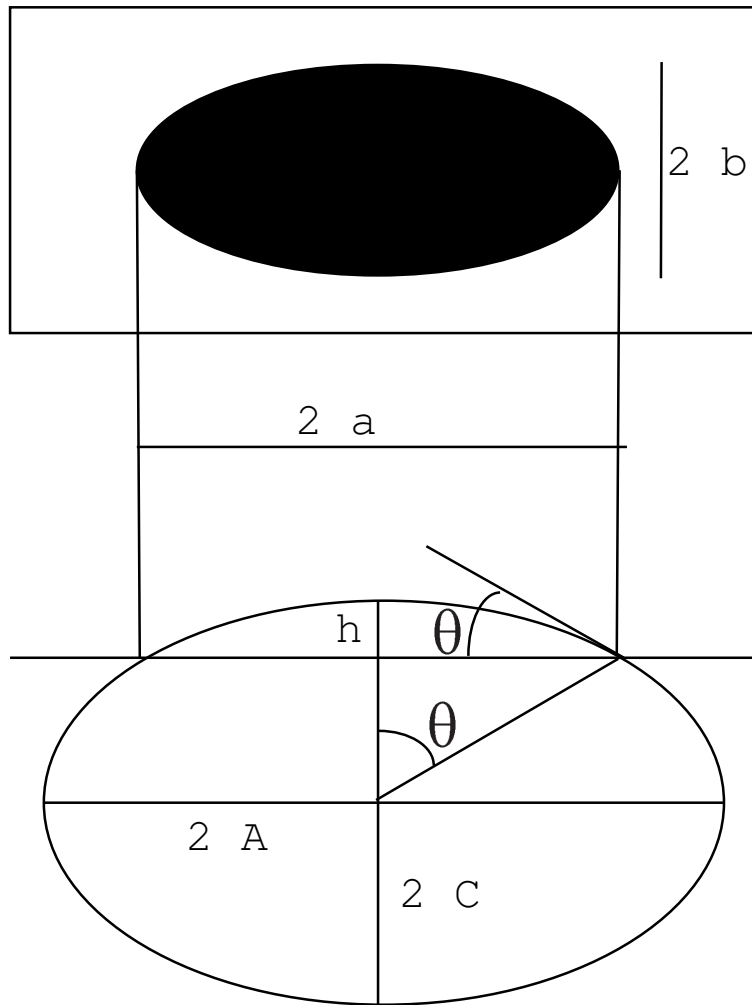
Figure 4: Drawing of the ellipsoid model of a sessile drop

The figure 4 gives also this equation:

$$tan\theta = \frac{a}{C - h} \qquad (4)$$

The 3 last equations allow to determine the value of θ. This model allows using bigger volumes for the drops, since the gravity plays here a role that is indirectly taken into account. So, all the measurements are more precise and the determination of θ more accurate.

2.2.2 Protocol

This experiment will be performed in order to determine the evolution of the contact angle with:

Figure 5: Drops of limonene ready to be measured

1. The gas used for the plasma reaction, either hydrogen, nitrogen, oxygen or argon

2. The specific energy supported by the material, between 0 and 200 $J.mm^{-2}$

3. The material used as a substrate, PTFE, FEP

4. The power rate at which the material is processed

For each point, a sample will be prepared. This sample should be big enough to allow 3 experiments on it. Doing the 3 experiments on the same sample avoids a possible error due to a change in the experimental conditions. Then, the values of a,b,h and V are measured for each drop with a monocular lens. The liquid used on this experiment is limonene. A picture of a sample with drops ready to be measured is on figure 5 on page 14.

The system used to measure the dimensions of the drops is illustrated on the figure 6 on 15. This system consists of a monocular lens with a graduated scale on one side with a precision of the tenth of millimetre. It is supported by a Petri dish in order not to touch the drops. A calibration is made regularly in order to take into account the parallax due to the distance between the graduated scale and the drop.

2.3 Scanning electron microscopy

In order to determine the reasons of the diverse behaviour of plasma treated fluoropolymers, a study of the surface state of the treated samples is made using surface electron microscopy. The samples, of approximately $0,4cm^2$, are plasma-treated and then studied by scanning electron microscopy (SEM). This allows determining the roughness of the surface. Studying the roughness of the surface can help understanding the macroscopic behaviour of these surfaces.

The parameters tested here are the influence of the specific energy on the surface state as the influence of the plasma gas, the effect of the substrate and finally the power rate. These different parameters are those used on the previous experiments and are chosen in order to have a first explanation of the behaviours encountered in the different experiments.

Figure 6: Lens ready to measure the dimensions of a drop

Material	Melt Temperature (K)
PTFE	321
FEP	256

Table 1: Melt temperatures of PTFE and FEP

Dose ($J.mm^{-2}$)	$\delta - 1$	γ	R^2
0	0	$4.38 * 10^1$	1
80	$3.98 * 10^{-1}$	$6.35 * 10^2$	0.97
120	$1.34 * 10^{-1}$	$3.41 * 10^2$	0.995

Table 2: δ and γ as a function of dose

3   Behaviour of fluoropolymers

The fluoropolymers used were kindly supplied by the Swedish Corrosion Institute and their melt temperatures, determined by DSC are summarized in the table 1:

3.1   Adhesion tests

3.1.1   Results with Teflon

The series of experiments covered 3 doses (0, 80 and 120 $J.mm^{-2}$) and the 4 gases for Teflon. This was done in order to have a brief overlook of the behaviour of this material, considered as representative of fluoropolymers. The results were then plotted as stress against molecular mass, with dose constant, and then stress against dose, with gas constant. Considering the effect of molecular mass, this graph studies the effect of the "pool" effect of the plasma gas, since the molecular mass is linked with kinetic energy. If one looks at the graph, see figure 7 on page 17, one can see that the results seems to follow a law which is:

$$\frac{\sigma}{M} = \gamma M^{-\delta} \tag{5}$$

The values of the parameters as a function of dose are compiled in the table 2 on page 16.

