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Graft polymerization of acrylic acid and methacrylic acid onto poly(vinylidene fluoride) powder in presence of metallic salt and sulfuric acid

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ABSTRACT

Poly(vinylidene fluoride) (PVDF) powder was grafted with acrylic acid (AAc) or methacrylic acid (MAA) by the pre-irradiation induced graft polymerization technique. The presence of graft chains was proven by FT-IR spectroscopy. The degree of grafting (DG) was calculated by the acid–base back titration method. The synergistic effect of acid and Mohr's salt on the grafting kinetics was examined. The results indicated that adding sulfuric acid and Mohr's salt simultaneously in AAc or MAA solutions led to a strong enhancement in the degree of grafting. The grafted PVDF powder was cast into microfiltration (MF) membranes using the phase inversion method and some properties of the obtained MF membranes were characterized.

1. Introduction

PVDF is one of the major materials used for preparation membranes due to its favorable properties including good thermal stability, chemical resistance, excellent membrane forming properties and high weathering resistance (Hashim et al., 2009; Betz and Begue, 2003; Clocharda et al., 2004).

Under ionizing radiation from γ-rays or electron beams, free radicals are produced in fluoropolymers. Therefore, a convenient method of getting modified fluoropolymers is by use of the radiation-induced graft polymerization technique (Dargaville et al., 2003; Nasef and Hegazy, 2004). In this way, functional membranes, which possess selective mass transfer properties, such as proton exchange membranes (PEMs) and antifouling microfiltration (MF) membranes, can be fabricated by grafting monomers containing the desired functional groups (Li et al., 2004, 2005a, 2005b, 2006a, 2006b, 2006c).

Many works have been reported concentrating on the grafting of monomers onto membranes directly (Hashim et al., 2009; Betz and Begue, 2003; Clocharda et al., 2004; Boributh et al., 2009). Recently, we reported the modification of polymer powder by pre-irradiation induced graft polymerization and then fabrication of the grafted polymer into membranes (Deng et al., 2008, 2009, 2010; Li et al., 2010). This new routine has the advantage of improving the evenness of the distribution of the graft chains.

Hydrophilic filtration membranes are usually obtained by grafting hydrophilic monomers such as AAc and MAA onto the hydrophobic membranes. An interesting phenomenon reported by Nho and Jin (1998) was that by adding sulfuric acid and Mohr's salt simultaneously to the AAc or MAA grafting solutions led to an unusual enhancement in the DG of grafted PE membranes. This is very valuable for increasing the monomer conversion.

Here, a study of the grafting kinetics for the pre-irradiation induced graft polymerization of AAc and MAA onto PVDF powder is reported. Hydrophilic MF membranes were prepared from AAc and MAA grafted PVDF powder using the phase inversion method.

2. Experimental

2.1. Materials

PVDF ($M_w = 420{,}000$) in powder form with diameter of 0.1 mm was purchased from Solvay Chemicals Company, Belgium. AAc, MAA, 1-methyl-2-pyrrolidone (NMP), poly(vinyl pyrrolidone) (PVP) K30 ($M_w = 50{,}000$), sulfuric acid and ferrous ammonium sulfate hexahydrate were purchased from Sinopharm Reagent Co. Ltd., Shanghai. All of the materials mentioned above were used without further purification.

2.2. Pre-irradiation induced graft polymerization

PVDF powder was irradiated to 15 kGy in air using γ-ray from a ^{60}Co source at room temperature, and then stored at $-24\,^{\circ}$C in a refrigerator before use.

70 mL deionized water, 5 g of irradiated PVDF powder and 30 mL of AAc or MAA were added to a 150 mL Erlenmeyer flask

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successively. The flask was then bubbled with nitrogen for 15 min to remove oxygen. After that, it was sealed, and graft polymerization was started at 60 °C under continuous stirring.

After a defined period, graft polymerization was stopped, and the grafted PVDF powder was filtered and washed. Then it was washed with 1 M NaOH solution at 60 °C under stirring for 2 h. During the wash, NaOH solution was replaced three times to remove all of the homopolymer completely. After that the powder was filtered and recovered by washing with an excess of 1 M HCl solution. Then the powder was washed repeatedly with deionized water until the pH value of the exhausted liquid was 7.0. Finally, the PVDF-g-PAAc or PVDF-g-PMAA powder was dried to constant weight at 60 °C in a vacuum oven.

The DG values of PVDF-g-PAAc or PVDF-g-PMAA powder were determined by acid–base back titration. The details of acid–base back titration were described in our previous papers (Deng et al., 2008, 2009, 2010).

2.3. *Infrared spectroscopy of pristine and grafted PVDF powder*

Pristine and grafted PVDF powders were pressed into pellets with KBr. Then FT-IR spectra were taken using a Nicolet Avatar 370 FT-IR spectrometer by the accumulation of 32 scans at a resolution of 4 cm^{-1}.

2.4. *Membrane preparation*

MF membranes were cast from NMP solution of pristine PVDF powder or grafted PVDF powder using the phase reverse method with PVP as the pore former as follows.

