

Short communication

ESR and vibrational spectroscopy study on poly(vinylidene fluoride) membranes with alkaline treatment

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Abstract

Poly(vinylidene fluoride) (PVDF) membranes treated with alkaline solutions were studied by electron spin resonance (ESR), FT-IR and FT-Raman spectroscopy. Alkaline treated samples produced free radicals, the concentrations of which were calculated. The vibrational spectroscopy showed the existence of conjugated carbon double bonds in the treated membranes. The degradation mechanism was discussed. And the effect of the alkaline concentration and treating time on the structure modification were also investigated.

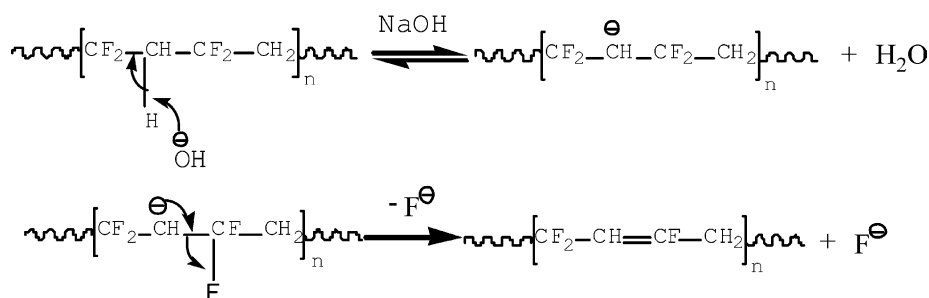
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1. Introduction

Poly(vinylidene fluoride) (PVDF) is a polymer with similar properties as fully fluorinated polymers, and is distinguished by its excellent resistance to heat, chemicals, oxidizing and radiation. These properties make its application possible in mechanical, chemical and electrochemical fields. When PVDF is used as the main chain of poly(vinylidene fluoride) grafted polystyrene sulfonated acid (PVDF-g-PSSA) membrane, a type of proton exchange membrane (PEM), it was found that pretreatment of PVDF in alkaline solutions could promote the grafting of PS [1]. This makes us interested in the effect of alkaline treatment of PVDF on its structure.

Previous investigations of the modification of PVDF involved treatment with chemicals [2,3], irradiation [4,5], heat and microwave. Modified PVDF possesses specific properties due to the changes of its functional group, structure of the chain and crystal configuration. Kise and Ogata [2] described the structure change in PVDF reacted with sodium hydroxide in aqueous solutions in the presence of phase transfer catalysts, which seems to be the production of C–C double and triple bonds. Ross et al. [3] proposed a mechanism for the alkaline degradation of PVDF on the basis of XPS, ToF-SIMS, FT-IR and Raman analysis. The mechanisms are shown below:



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But few reports have been found on the study of radicals produced in this process.

This work pretends to investigate the structure of alkaline treated PVDF with electron spin resonance (ESR), FT-IR and FT-Raman. Other differences between past work and the current investigations are the type of alkaline, the solvent and the reaction condition.

2. Experimental

PVDF powder was purchased from ShangHai San Ai New Material Co. Ltd. The PVDF membrane was prepared by casting a solution of PVDF in *N*-methyl pyrrolidinone (NMP) on a clean glass plate. After the removal of NMP, the PVDF membrane was formed and removed from the glass plate. The thickness of the membrane was about 50 μm . The PVDF membrane was treated in a solution of KOH in alcohol at 80 °C under the atmosphere of N_2 . Membranes (40 mm \times 30 mm) treated with different KOH concentration and different treating time have been analyzed with ESR, FT-IR and FT-Raman, respectively.

ESR spectra were obtained at X band (9.8 GHz) on a Bruker ER200 ESR spectrometer. The experimental conditions (power attenuation, field modulation, time constant and sweep time) were kept the same during the experiments on all samples. A double integration of the ESR signal was performed, and the corresponding spin numbers were calculated from a sample of known diphenyl picryl hydrazyl (DPPH, Aldrich, 95%) concentration. When we calculated the radical concentrations, the weight of the sample was taken into account.