The parameters γ and δ depending of everything possible except the molar mass of the gas, *e.g.* substrate or power rate. Since the error between the experiments and this law is quite low ($R^2 > 0,97$) no matter of the energy used, it seems that this law fits well the results. A quite interesting result is that, since results are well fitted by a law containing taking only into account the molecular mass for gas parameter, the "pool" effect seems dramatically superior, for these doses, to all the chemically possible reactions. Therefore, using a very light gas, therefore hydrogen or helium, seems the more efficient way to have a very high-modified polymer. This can be explained by the fact that a light, and so little, molecule will have only few ways to stock energy by intra molecular movements or by change of state, and a small molecule can go deeper inside the material before reacting. So, this molecule will have a high speed, since all the energy will be in form of kinetic energy of the whole molecule, and it will penetrate
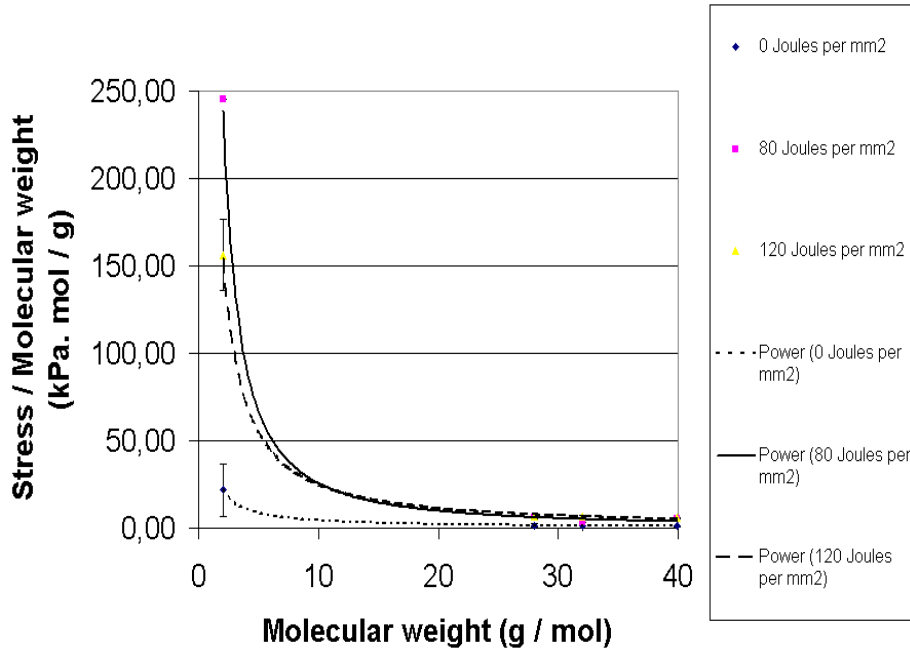
Figure 7: Plot of failure stress over molar mass against molar mass for Teflon

Gas	α	β	R^2
H_2	$5.59 * 10^1$	$1.84 * 10^{-2}$	0.76
N_2	$4.75 * 10^1$	$1.29 * 10^{-2}$	0.93
O_2	$4.24 * 10^1$	$1.28 * 10^{-2}$	0.99
Ar	$4.83 * 10^1$	$1.49 * 10^{-2}$	0.93

Table 3: α and β as a function of gas

deep inside the substrate to react and thus may punch away several atoms in its journey inside the polymer.

If one considers plotting the stress against the dose received by a Teflon sample, taking the gas as a constant, some interesting notes are to be done. The results are plotted in figure 8 on page 18.

A law seems to appear that is, if one notes D the dose:

$$\sigma = \alpha e^{\beta * D} \tag{6}$$

The values of the parameters as a function of the gases are presented in the table 3 on page 17.

If one tries to combine equations 5 and 6 obtained before, it appears difficult to find three constant parameters a, b and c to have an equation looking like:

$$\sigma = a M^b e^{c * D} \tag{7}$$

Therefore, it would need more experiments in order to have an idea of the behaviour of α and β as functions of M and γ and δ as functions of D.
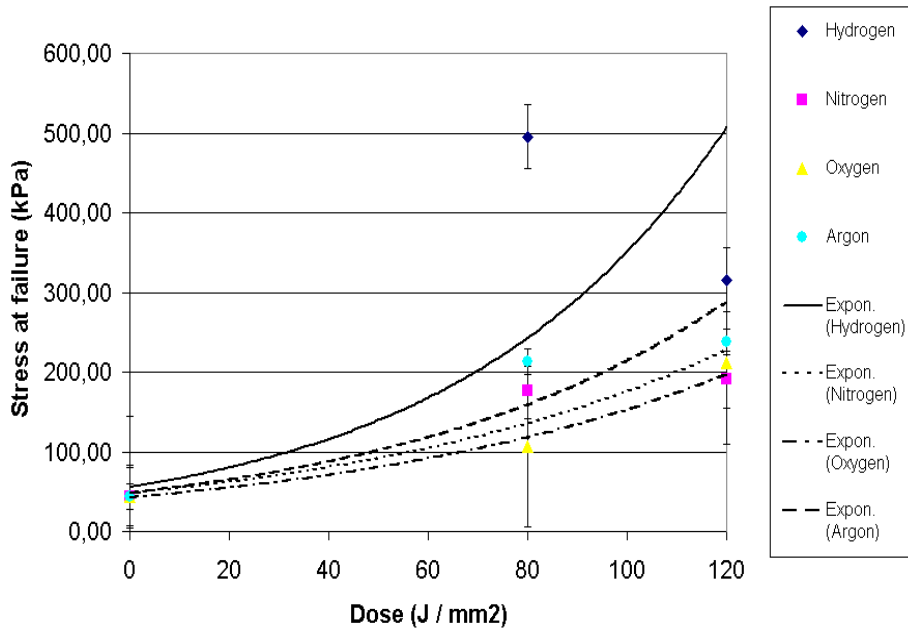
Figure 8: Plot of failure stress against dose for Teflon