Pristine or grafted PVDF powder and PVP were dissolved in NMP at 70 °C with a weight ratio of 12.5:3:84.5 for 6 days. Before casting, the solution was ultrasonicated for 30 min to eliminate bubbles. After that, the solution was cast onto a glass plate. Then, the new-born membrane was immersed in deionized water at 25 °C. The membranes were let stand in the coagulation bath for 3 days and then they were taken out and rinsed with deionized water 3 times to thoroughly remove any remaining solvent and then kept in fresh deionized water before further characterization.

A clear solution is required for membrane preparation; however, when the DG exceeded 30%, the solubility of the grafted PVDF powder became poor and the solutions were cloudy, even when heated for more than 7 days at 70 °C. Therefore, in this work only grafted PVDF powder with a DG lower than 30% were cast into MF membranes and then characterized.

2.5. *Water uptake measurement*

The water uptake (WU) of the MF membranes was determined by the weight change after soaking in deionized water.

MF membranes were rinsed with deionized water, and then dried in a vacuum oven at 60 °C for 24 h. After that, the dried membranes were immersed in deionized water for at least 24 h. Then the swollen membranes were taken out, and the excess water on the surfaces gently removed by a blotter. The swollen membrane weights were then quickly measured before drying the membranes under vacuum at 60 °C for 24 h. The dried membranes were quickly weighed and the WU was calculated according to the following relationship:

$$\text{Water uptake}\,(\%) = \frac{W_s - W_d}{W_d} \times 100 \qquad (1)$$

where W_s and W_d were the weight of the swollen and dry MF membranes, respectively.

3. Results and discussion

3.1. *FT-IR spectra*

PAAc and PMAA homopolymers are water-soluble acidic polymers and can be removed efficiently from the grafted PVDF powder by hot alkaline solution extraction. Therefore, the characteristic absorption attributed to the carboxyl groups in FT-IR spectra proves that AAc or MAA were successfully grafted onto the PVDF powder.

FT-IR spectra of PVDF-g-PAAc and PVDF-g-PMAA are shown in Figs. 1 and 2, respectively. All FT-IR spectra in Figs. 1 and 2 were normalized according to the absorption peak of CH_2 stretching mode located at 1411 cm^{-1}. In the spectrum of pristine PVDF powder, the characteristic absorption bands at 1168 and

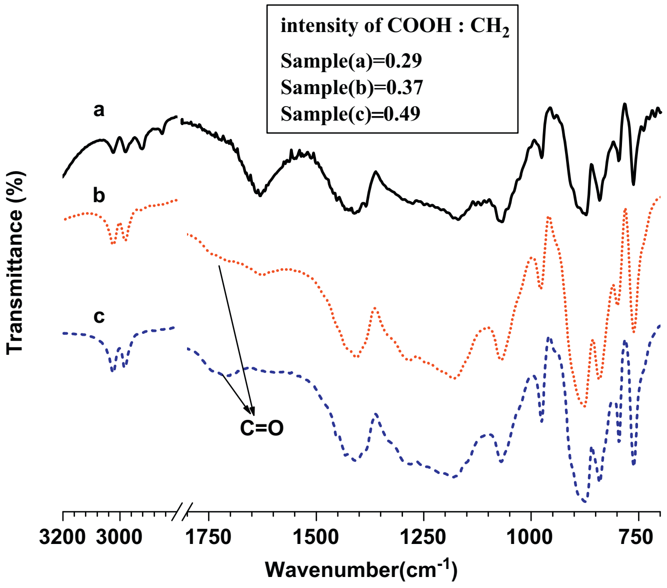

Fig. 1. FT-IR spectra of pristine PVDF (a) and PVDF-g-PAAc powder with DG of (b) 23.7% and (c) 47.1%.

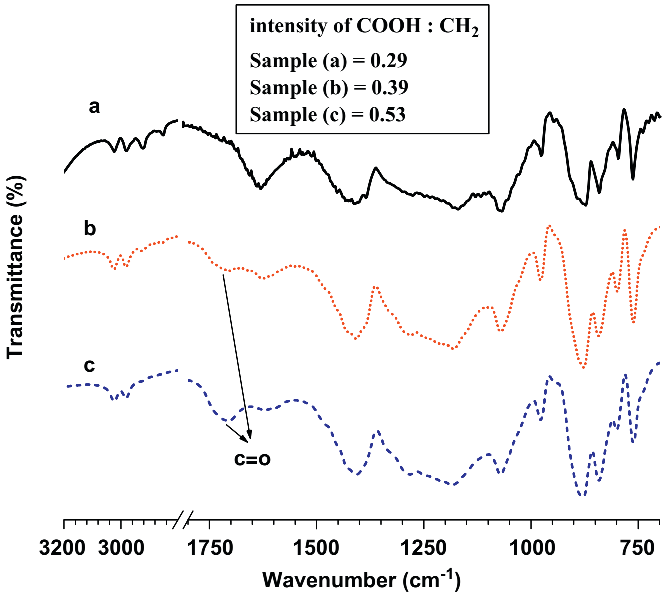

Fig. 2. FT-IR spectra of pristine PVDF (a) and PVDF-g-PMAA powder with DG of (b) 24.3% and (c) 48.4%.