Influence of Radiation-Induced Grafting Process on mechanical Properties of ETFE Based Membranes

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Abstract

We investigated the influence of irradiation dose, crosslinker concentration, graft level or styrene/DVB content on the tensile strength, elongation at break, yield strength and modulus of elasticity, of poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) based membranes. Grafted films were prepared by radiation-induced grafting and the membranes were obtained by subsequent sulfonation of the grafted films. It was found that the elongation at break decreases considerably beyond an irradiation dose of 50 kGy and tensile strength decreases gradually with dose. It was shown that the elongation at break decreases with increasing both the crosslinker concentration and graft level. However, tensile strength was positively affected by the crosslinker concentration. Yield strength and initial modulus of elasticity are almost unaffected by the introduction of crosslinker. On the other hand, yield strength and modulus of elasticity increases progressively with graft level. The elongation at break of the optimized membrane (graft level of ~ 25 %, 5% DVB (v/v)) obtained at lower irradiation dose (1.5 kGy) shows a pronounced decreases of ~ 56 % of its initial value after the grafting and sulfonation steps whereas the tensile strength was mostly affected by the sulfonation step. The obtained results were then correlated qualitatively to the other *ex situ* properties including crystallinity, thermal properties and water uptake of the ETFE-based grafted films and membranes.

Keywords: Radiation-induced grafting; Mechanical properties; Tensile strength, elongation at break, ETFE

1. Introduction

The radiation-induced grafting is a well established technology, which is used in an industrial level in many application areas (water desalination, biomaterials treatment, fuel cell, environmental waste treatment, etc) [1]. The attractiveness of this technique for the preparation of proton exchange membranes for fuel cell is based on its versatility and the possibility of using a wide range of low cost base polymer materials (perfluorinated, e.g., poly (tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), or partially fluorinated, e.g., poly (ethylene-*alt*-tetrafluoroethylene) (ETFE)), which are commercially available [2]. Thus, Proton exchange membranes for fuel cell prepared by radiation-induced grafting were developed as a cost effective alternative to replace the expensive perfluorosulfonic acid (PFSA) type membranes (e.g., Nafion®) [3].

The stability, reliability and cost effectiveness of the polymer electrolyte membrane in fuel cells are crucial issues to bring this technology to the commercial level. The Paul Scherrer Institut has been involved in the development of polymer electrolyte membranes using the radiation grafting method for several years. We reported on radiation-grafted crosslinked membranes based on styrene (divinylbenzene (DVB) as the crosslinker) and FEP base film, which exhibited comparable fuel cell performance to commercial Nafion®112 membranes and lifetimes of several thousand hours under steady state conditions at 80 °C [3, 4].

The partially fluorinated ETFE base film has been revisited as an alternative base polymer film in our laboratory. We reported on radiation-induced grafting of styrene onto ETFE in the presence of DVB as the crosslinker, as well as characterization of fuel cell relevant properties and fuel cell performance of the resultant membranes previously [5]. The influence of the crosslinker and graft level on the fuel cell relevant properties was systematically investigated [6-9].

The reliability of a fuel cell membrane is influenced mainly by the quality of the material and its properties (catalyst, gas diffusion layer, membrane, etc). The durability issue is closely related to the chemical and physical degradation of the membrane. In fact, the physical factors may lead to the membrane thinning and sometimes pinhole formation. This mechanical degradation can even be promoted by the chemical one, which accelerates the decrease in performance [10-12]. Yet, the mechanical properties (tensile strength, elongation at break, tear initiation and propagation resistance) have received a very low attention in order to define and understand the failure modes and their correlations with the mechanical integrity of membranes [13]. Works towards better understanding of mechanical behavior of Nafion® membranes under *in situ* operating environments e.g., humidity and temperature were carried out [14-16]. However, the failure mechanisms due to mechanical stresses are not yet clearly and fully understood.

Mechanical integrity is one of the important prerequisites for fuel cell membranes in terms of handling and fabrication of membrane electrode assemblies (MEA). Membranes should not only be robust to overcome both the mechanical and swelling stresses in fuel cell environment and during fuel cell stacks application but also tough to absorb energy upon deformation and prevent crack formation and tear initiation/propagation [2]. Furthermore, the material has to exhibit sufficient mechanical stability in order to fulfil its separator function [2].

Several articles have been published on styrene grafted films and membranes based on fluoropolymers such as FEP, ETFE, poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether) (PFA), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF), where changes in mechanical properties (tensile strength, modulus of elasticity and elongation at break) were highlighted [17-23]. Mechanical properties of styrene grafted PVDF based membranes have been investigated and compared with that of FEP and ETFE based membranes [21]. Chen *et a*l. [19] reported strain-stress curves for PTFE, FEP, PFA, FEP and ETFE based membranes. However, not many studies have been conducted addressing the effect of parameters like irradiation dose, graft level and degree of crosslinking onto the mechanical properties. These parameters are closely related to the hydration, conductivity, performances and durability of radiation grafted membranes under fuel cell operation. Previously, the effect of irradiation conditions on the base material and the mechanical properties of styrene grafted FEP and ETFE based membranes were investigated [23-25]. Yet the authors mainly focused on the effect of base film and the irradiation method and dose. We currently employ a different membrane preparation method (e-beam pre-irradiation, lower irradiation doses, a new grafting solvent mixture, mild sulfonation conditions) compared to our previous studies. Consequently, the resulting ETFE based membranes are expected to exhibit different *ex situ* properties, therefore it is desirable to characterize the resultant ETFE based membranes.

In this study, we evaluated in detail the mechanical properties of the pristine ETFE film, irradiated film, grafted film, and their sulfonated membranes. The influence of irradiation dose, crosslinker concentration and graft level on tensile strength, elongation at break, modulus of elasticity and yield strength were systematically examined. Mechanical properties were recorded with respect to both, the extrusion direction (machining direction) and transverse direction for each sample. The main objective is to quantify the changes of strength and toughness of our grafted membranes and explore the limits based on the preparation process.

