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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 behavior but concluded to a change of morphology due to chain scission. Since then, these abnormal behaviors 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 fulfill 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 4. These moieties can be, for example, radicals made of the polymer, or, if the plasma contains some reactive species, the corresponding radicals (e.g. $\text{OO}\cdot$) or some chemical functions, like carboxylic acids. Using this

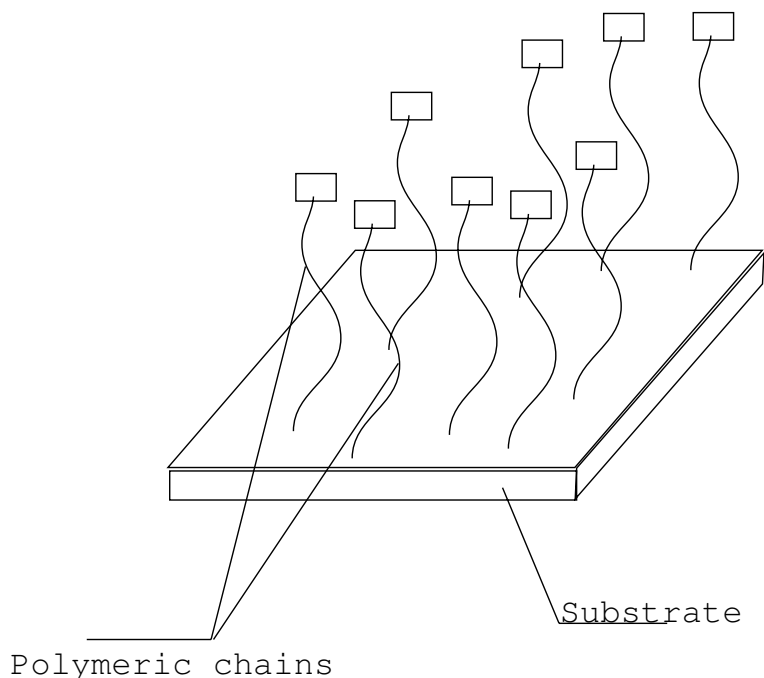


Figure 1: Product obtained by "graft-copolymerisation" on an inert solid

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 2.

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 4) and chemistry needs a copolymer to graft on the PTFE chains (see section 1.1 on page 1). 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 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 4.

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 1. 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°) 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 2 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 1 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 amount 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.

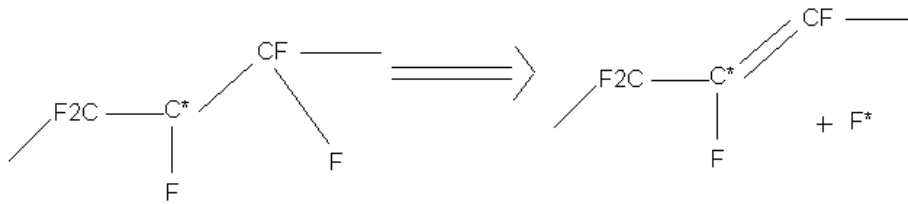


Figure 2: Transformation of a fluorinated radical into an unsaturated polymer

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 6

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 O₂. This will give birth to a peroxide radical (COO°) that may react easily with everything that may encounter the material in its future life.

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