Dose ($J.mm^{-2}$)	friction coefficient
0	1.63
40	2.03
120	2.17

Table 4: Friction coefficient of hydrogen treated PTFE

Some friction tests with hydrogen treated PTFE were also made in order to compare them with the adhesion results. The results are compiled in the table 4 on page 18. Adhesion and friction can be compared since the microscopic phenomena involved are basically the same.

3.1.2 Results with FEP

Experiments with FEP were done with hydrogen and the results can be seen on the figure 9 on page 19. The two sets of experiments show results astonishingly comparable, both in general aspects and in values for same doses. The "strange" behaviour of hydrogen plasma treated Teflon, as seen on the figure 8, can also be seen for FEP. Indeed, a high treated material has a quite low failure stress compared to lower treated ones.

A possible explanation of this can be that hydrogen, compared to other plasma gases, is a much more reactive gas. That is that it reacts quite easily and, when it reacts, it forms a dead end compared to e.g. oxygen that can create ether-like bonds. Therefore, at a high dose, the long polymeric chains can be cut in quite small chains that lack mechanical resistance. Thus, the
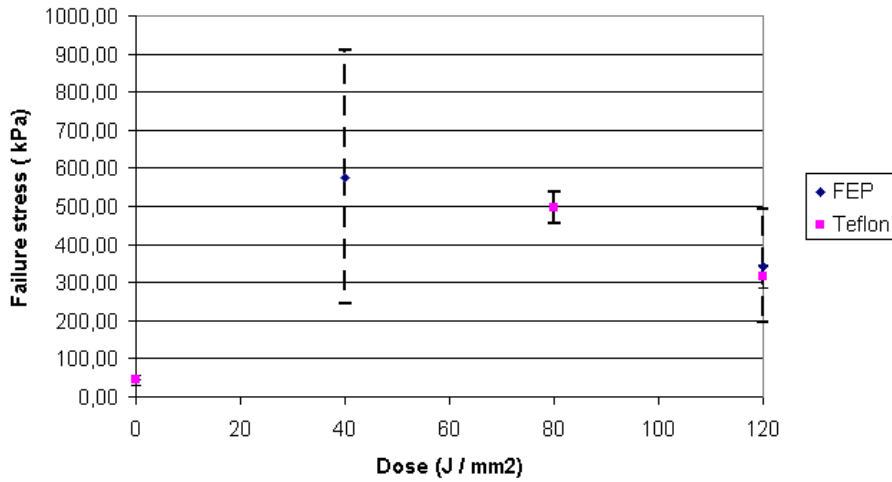
Figure 9: Plot of failure stress against dose for hydrogen plasma treated substrates

strengthening effect of crosslinking is only secondary to this loss on properties. Unfortunately, shortage of time made impossible to run an experiment in order to determine precisely if this assumption is true. A possible experiment to determine this is described in [BEX 02]. This experiment would have allow to know the concentrations of different elements as a function of depth on the different failure surfaces.

3.2 Contact angle

3.2.1 Results with Teflon

The contact angle experiment gives some interesting results that indicate the possibility of several phenomena involved in plasma processing. One can see the evolution of contact angle of limonene on Teflon on the figure 10 on page 21. It is interesting to see that the contact angle is lower for all processed samples than for virgin Teflon. The contact angle is increasing then with the dose between 40 and 120 $J.mm^{-2}$. Lastly, a drop occurs between 120 and 200 $J.mm^{-2}$. It seems that two phenomena, at least, occur. The first one, which is also described in other sections, is the creation of hydrophilic groups, double bonds or oxygen-, nitrogen containing functions. This, since limonene is hydrophobic, will make the contact angle higher. A second effect, which wasn't seen on adhesion tests, makes the contact angle lower than expected.

