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Pre-Irradiation Grafting of Styrene into Modified Fluoropolymers

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Summary: The grafting of styrene into commercially available fluoropolymer films by the pre-irradiation method has been investigated. Poly(tetrafluoroethylene) (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) (PFA) and poly(tetrafluorethylene-co-ethylene) (ETFE) were chosen as the base polymer material. The influence of the base material, the pre-irradiation dose, and the storage time between the irradiation and the grafting step on the yield of grafting was examined. The base materials were pre-treated by irradiation in the molten state under oxygen-free conditions in order to create branches and cross-links. The effect of pre-treatment on the yield of grafting was studied.

Keywords: cross-linking; Electron beam irradiation; fluoropolymers; graft copolymers; styrene

Introduction

A well-established technique for the preparation of polymer electrolyte membranes for fuel cells is the radiation-induced grafting. Generally, it is an attractive means of modifying the physicochemical properties of commercially available polymer films. The grafted materials frequently possess the superimposition of properties related to the backbone and the grafted chains. The grafting can be initiated by high-energy radiation, such as γ-rays and electron-beams, using the pre-irradiation method or the simultaneous radiation grafting.[1] In the pre-irradiation method, the grafted films are prepared by irradiation of the base films to generate reactive sites, followed by graft polymerization of vinyl monomers into the films. Typically styrene and its derivates have been used to graft because the grafted chains can be easily sulfonated to introduce sulfonic acid groups into the material. Reviews focusing on the preparation of radiation-grafted membranes have been published recently.[2,3]

Fluoropolymer films have been often chosen as the base materials because of their outstanding thermal and chemical stability. Perfluorinated polymers, such as poly(tetrafluoroethylene) (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), and poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) (PFA) predominantly undergo chain scission upon exposure to radiation.[4] In the case of PTFE, this behavior is unfavorable due to the drastic decrease in the mechanical properties of the pre-irradiated film. The copolymer FEP and PFA films have a significant higher radiation resistance then the homopolymer PTFE. Polymer electrolyte membranes based on FEP have been systematically investigated by G. Scherer et al. for about 15 years.[5] The partially fluorinated poly(tetrafluoroethylene-co-ethylene) (ETFE) undergoes cross-linking when irradiation is performed.[6] This advantage has made it a favorable substrate for radiation grafting. [7,8]

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Nevertheless, the interest in using PTFE films for the preparation of ion exchange membranes has been renewed after PTFE was found to be cross-linked upon irradiation in its molten state in an oxygen-free atmosphere.[9,10] Evidence for cross-links in PTFE was derived directly from structural information using ^{19}F solid-state NMR.[11] The radiation resistance of PTFE is much improved by radiation cross-linking.[12] Grafting of styrene into cross-linked PTFE has been studied by several groups.[13–21] It has been found that the yield of grafting of styrene into PTFE can be enhanced by the irradiation of the PTFE in the molten state prior to the pre-irradiation grafting.

Here, the influence of the base material, the pre-irradiation dose, the storage time between the irradiation and the grafting step, and the effect of pre-treatment on the yield of grafting of styrene into thin films of the perfluorinated polymers PTFE, FEP, and PFA as well as the partially fluorinated polymer ETFE is reported. The base materials were pre-treated by irradiation in nitrogen atmosphere at temperatures above their melting temperatures in order to create branches and cross-links.

Experimental Part

Materials

Commercially available PTFE peel film (PTFE Nünchritz GmbH, Glaubitz, Germany), Dyneon™ FEP 6107, Dyneon™ PFA 6510N and Dyneon™ ET 6235 (ETFE) films (Dyneon, Burgkirchen, Germany) with a thickness of 100 μm were used as received. Styrene (Fluka) was reagent grade and utilized without any further purification.

Irradiation for Grafting

The films were irradiated with 1.5 MeV electrons using an electron beam accelerator (ELV-2, Budker Institute of Nuclear Physics, Novosibirsk, Russia) described in detail in ref.[22] In order to initiate the grafting reactions in the subsequent step, the films were irradiated with different doses from 1 kGy to 50 kGy at room temperature in vacuum using a vacuum vessel as described in ref.[23] The vacuum vessel was mounted on the conveyor system of the irradiation facility, and passed under the electron beam at a velocity such that the specimens received the desired dose.

