Determining the degree of grafting for poly(vinylidene fluoride) graft-copolymers using fluorine elemental analysis

YU Yang[1,2]   ZHANG Bowu[1,2]   YANG Xuanxuan[1,2]   DENG Bo[1]
LI Linfan[1]   YU Ming[1]   LI Jingye[1,*]

[1]*Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China*

[2]*Graduate University of Chinese Academy of Sciences, Beijing 100049, China*

Abstract   Acrylic acid (AAc) and styrene (St) were grafted onto poly(vinylidene fluoride) (PVDF) powder or membrane samples by pre-irradiation graft copolymerization. The grafted chains were proved by FT-IR spectroscopy analysis. The degree of grafting (*DG*) of the grafted PVDF was determined by fluorine elemental analysis (FEA) method, and was compared with the *DG*s determined by weighing method, acid-base back titration method and quantitative FT-IR method. The results show that the FEA method is accurate, convenient and universal, especially for the grafted polymer powders.

Key words   Fluorine elemental analysis, Degree of grafting, Poly(vinylidene fluoride), Pre-irradiation graft copolymerization

1   Introduction

Poly(vinylidene fluoride) (PVDF) has been widely used in industries due to its outstanding properties of chemical resistance and thermal stability[1-3]. Many kinds of filtration and battery membranes are prepared from PVDF because of its good processability.

Some physical or chemical methods, particularly radiation-induced graft copolymerization of functional monomers, can endow PVDF membranes with special properties. For example, proton exchange membranes (PEMs) were prepared by grafting styrene (St) onto dense PVDF membranes and sulfonation, and antifouling microfiltration (MF) membranes were fabricated by grafting acrylic acid (AAc) onto porous PVDF MF membranes[4-6]. The degree of grafting (*DG*), defined as the weight percentage of the graft chains to the matrix, is the key parameter strongly affecting the performance of the modified membranes. Usually, the *DG* of grafted membranes is determined by weighing the samples before and after graft-copolymerization.

Recently, we reported the preparation of modified PVDF membranes by grafting functional monomers onto PVDF powders and then fabricating them into membranes. The PEM membranes from St-grafted PVDF powders were prepared using solution casting method[7], and the antifouling or pH-sensitive MF membranes from AAc grafted PVDF powders were prepared using phase inversion method[8,9].

However, due to unavoidable mass loss of the grafted PVDF powders during experimental procedures, such as filtration and extraction, the *DG* obtained by weighing method would be inaccurate and unreliable. Therefore, it is necessary to develop a convenient and accurate method to determine the *DG* of grafted PVDF powder. Considering that the PVDF matrix differs from the grafting monomers in its fluorine content, the fluorine elemental analysis (FEA) is a suitable way to determine the *DG* of the grafted PVDF powders. Moreover, FEA was applicable in determining the DG of both the non-fluoride monomers grafted fluoropolymers and the fluoride

monomers grafted non-fluoropolymers, regardless of the form of polymeric materials in powder, film, membrane, woven fabric or non-woven fabric.

In this paper, we report the *DG* determination of AAc- or St-grafted PVDF in powder or membrane form using FEA method. The results are compared with the *DG*s determined by other methods, including weighing, acid-base back titration, and quantitative FT-IR analysis.

2　Experimental

2.1　Materials

Powder PVDF of about 0.1 mm in grain size was purchased from Solvay Chemicals Company, Belgium. St, AAc, 1-methyl-2-pyrrolidone (NMP), acetic hydroxide, trisodium citrate dihydrate, NaCl, NaOH, NaF were purchased from Sinopharm Reagent Company, China. All the reagents were used without any further purification. PVDF membranes in thickness of about 50 μm were prepared from the PVDF powder via phase inversion method.

2.2　Pre-irradiation and graft copolymerization

PVDF samples in powder or membrane form were irradiated to 15 kGy in a ^{60}Co γ-ray source at room temperature. The irradiated PVDF samples were immersed in St or AAc solution to performing the graft copolymerization at 60ºC under nitrogen protection. The experimental details could be found in our previous papers[7,8]. The St or AAc grafted PVDF powder/membrane will be denoted as PVDF-g-PS or PVDF-g-PAAc powder/membrane in the following sections.

2.3　FT-IR measurement

After pressing the pristine and grafted PVDF powders into pellets with KBr, FT-IR spectra were taken on a Nicolet Avatar 370 FT-IR spectrometer by the culmination of 32 scans at a resolution of 4 cm^{-1}.