2. Experimental

2.1. Preparation of irradiated films, grafted films and membranes

In this study, Tefzel® ETFE 100LZ film (DuPont, Circleville, OH, USA), with thickness of 25 μm was employed as the base polymer film. The average molar mass (M_w) is 1’200’000 Da. ETFE base polymer film samples were pre-irradiated in an air atmosphere with an electron beam source at Leoni Studer AG (Däniken, Switzerland, accelerating voltage of 2.2 MV, beam current of 5-20 mA, dose rate 15.1±1.1 kGy s^{-1}). In order to study the influence of irradiation dose, ETFE films were irradiated with varying doses: 1.5, 5, 10, 25, 50, 100 and 200 kGy. The samples were stored at –80 °C after irradiation until tensile test or grafting reaction were performed.

An irradiation dose of 1.5 kGy was employed for the preparation of all ETFE based grafted films and membranes. A solution of styrene (purum grade; Fluka) and DVB (technical grade, ~80%, mixture with isomers 3- and 4-ethylvinylbenzene; Fluka) with styrene:DVB, varying (v/v)) in an 11:5 (v/v) isopropanol (analytical grade; Fisher Scientific) / water mixture was used as grafting solution.

All the grafting reactions were performed at 60 ºC with varying grafting times to achieve the desired graft level (GL). The GL of each film was determined from the weight of irradiated film (W_0) and grafted film (W_g):

$$GL = \frac{W_g - W_0}{W_0} \cdot 100\%$$

After grafting, the grafted film samples were immersed in toluene overnight and then dried at 80 °C overnight.

ETFE based membranes were prepared using 2% (v/v) chlorosulfonic acid (Fluka) in dichloromethane (Fluka) for the sulfonation of the grafted films (5 hours at room temperature) and then hydrolysis of sulfonyl chloride groups with sodium hydroxide solution and treatment with hydrochloric acid to regenerate the acid form of the membranes was carried out. Water swollen membranes were obtained by subsequent swelling in deionized water for 2 hours at 80 °C.

2.2. Mechanical Properties

The mechanical properties of the base films, grafted films and membranes based on ETFE were investigated utilizing a Universal Testing Machine (Zwick Roell Z005) at a cross head speed of 100 mm·min^{-1}.

A special cutting die was employed for the preparation of test samples. In this work, rectangular specimens (1 cm x 10 cm) were used. An ensemble of 10 specimens was prepared and each film or membrane sample subjected to a tensile test. All the samples were analyzed in machining and transverse directions. The membranes were converted to salt form in KCl solution (0.5 M) and then dried at 50 °C in an oven for at least 24 h. All measurements were carried out at room temperature.

Engineering strain-stress curves based on the initial sample dimensions were recorded and the modulus of elasticity and the yield stress were extracted as shown in Figure 1. The yield onset was evaluated by the tangents method for the strain-stress curves, in which the onset point was not possible to identify (Figure 1) [26].

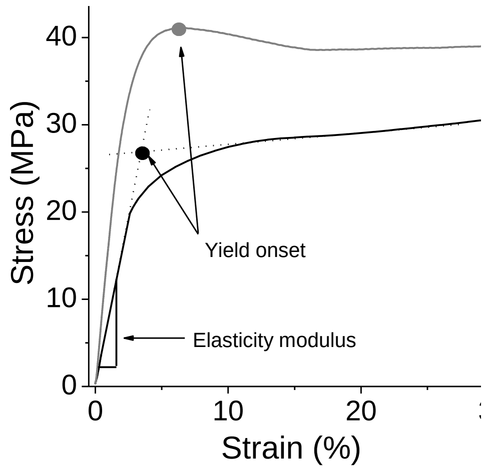

Figure 1: Determination of the modulus of elasticity and the yield onset by the tangents technique.

Thickness measurements were carried out using a digital thickness gauge (Heidenhain, Germany).

3. Results and Discussion

3.1. Effect of pre-irradiation dose on the mechanical properties of ETFE base films

The irradiation of polymers is well known to have several effects on their structures and properties [27]. Depending on the base material and the irradiation conditions, it is known that a base polymer undergoes irreversible mechanical degradation to some extent at certain irradiation dose. The influence of electron beam irradiation in air and the variation of irradiation dose on mechanical properties of pristine ETFE film were evaluated employing irradiation doses ranging from 1.5 to 200 kGy. It was found that irradiation did not affect the shape of the strain-stress curves, however, their characteristic values (elongation at break and tensile strength) were altered (Figure 2).

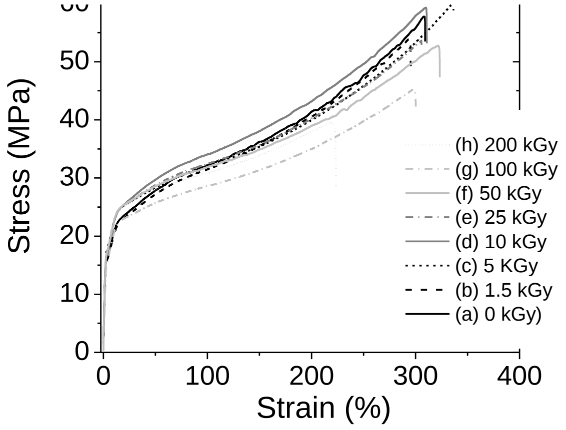

Figure 2: Tensile strain-stress curves of ETFE films for varying irradiation doses in the MD. (a) 0 kGy (unirradiated base film), (b) 1.5 kGy, (c) 5 kGy, (d) 10 kGy, (e) 25 kGy, (f) 50 kGy, (g) 100 kGy, (h) 200 kGy.

The tensile strength of ETFE base film is markedly reduced upon irradiation and the values are almost constant for low doses, such as 1.5 and 5 kGy, whereas a significant decrease is observed beyond an irradiation dose of 25 kGy (Figure 3). The mechanical properties in both directions follow the same trend as a function of the irradiation dose. As expected, in machining direction a higher tensile strength is observed due to the orientation induced by the anisotropy of the base film introduced during the processing, where the crystalline domains were pointed out to be oriented perpendicular to the machining direction [28].