So, at low doses, the predominant effect is surface roughening. The dose is not important enough to create enough polar groups to counteract it. At medium doses (40 to 120 $J.mm-2$), the trend is opposite and the increase of polarity is predominant over surface roughening. Lastly, at high doses, surface roughening and chain deterioration make the contact angle drop dramatically.
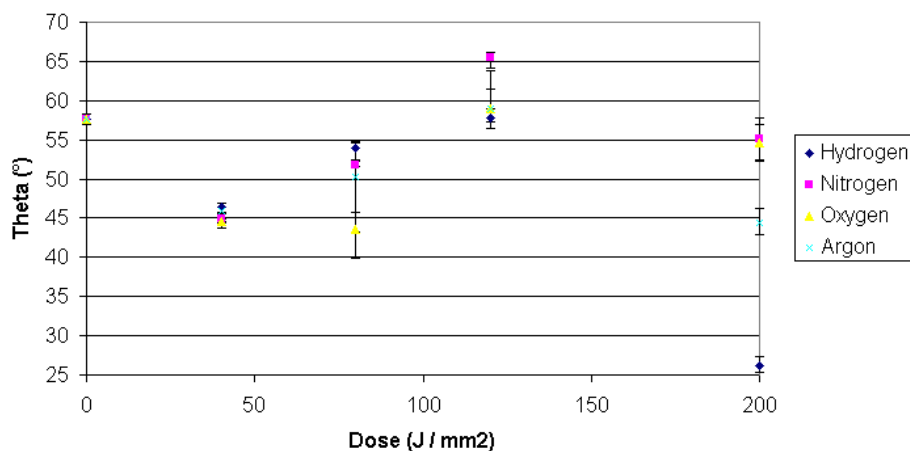
19

Figure 10: Plot of contact angle against dose for Teflon

This behaviour can have several explanations. The first one is that chain degradation can occurs under plasma processing. Another possibility is a change of the sample's topography. This change can come from the heating of the surface during the processing. This heating will make the chains more eager to move on the surface. Since plasma-building crosslinking points, like a classical curing process, makes the chains move closer, the hot chains will be able to move on the surface and "fill the voids". When the material cools down, the crosslinked parts won't contract as much as the others and thus a rough surface is created.

The first explanation should lead to an effect visible for adhesion tests. Also, the rough surface should lead to a higher adhesion and should be detected with SEM or when touching the surface. Since the failure stress is not dropping between a virgin polymer and a processed one (see section 3.1 page 16) and the surface is rough enough at high dose to be felt at touch, this explanation should be the right one. Some more experiment are made on this and described later in the section 4.2 on page 25.

This second phenomenon, which wasn't seen with adhesion tests, is interesting since it is obviously non-linear and should improve the adhesion of drops on it. Therefore, this phenomenon is expected to improve, in the conditions of industrial use of this material, the diffusion of a liquid through it.

3.2.2 Results with FEP

For FEP, the results show that the material go through less dramatic changes. The contact angles of limonene on the processed surfaces are more constant. The surface roughing occurs also as soon as the surfaces are processed. This is showed on the figure 11 on page 21 by the drop of the contact angle value between the zero values and the others. But after this, since FEP is stiffer than Teflon, the roughness of the surface plays is less important for FEP.
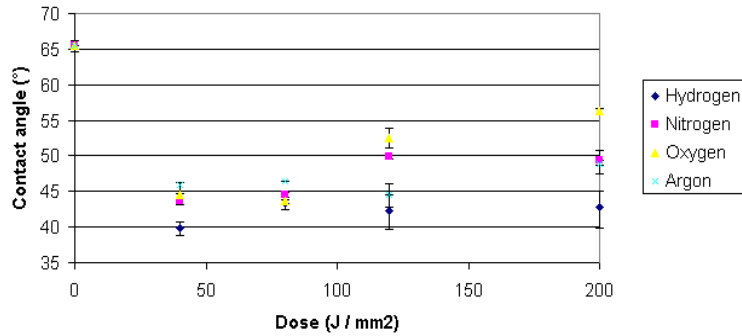
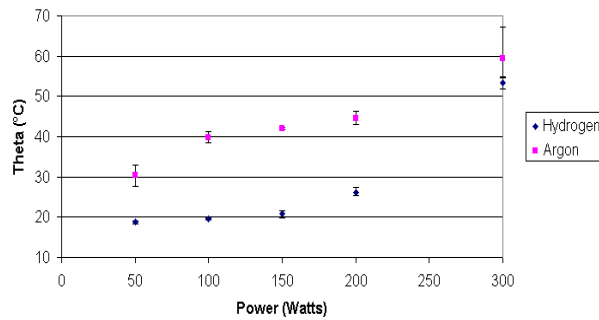Figure 11: Plot of contact angle against dose for FEP

Figure 12: Effect of power rate on the contact angle of limonene on Teflon

3.2.3 Effect of power rate

The dose is defined at the amount of energy received per surface unit. Therefore, for a given dose (D), three parameters exists, the surface(S) at constant energy, the power rate or the time of treatment, since energy is the product of power rate (P) and time (t).

$$D = \frac{P.t}{S}$$

Studying, for a given dose, the effect of power rate means to study the effect of the time of process. The results are presented on the figure 12 on page 22. This figure shows that the higher the rate, and thus, the shorter the treatment, the higher the contact angle. Since, these experiments were made at a constant dose (200 $J.mm^{-2}$), the explanation may come from the speed of reaction. One can see a fast reaction like a quenched one. When the reaction stops and the sample put away of the oven, its temperature drops dramatically and the thermoplastic matrix is frozen. Thus, this matrix couldn't fill the voids made by the creeping of the cured polymer. So, the surface will stay more or less even and so the contact angle will be higher.

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3.3 Conclusions of the behaviour experiments

The different experiments made in this section leads to interesting results that gives to several assumptions on the effect of plasma treatment:

1. Plasma treatment creates new chemical functions depending on the gas used. Crosslinking and double bondings are created regardless of the gas used. The efficiency of the treatment depends on the interactivity between the gas and substrate, the time of treatment and the energy of treatment.

2. Plasma treatment makes the surface rougher. This roughness seems to depend on all possible parameters of the treatment.