Grafting

The styrene was placed in a glass flask and flushed with nitrogen for at least 30 min prior to grafting. The pre-irradiated films were cut into strips, and immersed in styrene. The grafting reaction was initiated by placing the reaction flask in a water bath at 60 °C. The bubbling of nitrogen was continued for the whole grafting time. After desired reaction period the films were removed, and extracted with toluene in a Soxhlet for 5 h to remove excess styrene and homopolymer adhering to the surface of the grafted films. After that, the films were soaked in methanol for 2 h. Finally, the films were dried in vacuum at 40 °C until a constant mass was gained. The grafting yield Y_{mass} was determined gravimetrically as the mass increase of the films according to Equation 1, where m_g is the mass of the film after grafting and m_0 is the mass of the film before grafting.

$$Y_{mass} = (m_g - m_0)/m_0 \tag{1}$$

Pre-Treatment

The films were irradiated at elevated temperatures (PTFE: 385 °C, PFA: 350 °C, FEP: 290 °C, ETFE: 290 °C) above their melting temperatures under nitrogen atmosphere using the electron beam accelerator and the vacuum vessel mentioned above. The films were placed on an electrically heated carrier. The temperature of the carrier was controlled via a resistance thermocouple. Before the vessel was filled with nitrogen, it was evacuated to 10^{-2} Pa in order to minimize the concentration of oxygen. The total dose of 500 kGy was realized on a step-by-step basis with a dose of 50 kGy per pass. After irradiation, the controlled heating was continued for 20 min.

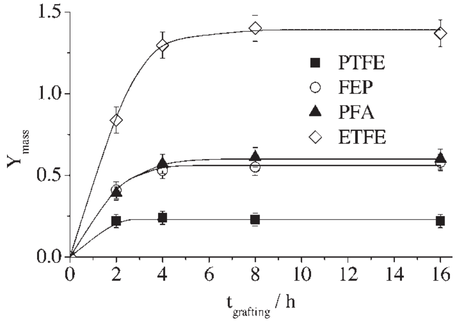

Figure 1.
Yield of grafting Y_{mass} as a function of the grafting time $t_{grafting}$ for various fluoropolymer films. All films were irradiated with a dose of 50 kGy and grafted at a temperature of 60 °C.

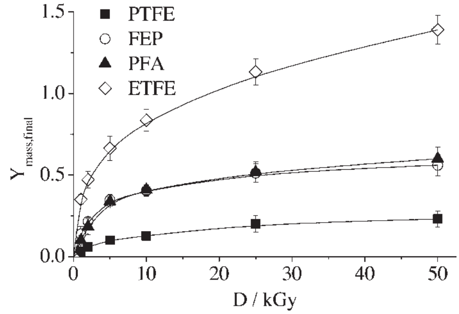

Figure 2.
Final yield of grafting $Y_{mass,final}$ as a function of the grafting dose D for various fluoropolymer films. All films were grafted at a temperature of 60 °C for 8 hours.

Results and Discussion

The dependence of the yield of grafting on the grafting time is illustrated in Figure 1. The grafting yield shows an initial rapid increase and then levels off with increasing grafting time. In the case of all polymers, a nearly constant level is reached after 8 hours. The radiation-induced grafting is assumed to occurs by the grafting front mechanism.[1] The grafting reaction initially starts at the surface of the polymer films which is in contact with the styrene. The grafted surface layer swells in styrene and the styrene diffuses further into the film. The two grafting fronts meet in the middle of the film. Continue the grafting the yield of grafting only changes slightly.

Figure 1 shows that the yield of grafting reached in the four fluoropolymers after 16 hours grafting varies significantly. The lowest yield of grafting was obtained for PTFE. The graft levels of FEP and PFA are similar in magnitude and much greater than those of PTFE. The reason is assumed to be the lower crystallinity of the copolymer films compared to the PTFE film. The crystallinity of the polymer material has an influence of the yield of grafting because grafting is expected to occur primarily in the amorphous or amorphous/crystalline interfacial regions.[24] The highest yield of grafting was observed in the case of the partially fluorinated ETFE. The extent of radical generation per unit irradiation dose is assumed to be greater in the case of the partially fluorinated ETFE in comparison to the perfluorinated polymers.

The yield of the graft polymerization of styrene into FEP films is known to be strongly affected by the reaction conditions such as grafting time and pre-irradiation dose.[25] Figure 2 shows the effect of the dose applied in the irradiation step on the final yield of grafting for the four fluoropolymer films. A pre-irradiation dose of 1 kGy is sufficient to initiate the grafting reaction. The final yield of grafting shows an increasing trend with the increase of the dose, but the extent of grafting per unit irradiation dose decreases. The behavior may be attributed to the fact that the concentration of radicals generated during the pre-irradiation step also increases. More radicals are, therefore, available for the grafting reaction with increasing dose. However, with rising dose considerable recombination of radicals takes place during the irradiation.