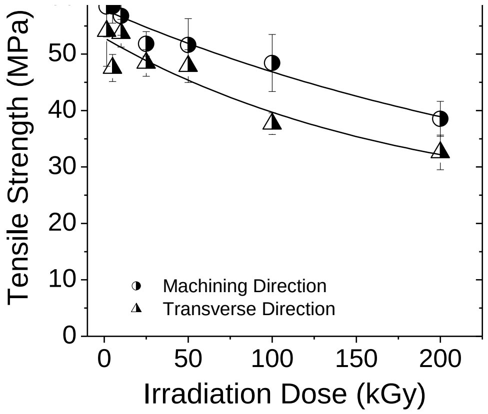

Figure 3: Effect of irradiation dose on tensile strength of the ETFE films in both directions.

No significant change in elongation at break values for ETFE films were observed for both directions up to an irradiation dose of 50 kGy (Figure 4). However, as the irradiation dose increases beyond a dose of 50 kGy, the elongation at break decreases gradually. The elongation at break decreases by about 25 % of its initial value measured for the unirradiated film at an irradiation dose of 200 kGy. In the dose range studied, it is clear that both machining and transverse directions display a similar trend with increasing irradiation dose. Moreover, the elongation at break values are obviously lower in machining direction (MD) compared to those in transverse direction (TD) as stated previously (anisotropy of the base film acquired during the processing) [28].

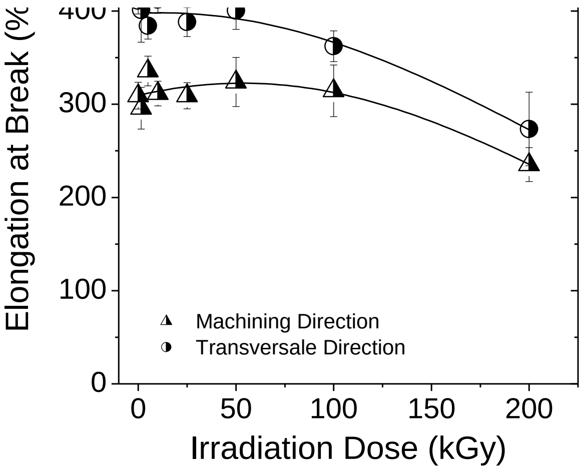

Figure 4: Effect of irradiation dose on elongation at break of ETFE films in both directions.

The yield strength is unaffected by the irradiation and only a decrease of the modulus of elasticity beyond a dose of 25 kGy was observed and then no further decrease was observed (Figure 5).

The obtained results of the different mechanical properties are in good agreement with the previous investigation on the effect of irradiation dose (up to 30 kGy) on the crystallinity of ETFE base film [6]. Indeed, we previously reported that there was no significant change in the melting temperature and the crystallinity occurring with increasing irradiation dose from 0 kGy to 30 kGy. Based on that, it is assumed that at low irradiation dose (25 kGy) no significant changes in the structure and in the physico-chemical properties occur.

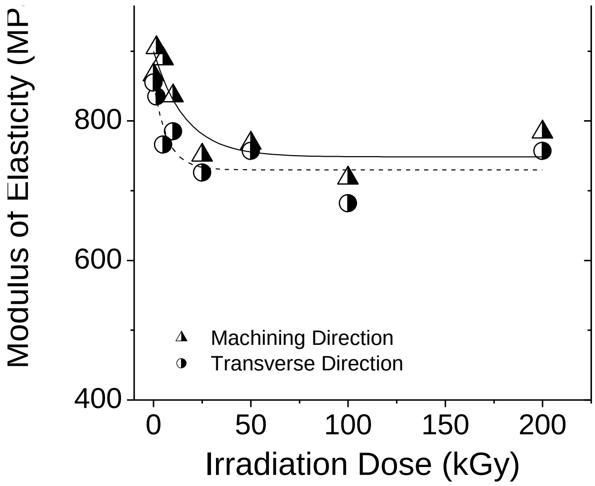

Figure 5: Modulus of elasticity of ETFE films as function of the irradiation dose in both directions.

The increase of the irradiation dose in the presence of oxygen over certain dose of 30 to 50 kGy leads to considerable deterioration of the mechanical properties of pristine ETFE films. The observed changes in the mechanical properties are attributed to increased radiation damage to the trunk polymer. In fact, the increase of the melt flow index (MFI) of the ETFE base film irradiated under air due to chain scission was reported [23]. Previously, Nasef *et al*. reported on mechanical properties and structural changes of ETFE, PVDF and PFA Films [17, 18]. These authors reported improved tensile strength values for PVDF films due to irradiation (e-beam irradiation under air), whereas the tensile strength decreased for PFA and ETFE films. In all cases, elongation at break was reduced by irradiation and the presumed reactions of crosslinking and/or chain scissions, interacting in a complex combination, were suspected to take place under specific conditions. Chen *et al*. investigated the effect of gamma ray irradiation (0-52 kGy) on various base films, including FEP, ETFE PVDF, PVF, PTFE, crosslinked PTFE and PFA [19] and a similar decrease in elongation at break and tensile strength was reported by the authors.

3.2. Effect of graft level

The graft level (GL) is one of the important quantities which has a direct and major influence on the different *ex situ* and *in situ* properties of the grafted films and, subsequently, on the membranes. Therefore, the variation of mechanical properties with GL was examined in detail during this study. A set of ETFE based grafted films and membranes with GL varying from

7% to 44% were investigated. The styrene/DVB volumetric ratio was varied from a value of 10/0 to 9/1 in the initial grafting solution in each series.