3. Lastly, plasma treatment can lead to chain scission. This phenomenon leads to a loss of mechanical properties, especially in terms of shear resistance. The extent of this phenomenon is very dependant on the nature of the plasma gas and hydrogen is a very efficient gas in this degradation process.

The first assumption has been described in several articles and in the section 1. This could also be determined via ESCA experiments that are planned to be run in the coming weeks. The second assumption was described for plasma sputtering of fluoropolymers, which is the use of fluorocarbon plasma on a polymer. It is summarized in the section 1.3.3 on page 8. A series of SEM observations of the surfaces of plasma modified samples is to be done in order to confirm or infirm this assumption. The third and last assumption can be linked to the first observations on irradiated fluoropolymers. Indeed, as described in the section 1, irradiating a fluoropolymer can lead to chain scission and thus a severe loss of properties. Indirect observations of this, via the observation of failure surfaces for adhesion tests are presented in the following section in order to add credit to this assumption.

Figure 13: Scheme of a adhesive sample viewed as a laminate

4 Surface modifications created by plasma treatment

This section is intended to determine if the different assumptions made in the previous section to explain the behaviour of treated fluoropolymers are true. Several experiments are made, from simple observations of the surface to electron scattering or scanning electron microscopy (SEM).

4.1 Simple observations of the sample surfaces

4.1.1 General observations of samples

When one touches a plasma treated sample, one can feel a rougher surface than the one of a virgin sample. It should be noted that the roughness is more important for high treated samples and, for a given energy, hydrogen treated samples appears to have a rougher touch than the other ones. These observations leads to the SEM observations made in the section 4.2.

4.1.2 Failure samples

A failure sample used in the experiment described in 3.1 can be considered as a laminate made of 5 layers that are from top to bottom, see figure 13 on page 24 for more details:

1. some virgin substrate

2. a thin layer (some nanometers) of plasma modified substrate

3. the adhesive

4. another thin layer of plasma modified substrate

5. some virgin substrate

Figure 14: Surface of H_2-plasma treated FEP. (a) is virgin FEP, (b) is treated with 40 $J.mm^{-2}$, (c) with 120 $J.mm^{-2}$

The delaminating of this composite can be done at the interface between the adhesive and the plasma-modified substrate (so between layers 2 and 3) or between layers 1 and 2, or even inside the layer 2. If one looks at the surfaces of the delaminated samples, especially the surface of the adhesive, see figure 14, one can see that it is bright and clear for samples that suffered a low treatment (figure 14(a)) and blurry for samples with a high treatment (figure 14(c)). Therefore, there seems to be much more polymer on the adhesive left for high treated polymers. So, the fracture occurs between the 2nd and 3rd layers for low treated polymers and between the 1st and 2nd or inside the 2nd in case of highly treated samples.

This change of failure interface proves that the link between the adhesive and the modified surface is stronger than the one between the modified surface and the virgin material. The latter interfacial strength comes from the interactions between chains that are proportional to the chain size. Since there is a drop of shear strength for treated samples over 80 $J.mm^{-2}$ for hydrogen, it means that depolymerization occurs at high-energy treatment. Several reasons can be stated to explain why it happens for hydrogen at these energies and not for other gases. First of all, since hydrogen is a much smaller molecule than the other gases, it should have the possibility to attack the substrate deep inside and bounce in several chains compared to a big molecule that can only interact with the first layers of chains. A second reason can be that reactions between FPs and hydrogen cannot create bridges in the polymeric chains but just dead ends.

Some further experiments should be done to precisely determine this. A possible experiment should be the one used in [BEX 02] in order to have, on each surface after failure the concentration of the different atomic species as a function of depth. Therefore, this can give results on quality of the treatment and in terms of adhesion of the modified layer.

4.2 Observations of the surface by SEM

As seen in the previous sections, especially the section 3.3, it seems that the surface become uneven when treated by plasma. This section intends to present results from scanning electron microscope observations of a fluoropolymer treated by plasma.
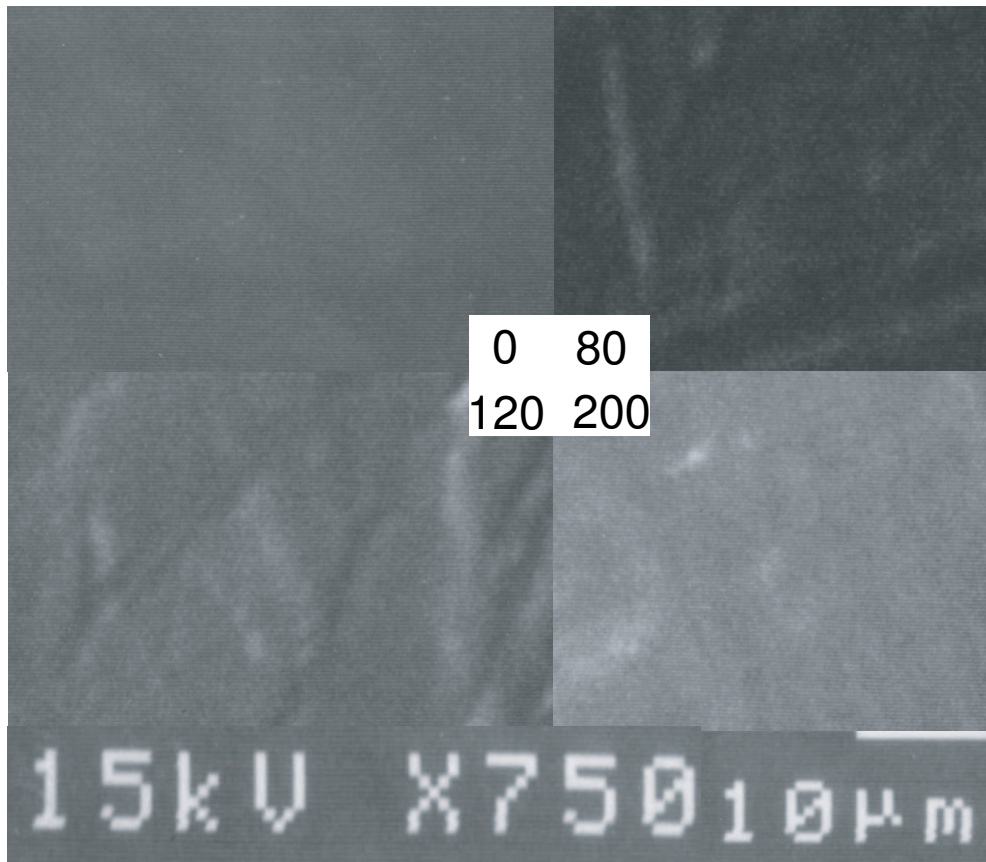
Figure 15: Surface state of plasma-treated PTFE. The treatment is made with hydrogen. The figures are the energy in $J.mm^{-2}$

