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Crosslinking of poly(vinylene fluoride) separators by gamma-irradiation for electrochemical high power charge applications

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ABSTRACT

Macroporous poly(vinylene fluoride) (PVdF) separators were prepared by phase inversion method and introduced to a gamma (**γ**) radiation with and without cross-linking agents. Triallyl isocyanurate (TAIC) and a macromonomer of ethylene oxide- propylene oxide (MEP) were used as a cross-linking agent. The resulting membranes were characterized in terms of thermal and mechanical properties. Ionic conductivities were determined in a molar solution of tetraethylammonium tetrafluoroborate ($TEABF_4$) in acetonitrile (AN) and propylene carbonate (PC). Excellent mechanical properties (250 MPa at 25 °C) and conductivities (14 mS cm^{-1}) were obtained for the cross-linked separator prepared with TAIC.

1. Introduction

Previously macroporous PVdF based separator for supercapacitors demonstrated as a novel and promising separator for supercapacitors [1–4]. This separator showed a high conductivity due to its highly porous structure (80% porosity). However, this high porosity leaded to have lower mechanical properties compared to the commercial separators such as Celgard® (Polypropylene) or cellulosic (Batscap) separators.

Mechanical strength of membranes can be improved by either addition of reinforcing additives to a polymer or cross-linking the membrane [5–12]. Fluorinated polymers can be cross-linked by chemical reactions or irradiation methods. Due the relative inertness of these types of polymers, their chemical cross-linking is rather difficult, however cross-linking agents such as polyamines, polyphenols or peroxides can be used to facilitate the reactions. The combination of the peroxide/ triallylisocyanurate is the most effective one which undergoes a radical reaction for cross-linking [13].

On the other hand irradiation is a very useful method especially for low-thickness films. Due to the polarity of PVdF, it is easy to create *in situ* radicals allowing the formation of a crosslinked network through the addition of an agent (TAIC, peroxides, etc.) (Fig. 1). Moreover since radical species are involved, the presence of quenching agent has to be avoided. This is particularly involved in the presence of molecular oxygen which leads to the formation of peroxides (Fig. 2).

Electron beam, X-ray, UV or gamma (γ) radiations can be used to modify the structure of the polymer. In our study, due to the efficient and easy respond of PVdF to γ-ray, our separators were subjected to γ-radiation with and without cross-linking agents. Triallyl isocyanurate (TAIC) and macromonomer of ethylene oxide/propoylene oxide (MEP) (Fig. 3) were used as co-agents.

2. Experimental

Porous PVdF membranes were prepared as described previously [4] with using acetone as a solvent and xylene as a non-solvent by the phase inversion method. The polymer powder (Kynar® 741) was supplied from Arkema. Resulting PVdF solutions were casted on an aluminum plate then they were placed in an oven at 60 °C to evaporate solvents. The films were then maintained under-vacuum at 100 °C for 2 days.

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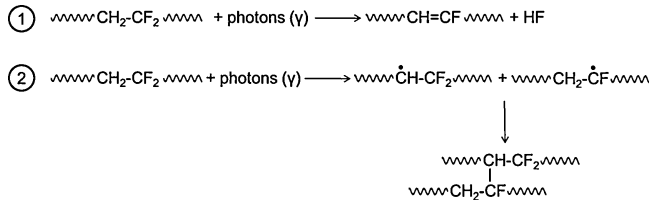

Fig. 1. Possible reactions of PVdF under gamma irradiation.

The separators containing co-agents were prepared with the same method and co-agents added to PVdF before addition of the solvent and non-solvent. Co-agent TAIC was supplied from Natrochem (TAIC DLC-A). MEP co-agent is not a commercial product and was synthesized according to the procedure proposed by Kono et al. [14].

The samples were irradiated at 2 different doses (150 and 300 kGy), using an industrial Co^{60} gamma rays (IONISOS SA, Dagneux, France) with a dose rate of 0.7 kGy per hour at 25 °C. An annealing at 100 °C under argon was performed after irradiation in order to favor the reaction of remaining radicals.

SEM observations were performed on a LEO S440 SEM instrument. The membrane surfaces and cross-section were observed. For the cross-section observation, the membrane was freeze-fractured in liquid nitrogen.

The thermal and mechanical characterizations were carried out using the same protocol described in a previous paper [4].