The uncrosslinked grafted films undergo the so-called necking phenomenon, typically observed in the case of strain softening causing a decrease of the samples cross section (Figure 6) [26, 29]. Beyond the yield point the deformation proceeds and the chains orient along the deformation axis and the observed increase in the strain-stress curve (strain hardening) is attributed to the existence of entanglements (physical crosslinks). For the crosslinked grafted films (5 % and 10 % DVB) no necking phenomenon or strain softening were observed with increasing the graft level. However, the strain hardening slope was much more pronounced as the graft level increases for the crosslinked samples. Assuming that the overall changes on the film during strain-stress test is superimposition of different deformation type (inter-atomic bonds stretching, uncoiling and inter-chain slippage), we can conclude that the entanglement and branching increases with the graft level for the crosslinked films. The effect of crosslinking decoupled from the influence of graft level will be discussed in the next section.

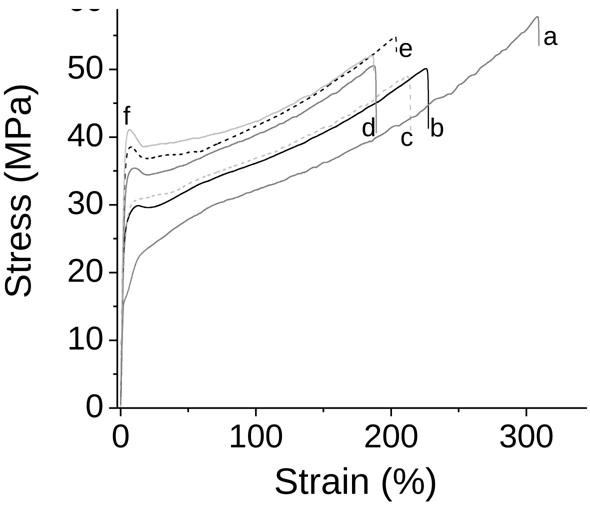

Figure 6: strain-stress curves of ETFE and ETFE-g-styrene films (MD) with different graft levels: (a) ETFE base film, (b) 13%, (c) 17%, (d) 25%, (e) 31%, (f) 44%.

The strain-stress curves show clearly that the yield strength of the grafted films (uncrosslinked and crosslinked) increases with the graft level (Figure 7). As an example, yield stress increases from 25 MPa to 48 MPa as graft level increases from 5 % to 51% for machining direction (DVB concentration of 5%). Similarly, the modulus of elasticity increases with graft level (Figure 9). In fact, by grafting styrene on ETFE base film, the initial dimensions of the films change in both directions, particularly in the machining direction (MD). This introduces important stresses to the polymer chains, which explains the change of the elastic deformation for each graft level. Indeed, with increasing the graft level, we need a higher load and a lower elongation before an irreversible deformation occurs.

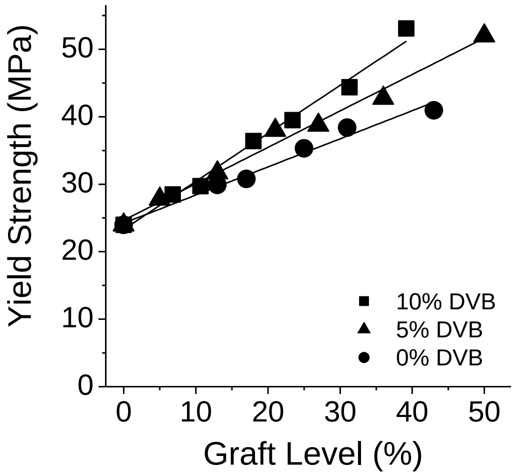

Figure 7: Evolution of the yield strength of ETFE-*g*-styrene films (MD) as function of the GL. Grafted films with different DVB concentration in the initial grafting solution.

The slope of the yield strength values versus the graft level are slightly increasing with the crosslinking extent of the grafted films (Figure 7). The yield strength appears to be relatively independent of the crosslinker concentration at lower graft levels (less than 15 %), and slight differences are observed up to a graft level value of 25 %. The deviation at high graft levels (graft level values > 30 %) between the uncrosslinked and crosslinked grafted films is due to the fact that the crosslinking with DVB resulted in a decrease in the ductility of the ETFE base film and its deformation capability. Thereby, the yield strength of the base film is mainly affected by the increase of the graft level (graft level values < 30 %) and also by the crosslinking (graft level values > 30 %). It is well known that the yield strength of the semi-crystalline polymer gives qualitative insight into the mobility of the chains and their degree of freedom. Therefore, the molecular and chain flexibility have a predominant impact on the relative mechanical properties of the grafted films and resulting membranes. Yet, the observed improvements can be attributed to the possible chain entanglement and branching occurred upon grafting.

Compared to the values obtained for the uncrosslinked grafted films, the elongation at break decreases more in the case of crosslinked films as the graft level increases (Figure 8). Based on our previous thermogravimetric analysis study of ETFE grafted films indicating two phase system [6], it is necessary to explain the mechanical properties of the grafted films by considering the mechanical properties of the two phases, polystyrene and ETFE base polymer. In fact, the bulky pendant phenyl group creates steric hindrance which results in a stiffer polymer chain. Therefore, the decrease in elongation at break is a consequence of the stiff polystyrene chain. In addition to the discussed factors, the decrease in crystallinity may also explain the observed deterioration in mechanical properties as mentioned. In fact, the crystallites of the base film were already reported to behave as virtual crosslinks [23]. We previously observed the tendency of the inherent crystallinity of ETFE base film (initially of a value of about 34 %) to decrease to some extent as GL increases [6].

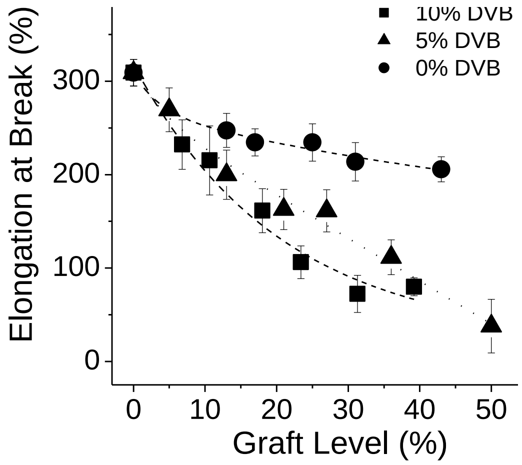

Figure 8: Elongation at break of ETFE-g-styrene films (MD) as function of the GL. Grafted films with different DVB concentrations (0, 5, 10 %) in the initial grafting solution.