Infrared spectra (IR) were recorded on an AV360 infrared spectrophotometer with an ATR (attenuated total reflection) crystal over the range from 4000 to 700 cm^{-1} . FT-IR was complemented by FT-Raman spectroscopy, using a Perkin-Elmer Spectrum GX instrument with 0.1 cm^{-1} resolution.

3. Results and discussion

3.1. ESR results

Alkaline treated PVDF samples were immediately placed in a quartz ESR sample tube, which is introduced into the ESR cavity. The spectra were obtained by sweeping the static magnetic field (from 3377 to 3577 G) and by recording the first derivative of the absorption spectrum on a computer. Figs. 1 and 2 show the ESR spectra of PVDF samples related to the alkaline treating time and the concentration of alkaline solution. Untreated samples produced no signal. This indicates that free radicals were produced when PVDF membranes were treated with KOH–alcohol solutions. The g -value is 2.0031, obtained by measuring the resonance field and the microwave frequency. This peak can be assigned to the radical of $-\text{CF}_2-\text{C}^\bullet\text{H}-\text{CF}_2-$ according to Refs. [4,5]. It is produced when the OH^- attacks the main chain of PVDF, and deprotonisation occurs [2]. The produced radical concen-

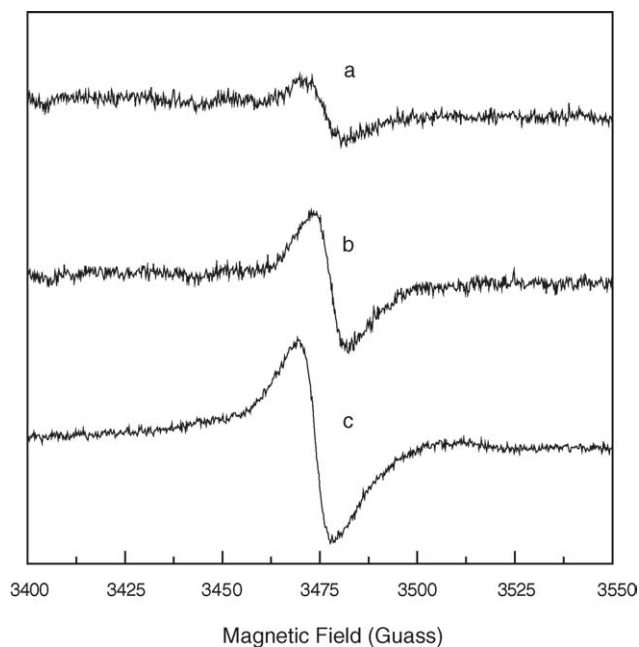


Fig. 1. ESR spectra of PVDF membranes treated with 4 g L^{-1} KOH–alcohol solution for: (a) 45 min; (b) 70 min; (c) 130 min. Untreated samples produced no signal. Frequency = 9.765 GHz. Gain = 2.5×10^5 .

trations of all measured samples were calculated, the result of which is of 10^{16}g^{-1} magnitude (Fig. 3). The radicals produced are not so many as that produced by electron irradiation [4,5], but could exist at least for 2 h exposed to light in air and no ESR signal could be observed on the sample 12 h after treatment.