4.2.1 Effects of energy

As seen in the contact angle section on page 20, a drop in the contact angle occurs when a fluoropolymer is plasma-treated. If one have a look at the surface of PTFE treated at different energies with an hydrogen gas, like in the figure 15 on page 26, one can see that the surface becomes rougher as the energy grows. These pictures were made with a constant power rate of 100 W.

4.2.2 Effects of power rate

In the contact angle section, the figure 12 on page 22 showed that the contact angle of limonene on PTFE increases with the power rate for a given energy. If one looks at the first conclusions drafted in the section 3.3, it seems that the power rate has an effect on the surface roughness. If one looks at the figure 16 on page 27, one can see that the surface roughness is increased at low power rate.

A possible explanation of this effect can come from the warming up of the sample during the treatment. Since the process heats the substrate, the surface
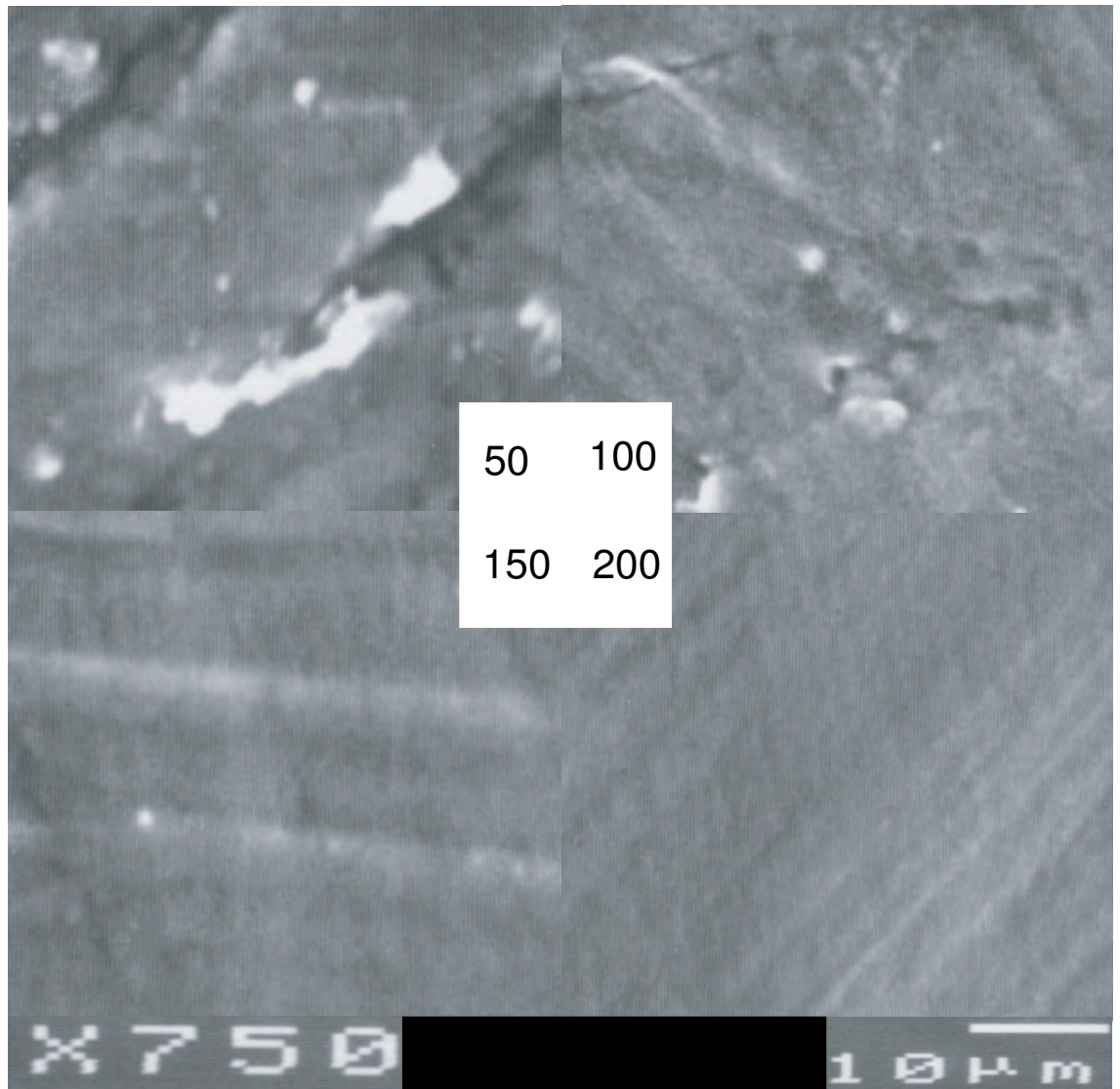
Figure 16: Surface state of plasma-treated PTFE. The treatment is made with hydrogen at 200 $J.mm^{-2}$. The figures are the power rate in Watts