It has to be pointed out that notable differences are observed at lower graft levels between machining and transverse directions of the grafted films as far as yield strength and elongation at break are considered.

The same trends shown for the grafted films in term of tensile strength, modulus of elasticity, yield strength and elongation at break versus the increase of the graft level were observed for the resulting membranes (Figure 8 and 9).

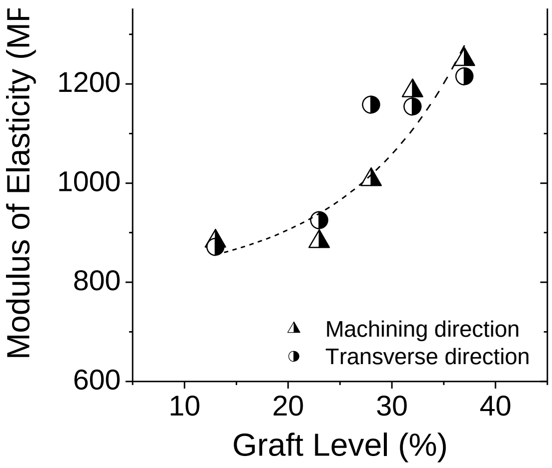

Figure 9: Modulus of elasticity of ETFE-*g*-styrene based membranes as function of the GL in the MD and TD.

In fact, the elongation at break decreases with the increase of the graft level, whereas the opposite is observed for the yield strength and the modulus of elasticity. The same behavior was observed for perfluorinated vinyl monomer grafted into crosslinked PTFE film [30].
The comparison of the obtained results for the grafted films and their membrane counterparts showed that the latter possess inferior mechanical properties with the increase of the graft level as predicted.

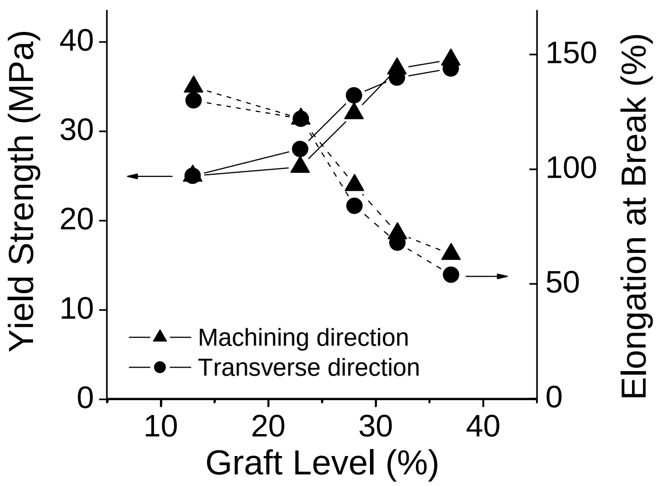

Figure 9: Elongation ate break and modulus of elasticity of ETFE-*g*-styrene/DVB (5% DVB) based membranes with varying graft level.

3.3. Effect of crosslinker concentration

The crosslinking is a key parameter which has a direct influence on several important properties for the grafted membranes (water uptake, conductivity, fuel cell durability, etc) [7-9]. To ensure good performance and improve the lifetime of the grafted membrane during fuel cell operating, the crosslinker content has to be optimized. A set of strain-stress experiments on grafted films and membranes with a fixed graft level of around 25 % with varying crosslinker (DVB) concentration in the initial grafting solution from 0 % to 15 % of DVB were performed. Thus, the influence of the crosslinker concentration on the mechanical property changes of ETFE based grafted films and their respective membranes was studied.

As shown in the Figure 10, the tensile strain-stress curves do not show any significant difference regarding the yield strength at a fix graft level value of ~ 25. However, we observed a clear trend concerning the other parameters. An increase of the strain hardening slope is observed as the crosslinker concentration increases. This suggests that the increase of DVB not only reduces the toughness of the base film but increases the brittleness of the grafted films.

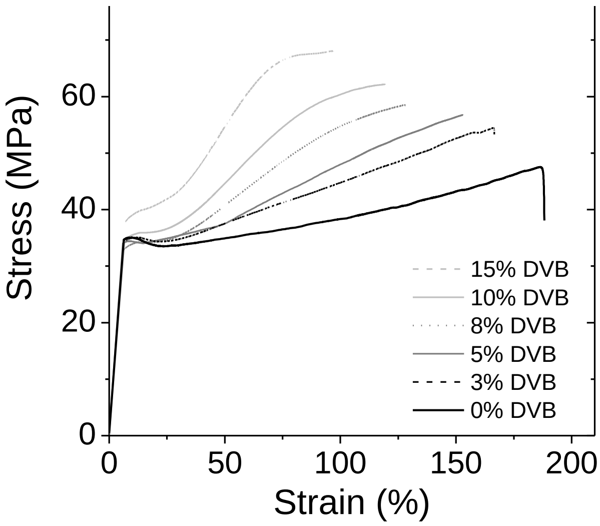

Figure 10: Strain-stress curves of ETFE-*g*-styrene/DVB films (MD) with different DVB concentration in the initial grafting solution.

The tensile strength of ETFE based grafted films and membranes increases with the DVB concentration, while the elongation at break decreases significantly (Figure 11 and 12). Furthermore, the observed decrease for the elongation at break was markedly high, where it is of about 280 % for the uncrosslinked grafted films and it becomes 100 % for DVB concentration of 15 %. The observed trend may be resulting from the significant changes occurring in the structure of the films by crosslinking. Thus, the tensile strength and elongation at break are closely related to the crystallinity of the base film and its structure. Recrystallization experiments on these films show a multiplicity pattern in the exothermic peaks of the crosslinked grafted films, whereas the crystallinity itself was not substantially affected [31]. It is assumed that two types of crystallites are present in the crosslinked grafted films, leading to completely different chain mobility. One crystallite type is slightly affected by the crosslinking, while the chain flexibility of the second type is hindered even if it is assumed that the most of grafting occurs on the amorphous zone of the base film [32].