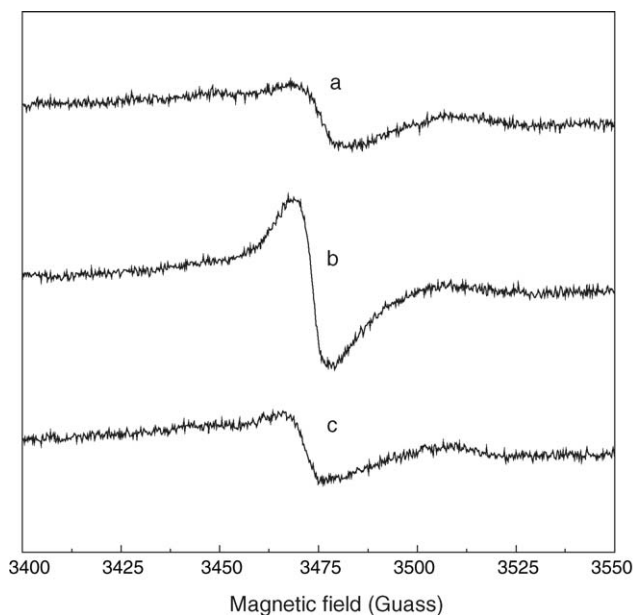


Fig. 2. ESR spectra of PVDF membranes treated with (a) 2.1 g L^{-1} ; (b) 6.1 g L^{-1} ; (c) 10.0 g L^{-1} KOH–alcohol solution for 100 min. Untreated samples produced no signal. Frequency = 9.758 GHz. Gain = 2.5×10^5 .

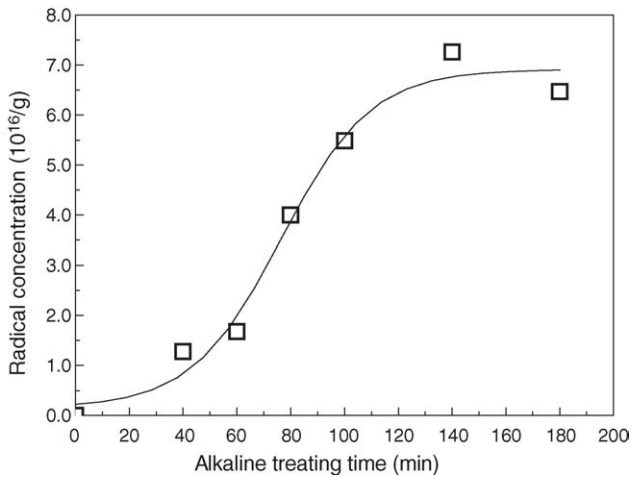


Fig. 3. Radical concentrations in relation to the alkaline treating time (in 4.0 g L^{-1} KOH–alcohol solution).

With the treating time increased, the spectra peaks increased in intensity as shown in Fig. 1, which is also shown in Fig. 3, indicating the increase of the concentration of free radicals. But after 2 h, the increase tends to be slower. The radical concentrations also increase with the alkaline concentration under 6 g L^{-1} , above which radicals became fewer (Figs. 2 and 4). We can infer from it that the free radicals may have collided with each other and combined to form a bond.

3.2. FT-IR results

Figs. 5 and 6 show the FTIR-ATR spectra of PVDF membranes treated with KOH–alcohol solutions for increasing time and of different concentrations, respectively. The spectrum of original PVDF, reported in Fig. 5a, is characteristic of the polymer in the form III [6]. Compared with the spectrum of Fig. 5b and c, it is apparent that the polymer does not change appreciably with the alkaline treating time increased. But a broad band occurs from 1750 to 1500 cm^{-1} , with maxi-

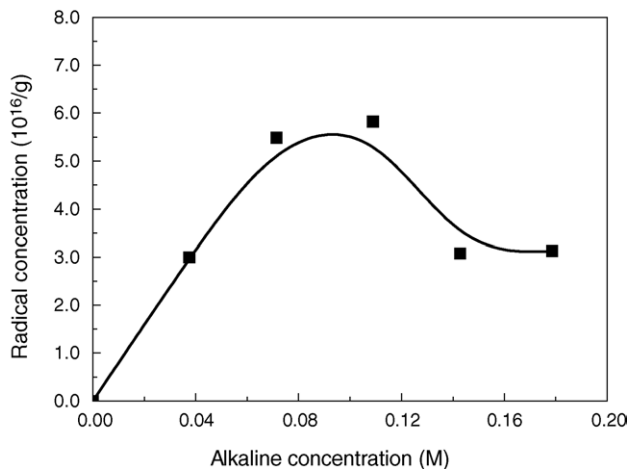


Fig. 4. Radical concentrations in relation to the alkaline concentration (for 100 min).