becomes softer and can flow. Considering that the specific energy is constant, the time of treatment is inversely proportional to power rate. If one looks at the following parameters of the experiment:

- the temperature of treatment, T, which depends on the power rate

- the viscosity of the material, η, which is a function of temperature and material.

- the volumic mass of the material, ρ.

- t, the time of treatment

The units of these different parameters are:

Unit	Length	Mass	Time
η	-1	1	-1
ρ	-3	1	0
t	0	0	1

A brief look at the units of these parameters gives that the quantity L defined as following has the dimension of a length:

$$L \propto \sqrt{\frac{\eta \, t}{\rho}}$$

L can be considered like the height the molecules can fall from during the processing time. Therefore, the higher this value, the more the flowing molecules can fill the voids created in the crosslinked parts of the surface. Thus, this high value will lead to a high difference of concentration of polymer between reacted and non-reacted areas. So, when the sample will cool and creep, the surface will be rougher. Therefore, one can imagine that the roughness of the sample h will be proportional to this value L. Unfortunately, it was impossible to run, mainly for time reasons, an experiment that would allow determining the degree of accuracy of this assumption. However, a atomic force microscopy observation of treated samples should be sufficient to have fairly good results for this experiment.

4.2.3   Influence of the material

In this section the surface state of hydrogen plasma modified FEP and PTFE are compared. If one looks at the observations of samples *via* MEB, the surface states of FEP and PTFE samples treated with the same plasma has different surface states, see figure 17 on page 29.

PTFE has a rougher surface that can be compared to the higher modulus of FEP. Since FEP has a higher modulus, it should be more difficult to have it flow across "long" distances and thus the roughing process described in the previous subsection cannot have such an extent than for PTFE. This is dramatically proven with the contact angle experiments. In these experiments, contact angle of FEP is relatively constant while the one of PTFE decreases at high doses.
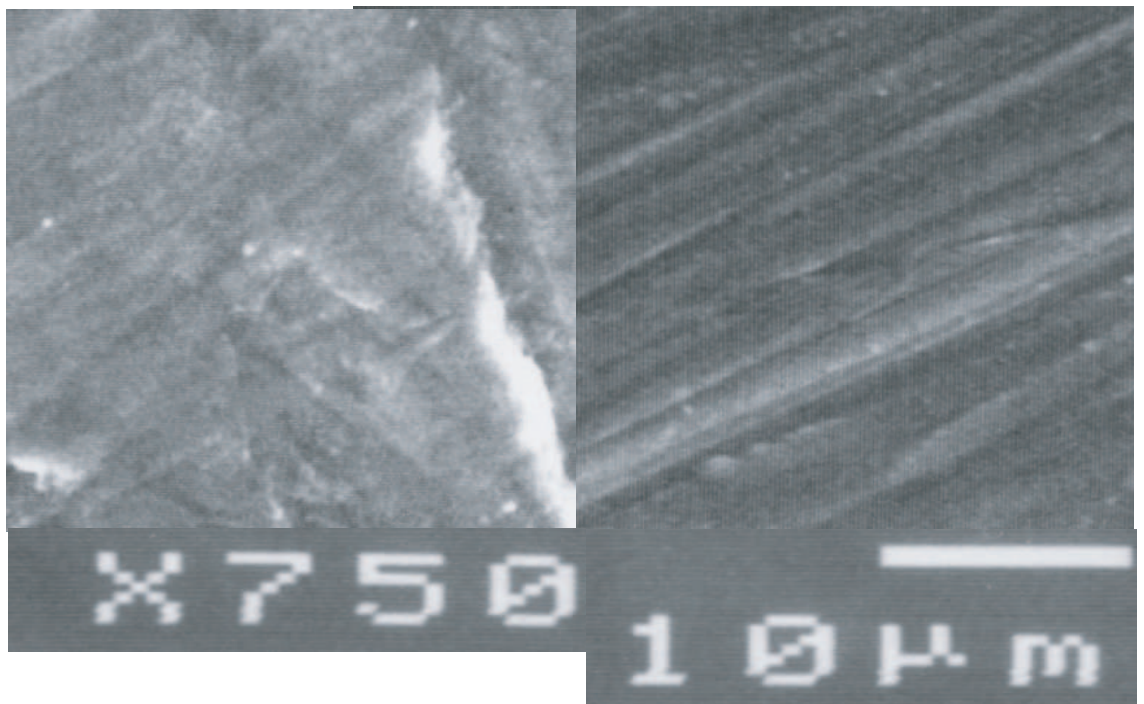
Figure 17: Surface state of plasma-treated PTFE (left) and FEP (right). The treatment is made with hydrogen at 200 $J.mm^{-2}$ with a power rate of 100W.