In addition, it is expected that the brittleness of the grafted films and the resulting membranes increases with the DVB content. The increase of the crosslinker concentration is assumed to create a denser network and induce more entanglement between the grafted chains and the base film. This is in agreement with the diffusion limitation observed during grafting at high DVB concentrations [7]. Likewise, the investigation of the thermal stability (TGA results) revealed that the amount of the thermal degradation residue of the crosslinked samples increased with the increase of the DVB content [7].

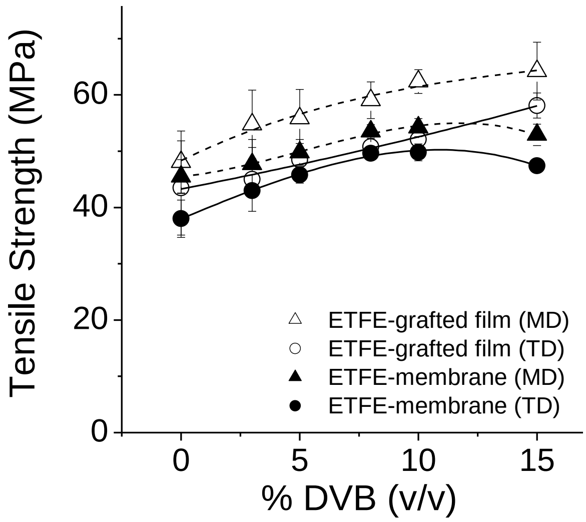

Figure 11: Effect of DVB concentration in the initial solution on the tensile strength of ETFE-*g*-styrene/DVB films and membranes (GL ~ 25%) in both direction (MD and TD).

Although, both machining and transverse directions exhibit similar tendency in terms of tensile strength and elongation at break, slight differences are observable. Indeed, starting from a value of 8% DVB, the tendency of elongation at break for the machining and the transverse direction becomes different. It was observed previously that the machining direction expanded slightly more than the transverse direction after the grafting reaction (independently of the crosslinker concentration) and this tendency disappeared after sulfonation [7].

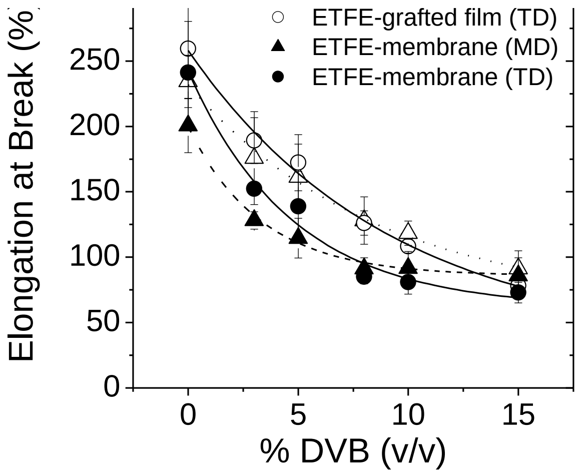

Figure 12: Effect of DVB concentration in the initial solution on the elongation at break of ETFE-*g*-styrene/DVB films and membranes in both direction (MD and TD).

The other observation is that the mechanical properties of the grafted films are superior to those of their resulting membranes in both directions (elongation at break value of 161 % of grafted film decreases to a value of 114 % after sulfonation). In fact, the observed differences are expected due to the changes happening in dimensional stability, crystallinity, structure and morphology after grafting and sulfonation. The grafted films showed a higher crystallinity than the resulting membranes as a function of the studied crosslinker concentrations [7, 31]. Indeed, the observed decrease in the membrane crystallinity in comparison with the grafted film is mostly due to the strong hydrophilic-hydrophobic stress induced by water uptake (crystallites disruption) [6].

Although, the crosslinking increases in one hand the brittleness of the grafted membranes it was found in the other hand to reduce the area shrinking (wet→dry). Recently, simulations and experimental studies on Nafion membrane under fuel cell environment were performed, whereas, the influence of humidity and temperature on the mechanical properties were established [14-16]. The in-plane stress in the membrane due to humidity cycling (hydration-dehydration) was found to be the most affected parameter, which has to be improved to reduce the fatigue behaviour in the membrane.

3.4. Influence of the membrane preparation process on the mechanical properties of ETFE based membrane

In order to evaluate the changes on the mechanical properties of the base film occurring during the overall preparation process (irradiation, grafting and sulfonation), strain-stress tests were performed for the optimized ETFE based membrane. For this, ETFE base film, irradiated film (irradiation dose of 1.5 kGy), grafted film (5% DVB and GL~25%) and membrane were prepared and tested.

To begin with, both ETFE and FEP, the radiation grafted membranes prepared based on electron beam irradiation under inert atmosphere have better mechanical properties than the membranes prepared from gamma irradiated films under air [2]. It has been reported that ETFE based grafted films and membranes exhibit comparably better mechanical properties than FEP based ones since ETFE films are available at higher molecular weight which enhances breaking strength and toughness [5]. In addition, FEP undergoes a greater extent of chain scission reactions when irradiated compared to ETFE [23].

Comparison was made between the ETFE-based membrane (5% DVB and GL~25%) and the Nafion®-112 (Figure 13). In fact, the choice of such DVB concentration for the ETFE-based membrane was suggested from the obtained result of the *in situ* fuel cell test. Indeed, it was shown that the presence of crosslinker at that concentration in ETFE grafted films improves the electrochemical performance in fuel cells [8].