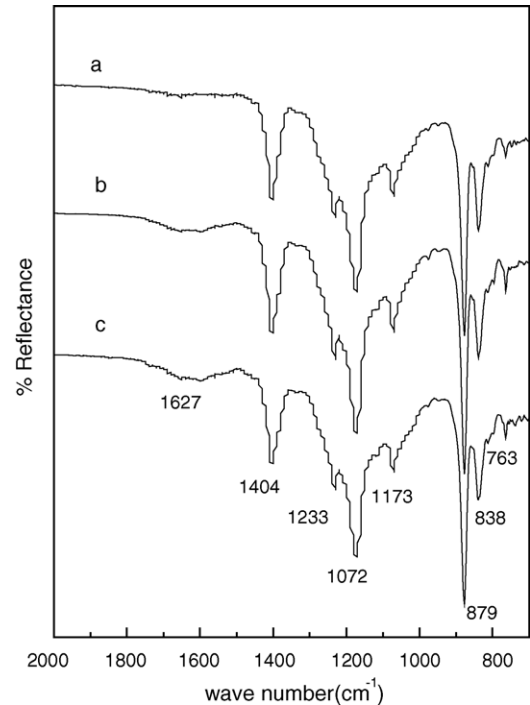


Fig. 5. FTIR-ATR spectra of PVDF membranes treated with 4.0 g L^{-1} KOH–alcohol solution for: (b) 60 min; (c) 100 min and (a) untreated sample.

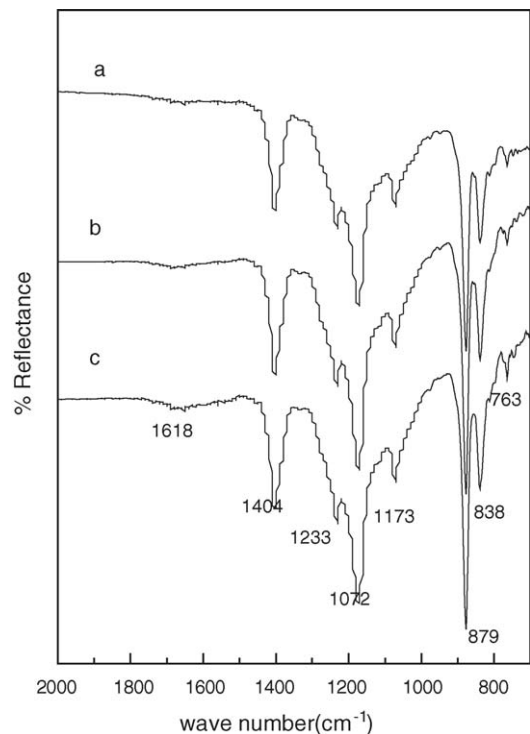


Fig. 6. FTIR-ATR spectra of PVDF membranes treated with: (b) 6.2 g L^{-1} ; (c) 10.1 g L^{-1} ; KOH–alcohol solutions for 40 min and of (a) untreated sample.

imum intensity around 1630 cm^{-1} . This band can be assigned to the formation of C=C double bonds, due to a dehydrofluorination process [2].

Kise and Ogata [2] treated the PVDF powder in aqueous NaOH solution in the presence of catalyst and they assigned the new band around 1590 and 2100 cm^{-1} of the product IR spectra to the stretching bands of C–C double and triple bonds, respectively. In the present work, we did not find the characteristic peak of C–C triple bond and the characteristic band of PVDF ($1404, 1072, 879, 838, 763\text{ cm}^{-1}$) did not changed much, which means that the reactions are not so bitter as to destroy the skeleton structure of PVDF.

The same trend appears when only the alkaline concentration changes. This was proved more clearly by the FT-Raman results.