In the pre-irradiation method, the polymer film is activated in a irradiation step and then grafted with the monomer in a subsequent step. These method is attractive because the grafting may be performed later far away from the radiation source. The storage of the irradiated films prior to the grafting is an important factor which might influence the concentration of reactive sites. It was found that irradiated FEP films stored at a temperature of −60 °C for four months retain their activity.[25] The influence of the storage time between the irradiation and the grafting step on the yield of grafting was investigated to ascertain the efficiency of the irradiation in initiating grafting into the four fluoropolymer films with the storage. The polymer films were irradiated with a dose of 50 kGy in order to produce radicals for the following grafting procedure and stored at a temperature of 5 °C in air. Figure 3 shows the yield of grafting in dependence on the storage time. The first grafting experiment was carried out one day after irradiation. Figure 3 shows that the yield of grafting stays nearly constant even after 12 weeks of storage for the perfluorinated polymers. The trapped radicals formed inside the perfluorinated polymers are assumed to be thermally stable during the storage at low temperature. For ETFE the yield of grafting slowly decreases with storage time. The reason may be due the formation of hydroperoxides, which is possible in ETFE in addition to the generation of radicals as opposed to reactions in perfluorinated polymers. The conclusion is that the grafting of styrene into PTFE, FEP and PFA films may be performed days or weeks after the irradiation, but ETFE films should be grafted within the next few days in order to use the reactive sites formed by pre-irradiation effectively.

In further experiments, the thermal stability of the reactive sites was studied. The influence of an annealing step on the yield of grafting was investigated. The polymer films were annealed at different temperatures for 8 hours in air. The results are illustrated in Figure 4. The four polymers studied show different behavior. The lowest yield of grafting was realized for PTFE, but the reactive sites in PTFE seems to be thermally very stable. Approximately the same yield of grafting was obtained for PFA and FEP, but the reactive sites formed in FEP are less stable than in PFA.

The reactive sites generated in ETFE possess the lowest stability. An annealing at 50 °C already results in a drastic decrease of the yield of grafting. The yield of grafting decreases by a factor of ten after annealing at 100 °C. The low thermal stability of the reactive sites in ETFE is not surprising, because a decrease of the yield of grafting was also found after storage at low temperature for several days.

The four fluoropolymer films were pre-treated by irradiation in oxygen-free atmosphere at elevated temperatures. Chemical structures like branches and cross-links are generated by this pre-treatment.[11,26–30] It was supposed that these changes in the chemical structure give rise to a higher

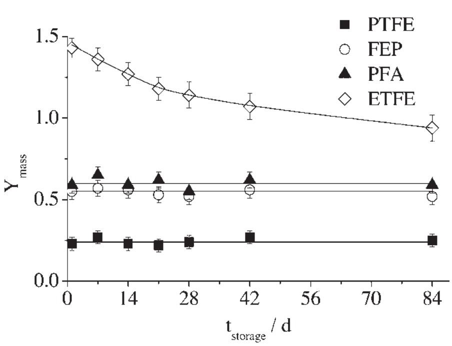

Figure 3.
Yield of grafting Y_{mass} as a function of the time between irradiation and grafting $t_{storage}$ for various fluoropolymer films. All films were irradiated with a dose of 50 kGy and grafted at a temperature of 60 °C for 8 hours.

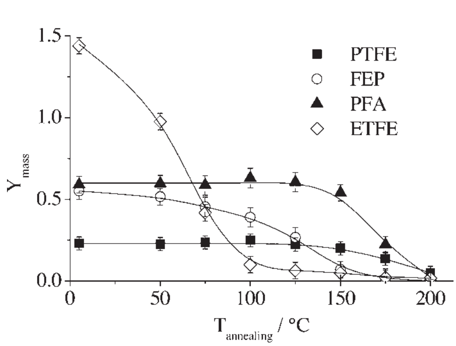

Figure 4.
Yield of grafting Y_{mass} as a function of annealing temperature $T_{annealing}$ for various fluoropolymers. All films were irradiated with a dose of 50 kGy, annealed in air at different temperatures for 8 hours and grafted at a temperature of 60 °C for 8 hours.

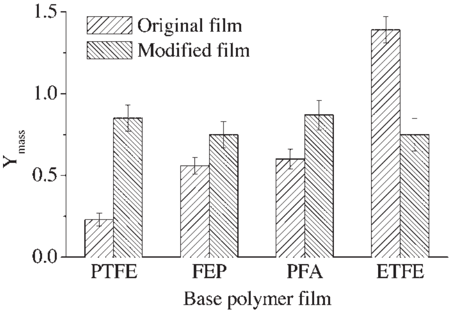

Figure 5.
Yield of grafting Y_{mass} for original and modified polymer films. All films were irradiated with a dose of 50 kGy and grafted at a temperature of 60 °C for 8 hours.