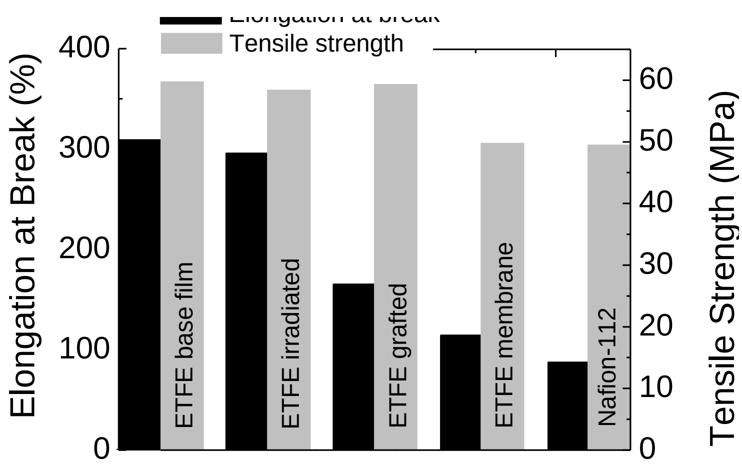

Figure 13: Effect of preparation process (irradiation, grafting and sulfonation) on the elongation at break and tensile strength of ETFE-g-styrene/DVB membrane (5% DVB (v/v) and GL ~ 25 %) in the machining direction. Membranes are exchanged to K^+ form and dried. Nafion®112 membrane is presented for comparison.

The general observation is that the major loss occurs for the elongation at break of the polymer after the grafting process. Indeed, we observed a decrease of about 50 % of the elongation at break value due to the grafting and then more loss occurs after the sulfonation process. No significant change on the tensile strength was observed after grafting of the base film, however, only a slight loss occurs after the sulfonation procedure.

The comparison of the Young's modulus of the ETFE-based material over the preparation process was also carried out (Table 1.).

Table 1: Modulus of elasticity of ETFE-g-styrene/DVB (5% DVB (v/v) and GL ~ 25 %) and Nafion®112 based membranes in both direction (MD and TD).

	Modulus of elasticity [MPa]	
	MD	TD
ETFE	866	855
ETFE-irradiated	905	835
ETFE-grafted	1267	1365
ETFE-sulfonated (membrane)	820	844
Nafion®112	567	575

The elasticity modulus does not show any significant changes after irradiation (1.5 kGy) and then a noticeable increase was observed after grafting. After sulfonation and swelling the observed increase in the modulus of elasticity is lost. This can be understandable from the occurring changes of the membrane structure, owing to its decrease in crystallinity (combination of crystallite disruption and dilution effect) [6].

A comparison of the mechanical properties of the ETFE (5 % DVB (v/v) and GL ~ 25 %), FEP (10 % DVB (v/v) and GL ~ 20 %) based membranes and Nafion®112 was performed. In fact, the measurements were carried out as described previously and the results of the tensile strength and the elongation at break are depicted in Figure 14. Moreover, the comparison of the elasticity modulus of the different type membranes (ETFE and nafion®112 results are listed in Table 3, whereas the values determined for the FEP based membrane are 880 MPa and 974 MPa in the machining and transverse direction, respectively) was carried out.

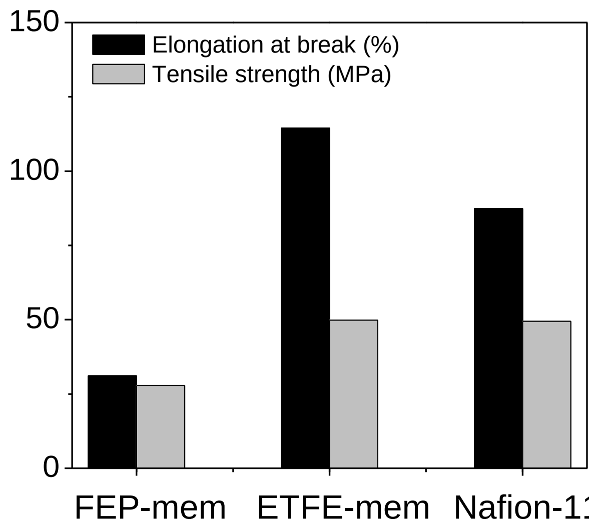

Figure 14: Elongation at break and tensile strength of ETFE-*g*-styrene/DVB (5 % DVB (v/v) and GL ~ 25 %), FEP-*g*-styrene/DVB (10 % DVB (v/v) and GL ~ 20 %) and Nafion®112 based membranes in the machining direction. Membranes are exchanged to K^+ form and dried.

Both tensile strength and elongation at break of **N**afion®112 and ETFE-based membrane are higher than the FEP base membrane values. However, the FEP based membrane shows a slightly higher modulus of elasticity value compared to the ETFE-based membrane in both directions. The modulus of elasticity and elongation at break of Nafion®112 appears to be lower in comparison with the grafted ETFE membrane under the specified conditions. We note here that both grafted membranes are crosslinked and posses lower thickness values (29 µm for FEP and and 33 µm for ETFE), while the Nafion®112 is uncrosslinked and is thicker (58 µm), which may explain its lower modulus of elasticity. In fact, the observed low values of the FEP based membrane can be easily attributed to the base film intrinsic properties and the process of grafting. Indeed, the FEP base membrane is obtained with 10 % DVB in the initial grafting solution and the used dose is double than that used in the case of ETFE (1.5 kGy).

4. Conclusion

The study of the influence of the irradiation dose, the crosslinker concentration and graft level on the mechanical properties reveals that the most affected parameter of the radiation grafted membrane is the elongation at break. Indeed, the plasticity of the ETFE based grafted film and membrane decreases drastically with the increase of the graft level and the crosslinker concentration. Furthermore, the ETFE based film shows a good mechanical stability at relatively high doses, which provides the opportunity to use it with other monomer systems which suffer from poor grafting kinetics, such as, alpha-metylstyrene/methacrylonitrile monomer combination [33].

Mechanical properties of the base polymer films were different and dependant on the initial sample orientation (either machining direction or transverse direction). In general, mechanical properties (tensile strength; elongation at break) of grafted films are poorer than those of pristine base polymers. Furthermore, the mechanical properties of the resulting membranes are poorer than their respective grafted films in dry state.