3.3. FT-Raman results

Raman spectroscopy provides more information about the conjugated structure and the chain skeleton of polymers. From Fig. 7, we can easily find the gradual changes in the Raman spectra when the treating time increased. By comparison with the untreated PVDF membrane spectrum (Fig. 7a), two new bands (1134 and 1530 cm^{-1}) appear in the treated membrane spectrum (Fig. 7b–e), though these two bands are observed only as shoulders for the membrane treated for 40 min (Fig. 7b). They are characteristic of the C=C stretching vibration modes of polyenes [7], indicating that the structure of conjugated C=C double bonds formed in the polymer when treated by alkaline solution. The length of the conjugated carbon double bond structure can be estimated by the distance between the two peaks, and the relationship

were studied [2]. According to Ref. [2], the lengths of the conjugated double bonds are about 8.5 from our Raman report using the maximum intensity. Another change in the spectra is the slight decrease of the peaks at 2980 and 1432 cm^{-1} , which are characteristic of CH_2 bending vibration mode and CH stretching vibration mode, respectively. This indicates the deprotonation of CH_2 when alkaline attacks the PVDF chain structure.

The content of C=C double bonds increases with treating time within 3 h (Fig. 7) and with alkaline concentration within 10 g L^{-1} (Fig. 8). As the membrane will become black and brittle, treatment above that concentration or longer than 3 h has not been conducted. It seems that the conjugated double bonds do not grow so quickly after 100 min as before that time. A turning point also exists in the case of concentration, which seems to be 6 g L^{-1} of the KOH alcohol solution.

3.4. Discussion

The ESR investigation indicated that a kind of free radical, $-\text{CF}_2-\text{C}^\bullet\text{H}-\text{CF}_2-$, was produced when KOH reacted with PVDF membrane. It is not stabilized and could exist only within 12 h. The FT-IR and FT-Raman spectra showed the formation of C–C double bond in the alkaline treated PVDF membrane. And the productions of the free radical and double bond showed some similarity in their relation against treating time, i.e., they all grow slowly first before 40 min, and rapidly between 40 and 100 min, then slow down. This means that they might have relation to each other. Ross et al. [3] suggested that the deprotonation and defluorination steps of the alkaline treatment could not occur simultaneously via an E2 (elimination, bimolecular) in chain reaction due to high steric

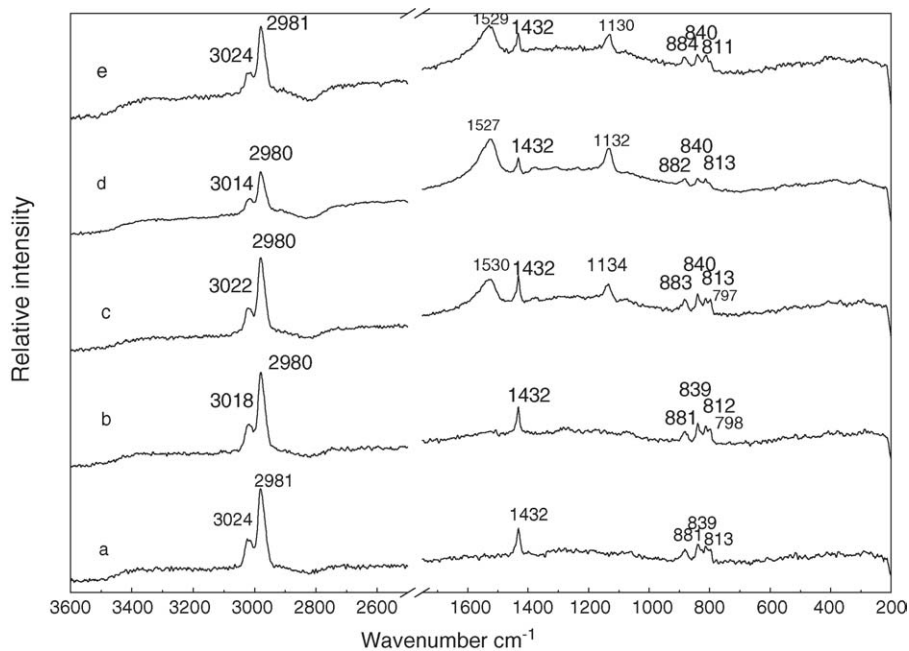


Fig. 7. FT-Raman spectra of PVDF membranes treated with 4.0 g L^{-1} KOH-alcohol solutions for: (b) 40 min; (c) 100 min; (d) 130 min; (e) 170 min; (a) for untreated membrane.