For conductivity measurements, the porous membranes were soaked in 1 M tetraethyl ammonium tetrafluoroborate ($TEABF_4$) in acetonitrile (AN) or propylene carbonate (PC) for supercapacitor applications and 1 M solution of $LiPF_6$ in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) for 30 minutes, and then sandwiched between two stainless steel electrodes in a dry box. Conductivities were determined by electrochemical impedance spectroscopy using an HP 4192A Impedance Analyzer in the frequency range 5 Hz–13 MHz. The measurements were performed from −30 °C to 60 °C. The temperature was equilibrated for 2 hours before each measurement. The thicknesses of the films are between 60 and 80 μm.

3. Results and Discussion

3.1. Membrane Morphology

First, incorporation of low amount of co-agent (wt 2%) does not lead to modification of the porous character of the membrane since in both cases, porosity (P) close to 80% has been obtained whereas SEM images are unchanged in the presence of TAIC or MEP. After irradiation, SEM analysis shows that for agent amount lower than 2% porous structure was not affected significantly from irradiation (Fig. 4) since pore sizes of membranes are the same and the pore diameters varied between 1 and 5 μm. However, the membranes prepared with higher concentration of cross-linking agents (5–10% per weight) showed skin formation on the surface of the separator after irradiation (Fig. 5).

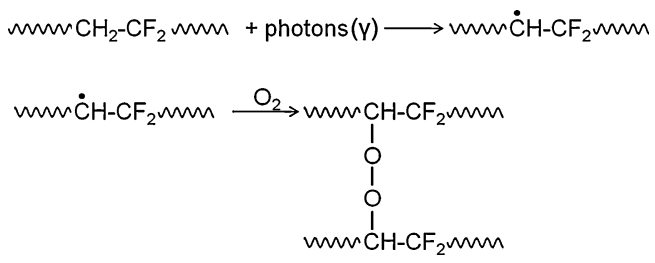

Fig. 2. Mechanism of the peroxide creation by irradiation.

3.2. Thermal properties

3.2.1. Results without cross-linking agent

Table 1 summarizes the thermal properties of PVdF separator before and after irradiation. The crystallinity of the separator increases with the dose of radiation. This increase in crystallinity might be due to creation of shorter polymer chains which reduces the chain entanglement and leads to easier organization of the chains. On the other hand, the melting temperature (T_m) of the separator decreases with the increase of dose which can be attributed to the creation of localized crystallites during the irradiation as proposed by Zhudi et al. [15]. The density of the separator was also determined and found that the irradiation causes slight increases of the density (from 0.32 to 0.35 g cm^{-3}) which is consistent with the increase of crystallinity.

3.2.2. Results with cross-linking agents

As a first step the influence of cross-linking agents on PVdF separators (before irradiation) were determined by DSC. The T_m of PVdF decreases with addition of both TAIC and MEP agents which confirms that these agents are plasticizer of PVdF (Table 2). However, after irradiation of the samples, T_m increases back but still lower than pure PVdF separators. The plasticizer effect of the cross-linking agents disappears when samples go under irradiation because they create a three dimensional network within the polymer structure. Increase in crystallinity shows that even with cross-linking agent, it is possible to produce crystallites in the amorphous region of PVdF.

3.3. Mechanical properties

As previously detailed, DMA results show porous PVdF which exhibits relative high mechanical properties up to close to 150 °C. On the other hand, irradiation leads to significantly decrease of the mechanical properties particularly for low dose of radiation, since the rupture temperature drops from 150 °C to 80 °C. Increasing the dose, better storage modulus can be retrieved. It is known that highly crystalline polymers have higher mechanical strength. Taking into account that the crystallites that we created on our

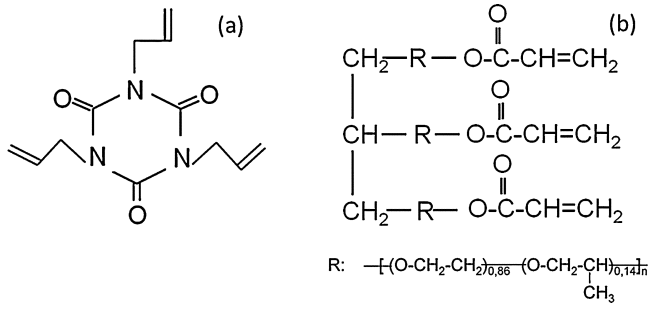

Fig. 3. Chemical structures of (a) Triallylisocyanurate (TAIC) and (b) POE-POP macromonomere (MEP).