5 Conclusions

This report shows that the plasma modification of fluoropolymers can have dramatic effects. These effects are mainly three, a chemical modification of the polymer, *via* among other phenomena crosslinking and inclusion of heteroatomic groups, a surface roughening and chain scission. These effects are, of course, highly dependant on the different parameters of the modification, including the gas and the polymer substrate. These modifications of the surface of the polymer occur in a depth of the order of magnitude of the nanometer. This leads to problems to determine the chemical composition of this surface by classical IR spectrometry. This very low thickness implies also a fragility of the treatment. Using sandpaper on a sample for a couple of minutes is enough to have a virgin-like surface. In terms of reactivity of the surface after modification, this treatment leads to an improved hydrophility of the surface. This phenomenon is ever increased with the higher roughness of the modified surface. This roughening of the surface leads also to an improved adherence of the sample when a polymeric adhesive is used on it. However, this is limited by chain scission that will make the sample in itself more fragile. A general overview of the effects of the different occurring phenomena on adhesion are to be seen on the figure 18 on page 31.

These different results can be compared to those obtained with other crosslinking methods used with fluoropolymers. Crosslinking of fluoropolymers can be obtained in various ways, from irradiation crosslinking to plasma deposition or even chemical crosslinking. Making the surface rougher was described before for plasma sputtering of fluoropolymers on substrate. For this method, it seems quite obvious since sputtering matter on a surface implies to add some material and it should be an extraordinary coincidence if the surface were smooth. Lastly, chain scission was the main reason why PTFE has been considered as a radiation degradative polymer until Tutiya found the conditions in 1972 that allow to crosslink PTFE by radiation.

So, plasma modification of fluoropolymers leads to important modification of the properties. These modifications can be done using several parameters that contains, for a given substrate:

- the gas used

- the power rate

- the energy

- the gas flow, that hadn't been tested in this report

- the plasma pressure, that hadn't been tested too.

These different parameters, which can have opposite effects or not for a given property, allow to finely crafting the different properties in order to have the "perfect" surface. It should be noted thus that the effects of these different parameters on properties like permeability have not been studied yet. However, it should been pointed that a crosslinked surface should be less permeable than a pristine one since crosslinking makes the chains closer one to another. This phenomenon should be opposed to the increased roughness caused by plasma modification that should allow a better contact and thus a more important permeability.
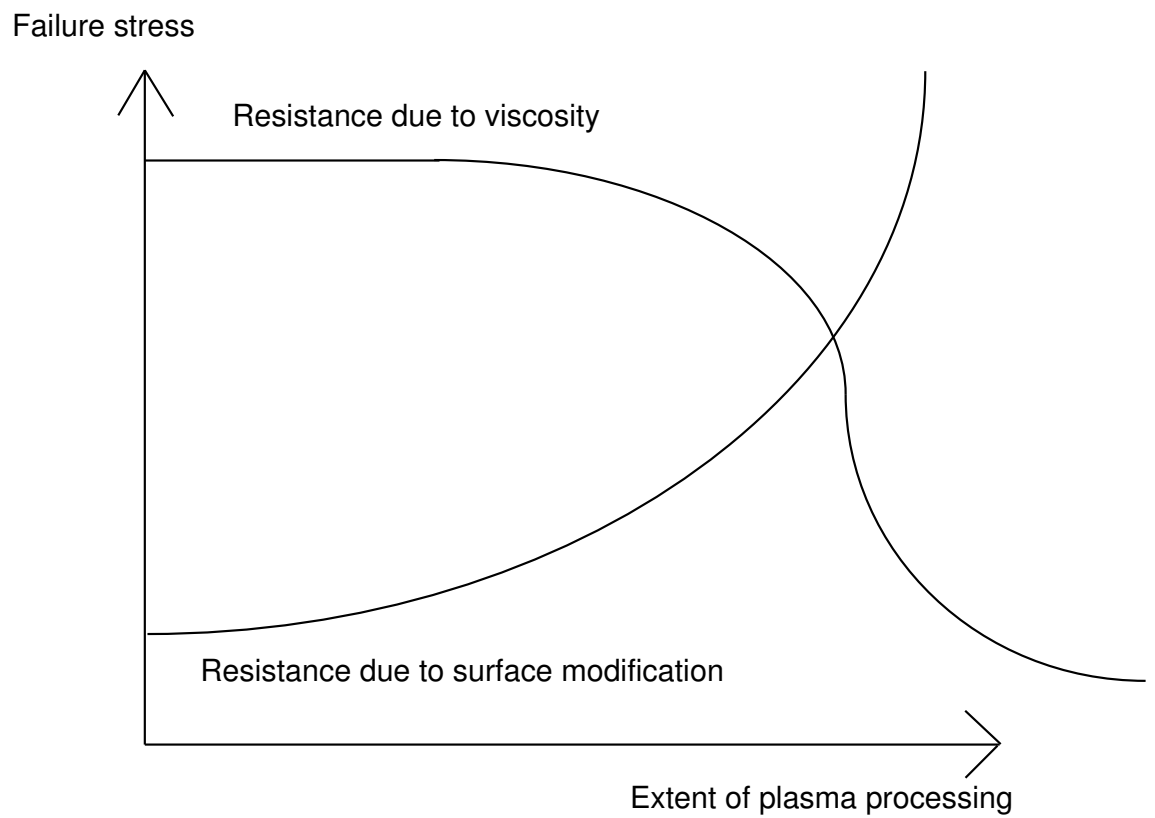
Figure 18: influence of the different phenomena triggered by plasma modification on adhesion properties

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