As general statement for the radiation grafted membranes, we found that the less we irradiate, the less we graft and crosslink, the better are the mechanical properties. Therefore, it is necessary to find a compromise between the mechanical robustness of the membrane and its proton conductivity. This study, in combination with previous work, leads to the conclusion that 5 % of DVB is a good proportion to increase the fuel cell's performance, and prevent at the same time the ETFE base membrane from excessive losses in the mechanical properties. Indeed, the tensile strength of both Nafion® 112 and the ETFE based membrane are fairly similar in the dried state and the latter shows slightly better elongation at break.

The mechanical properties of the grafted membranes in fully swollen state are better, owing to the plasticizing effect of water. Hence, the mechanical properties of the grafted membranes under realistic environments (fuel cell operation conditions: high temperature, humidity, pressure, etc) are not yet investigated and are the subject of ongoing work.

References

[1] M. M. Nasef and E. S. A. Hegazy, *Prog. Polym. Sci.*, 29 (2004) 499.

[2] S. Alkan Gürsel, L. Gubler, B. Gupta and G. G. Scherer, Adv. Polym. Sci., 215 (2008) 157.

[3] L. Gubler, S. Alkan Gürsel and G. G. Scherer, Fuel Cells, 5 (2005) 317.

[4] L. Gubler, H. Kuhn, T. J. Schmidt, G. G. Scherer, H. P. Brack and K. Simbeck, Fuel Cells, 4 (2004) 196.

[5] L. Gubler, N. Prost, S. A. Gürsel and G. G. Scherer, Solid State Ionics, 176 (2005) 2849.

[6] S. Alkan-Gürsel, J. Schneider, H. Ben youcef, A. Wokaun and G. G. Scherer, J. Appl. Polym. Sci., 108 (2008) 3577.

[7] H. Ben youcef, S. Alkan-Gürsel, A. Wokaun and G. G. Scherer, J. Membr. Sci., 311 (2008) 208.

[8] L. Gubler, H. Ben youcef, S. Alkan-Gürsel, A. Wokaun and G.G. Scherer, J. Electrochem. Soc., 155 (2008) B921.

[9] H. Ben youcef, L. Gubler, T. Yamaki, S. Sawada, S. A. Gursel, A. Wokaun and G. G. Scherer, J. Electrochem. Soc., 156 (2009) B532.

[10] J. Zu, C. Yu, M. Wu, Z. Jiao, J. Zhang and X. Liu, J. Appl. Polym. Sci., 99 (2006) 3396.

[11] S. Kundu, L. C. Simon, M. Fowler and S. Grot, Polymer, 46 (2005) 11707.

[12] L. Gubler and G. G. Scherer, Adv. Polym. Sci., 215 (2008) 1.

[13] L. Gubler and G. G. Scherer, in Polymer Electrolyte Fuel Cell Durability, M. Inaba, T. J. Schmidt and F. N. Büchi Editors, p. 133, Springer New York (2009).

[14] Y. Tang, A. M. Karlsson, M. H. Santare, M. Gilbert, S. Cleghorn and W. B. Johnson, Materials Science and Engineering: A, 425 (2006) 297.

[15] A. Kusoglu, A. M. Karlsson, M. H. Santare, S. Cleghorn and W. B. Johnson, Journal of Power Sources, 161 (2006) 987.

[16] A. Kusoglu, A. M. Karlsson, M. H. Santare, S. Cleghorn and W. B. Johnson, Journal of Power Sources, 170 (2007) 345.

[17] M. M. Nasef and K. Z. M. Dahlan, Nucl. Instrum. Methods in Phys. Res. Sect. B, 201 (2003) 604.

[18] M. M. Nasef, H. Saidi, H. M. Nor, K. Zaman, M. Dahlan and K. Hashim, J. Appl. Polym. Sci., 73 (1999) 2095.

[19] J. Chen, M. Asano, Y. Maekawa and M. Yoshida, J. Membr. Sci., 277 (2006) 249.

[20] A. Oshima, S. Ikeda, T. Seguchi and Y. Tabata, Radiat. Phys. Chem., 50 (1997) 519.

[21] N. Walsby, F. Sundholm, T. Kallio and G. Sundholm, J. Polym. Sci. Part A: Polym. Chem., 39 (2001) 3008.

[22] N. Walsby, M. Paronen, J. Juhanoja and F. Sundholm, J. Polym. Sci. Part A: Polym. Chem., 38 (2000) 1512.

[23] H. -P. Brack and G. G. Scherer, Macromol. Symp., 126 (1997) 25.

[24] H. P. Brack, H. G. Bührer, L. Bonorand and G. G. Scherer, *J. Mater. Chem.*, 10 (2000) 1795.

[25] B.-N. Kim, D.-H. Lee and D.-H. Han, Polym. Degrad. Stab., 93 (2008) 1214.

[26] I. M. Ward Mechanical properties of solid polymers, 2nd ed., New York: Wiley; 1983.

[27] D. W. Clegg and A. A. Collyer, "Irradiation effects on polymers", ISBN 1-85166-563-3, Elsevier (1991).

[28] K. Mortensen, U. Gasser, S. A. Gürsel and G. G. Scherer, J. Polym. Sci. Part B: Polym. Phys., 46 (2008) 1660.

[29] V. Shah, Handbook of Plastics Testing Technology, 2nd Ed, John Wiley & Sons, 1998.
[30] M. Zhai, J. Chen, S. Hasegawa, D. Li, H. Oku and Y. Maekawa, Eur. Polym. J., 45 (2009) 1668.
[31] H. Ben youcef, Dissertation ETH No. 18215, Swiss Federal Institute of Technology Zürich, 2009.
[32] M. M. Nasef and H. Saidi, Macromol. Mater. Eng., 291 (2006) 972.
[33] L. Gubler, M. Slaski, F. Wallasch, A. Wokaun and G. G. Scherer, Journal of Membrane Science, 339 (2009) 68.