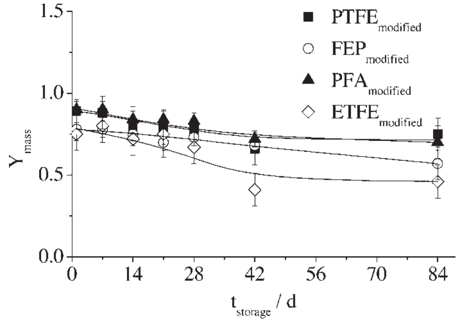

Figure 6.
Yield of grafting Y_{mass} as a function of the time between irradiation and grafting $t_{storage}$ for modified fluoropolymer films. All films were irradiated with a dose of 50 kGy and grafted at a temperature of 60 °C for 8 hours.

concentration of reactive sites for grafting in the following irradiation step. Figure 5 shows the yield of grafting Y_{mass} for original and modified polymer films, which were pre-irradiated with the same dose and grafted under the same conditions. It is quite evident that the pre-treatment has an influence on the yield of grafting in the case of the PTFE material. The yield of the graft polymerization of styrene into the pre-treated PTFE films is much higher than that of the original PTFE film. The yield of grafting is increased through the pre-treatment by a factor of about four. The reason for the higher yield of grafting of radiation-modified films compared to original PTFE film is assumed to be a higher content of trapped radicals. A higher concentration of trapped radicals is known to give more active sites for grafting, which results in higher yield of grafting under same reaction conditions. For the copolymers FEP and PFA the effect is less strong. In the case of the partially fluorinated ETFE, it is not possible to enhance the yield of grafting through a irradiation of the base film in the molten state. Quite the contrary, the yield of grafting was found to decrease significantly.

The influence of the storage time between the pre-irradiation and the grafting step on the yield of grafting was also investigated for the modified fluoropolymer films. Figure 6 shows that the yield of grafting decreases with increasing storage time for all modified fluoropolymers. Therefore, the modified films should be grafted within the next two weeks after the pre-irradiation.

Results about the thermal stability of the reactive sites in the modified fluoropolymer films are shown in Figure 7. Compared to the original films, the reactive sites in the modified films have a lower thermal stability. An annealing at 50 °C already results in a decrease of the yield of grafting for all modified films. The stability decreases in the sequence: PTFE > PFA > FEP > ETFE.

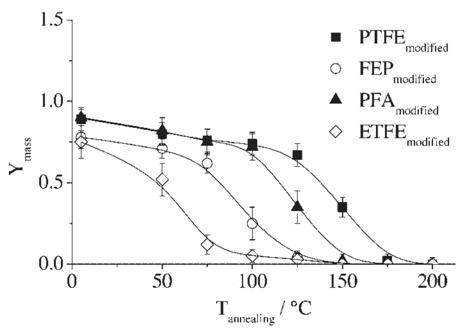

Figure 7.
Yield of grafting Y_{mass} as a function of annealing temperature $T_{annealing}$ for modified fluoropolymers. All films were irradiated with a dose of 50 kGy, annealed in air at different temperatures for 8 hours and grafted at a temperature of 60 °C for 8 hours.

Conclusions

The pre-irradiation grafting of styrene into different fluoropolymer films was studied. The nature of the base polymer film was confirmed to be an important factor in the grafting process. The yield of grafting realized using the same pre-irradiation and grafting conditions shows the following sequence: PTFE < FEP ≈ PFA < ETFE. For all fluoropolymers investigated it was found that the yield of grafting is influenced by the grafting time and the grafting dose. The storage time between pre-irradiation and grafting only has a influence on the yield of grafting into ETFE. The conclusion is that the grafting of styrene into the perfluorinated films may be performed days or weeks after the films were activated by pre-irradiation, but ETFE films should be grafted within the next few days in order to use the reactive sites formed by the pre-irradiation effectively. It was confirmed that the grafting of styrene into PTFE can be enhanced by a pre-treatment of the PTFE, which was realized by irradiation in the molten state. Similar results were found for the perfluorinated copolymers FEP and PFA, but the relative increase of the yield of grafting is lower than in the case of PTFE. It is not possible to increase the yield of grafting into ETFE through the irradiation of this polymer in the molten state.

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