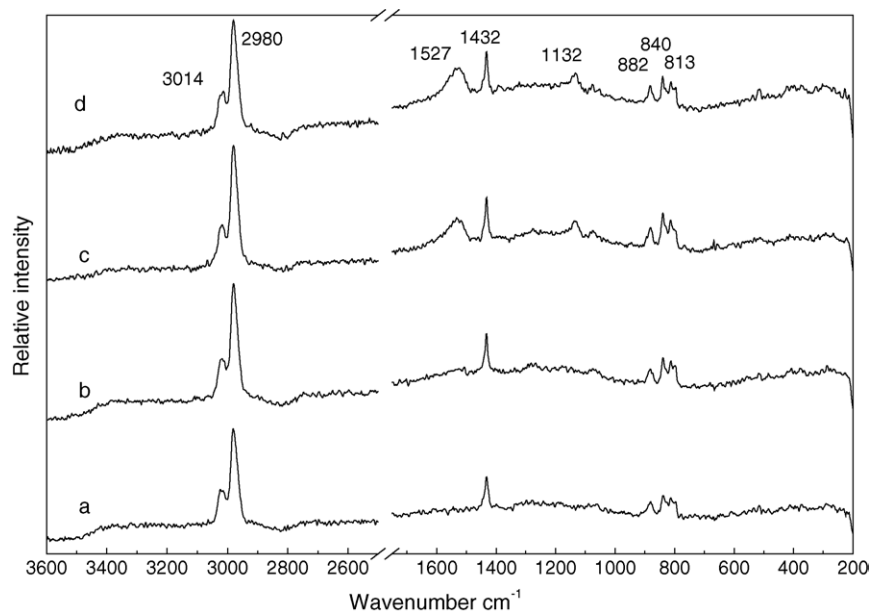


Fig. 8. FT-Raman spectra of PVDF membranes treated with: (b) 4.0 g L^{-1} ; (c) 6.2 g L^{-1} ; (d) 10.1 g L^{-1} KOH-alcohol solutions for 40 min; (a) for untreated membrane.

hindrance. In the mechanism they suggested, the product of the deprotonisation step is $-\text{CF}_2-\text{C}^{\ominus}\text{H}-\text{CF}_2-$. From work of this article, we can infer that the mechanism of the PVDF membrane reacting with KOH (alcohol solution) could possibly be as following. The hydroxide ion attacks the CH_2 group and the deprotonation occurs, resulted in the radical of $-\text{CF}_2-\text{C}^{\bullet}\text{H}-\text{CF}_2-$. The radicals are not stable and the more stable $\text{C}=\text{C}$ double bonds are formed through an elimination reaction. The second step is so rapid that only small amount of radicals could be detected with ESR. If the concentration of the OH^- is high enough (e.g., higher than 6 g L^{-1}), the second step becomes more rapid as to decrease the amount of residual free radicals.

With the help of ESR, FT-IR and FT-Raman spectroscopy, we could find that the production of the active sites, i.e., the free radicals and double bonds is in agreement with the degree of grafting concerning to alkaline treating time [1]. We can conclude that it is these structure modifications that promote the grafting of styrene on PVDF.

4. Conclusions

PVDF membranes treated with KOH-alcohol solutions were analyzed by ESR, FT-IR and FT-Raman. The results indicate that free radicals and conjugated $\text{C}=\text{C}$ double bonds have been produced in the polymer through alkaline treat-

ment, which increase quickly with alkaline treating time before 100 min and with the alkaline concentrations below 6 g L^{-1} . This kind of structure modification of the polymer favors grafting of styrene on it, by which a kind of PEM was made. We will take advantage of this type of treatment to prepare new PEMs by grafting other monomers to PVDF.

Acknowledgements

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