The surface chemical structure of the grafted PVDF membranes could be analyzed using ATR mode with the SMART Accessory by pressing the sample over a Zn-Se crystal. All the spectra were recorded in the ATR mode from 4000 to 650 cm^{-1}, with a resolution of 4 cm^{-1} and using 32 scans.

2.4　*DG* determination

2.4.1　FEA method

Total ionic strength adjustment buffer (TISAB) was prepared by putting acetic acid (10.0 mL), trisodium citrate dehydrate (10.0 g), NaCl (58.0 g), and deionized water into a 1-L beaker. The pH was adjusted to 5–7 by adding 5 mol·L^{-1} NaOH solution dropwise.

A series of NaF solutions in concentration of 5×10^{-2}, 1×10^{-2}, 5×10^{-3}, 1×10^{-3}, and 5×10^{-4} mol·L^{-1} were prepared. After measuring the potential of the solution by fluorine ion selective electrode, the standard curve of potential difference versus logarithm of the concentration was drawn according to Eq.(1):

$$V_\mathrm{F} = \mathrm{A}\log C_\mathrm{F} + \mathrm{B} \tag{1}$$

where V_F is numeric value of potential difference, C_F is fluorine ion concentration of solutions, and the A and B are constants.

Each sample of about 10-mg grafted PVDF in powder or membrane form was precisely weighed before wrapped into a package using a dust-free filter paper. Folding it into a square shape, the package was combusted in a 500-mL oxygen flask, in which 35-mL absorbent solution of TISAB was added and the oxygen was filled. The flask was shaken for 1 min, and kept for 15 min after combustion process, so as to ensure full absorption of the smoke by the solution. Then, 65-mL absorbent solution was poured into the flask, and then the flask was oscillated.

Using fluorine ion selective electrode, the concentration of fluorine ion in the solution was determined, and the fluorine percentage of the grafted sample was calculated according to the standard curve and Eq.(2):

$$P_\mathrm{s} = [10^{(V_\mathrm{F}-\mathrm{B})/\mathrm{A}} \times 0.1 \times 19/m_\mathrm{s}] \times 100\% \tag{2}$$

where P_s is fluorine percentage of the sample, 19 is atomic mass of fluorine, and m_s is the sample mass.

The *DG* of grafted PVDF samples was calculated using Eq.(3):

$$DG_\mathrm{FEA} = [(P_\mathrm{PVDF}-P_\mathrm{s})/P_\mathrm{s})] \times 100\% \tag{3}$$

where DG_FEA is the degree of grafting calculated by FEA method, P_PVDF is the fluorine percentage of PVDF, and P_s is the fluorine percentage of the grafted PVDF sample.

2.4.2 Weighing method

The *DG* of grafted PVDF samples was calculated using Eq.(4):

$$DG_W = [(W_g - W_0)/W_0)] \times 100\% \qquad (4)$$

where DG_W is degree of grafting calculated by weighing method, W_0 and W_g are the mass of PVDF samples before and after graft copolymerization, respectively.

2.4.3 Acid-base back titration method

Samples in certain mass of dried PVDF-g-PAAc were soaked into 100-mL NaOH solution and kept overnight under vigorous stirring. For every sample, 20-mL solution was titrated using HCl to determine concentration of the un-reacted NaOH. The titration was repeated for three times.

The same experiments were proceeded to determine acidity of the irradiated and washed PVDF powder samples. The *DG* was calculated using Eq. (5):

$$
\begin{aligned}
DG_T &= W_{PAAc}/W_{PVDF} \\
&= [(W_s Ac_{PVDF} - Ac_t)/(Ac_{PVDF} - 1/M_{AAc})] / \\
&\quad [(W_s M_{AAc} - Ac_t)/(M_{AAc} - Ac_{PVDF})] \\
&= [(W_s Ac_{PVDF} - Ac_t)/(W_s M_{AAc} - Ac_t)] / \\
&\quad [(M^2_{AAc} - Ac_{PVDF} M_{AAc})/(Ac_{PVDF} M_{AAc} - 1)]
\end{aligned}
\qquad (5)
$$

where, DG_T is degree of grafting calculated by acid-base back titration method, W_s is weight of PVDF-g-PAAc sample, Ac_t is the amount (in mole) of acid groups of PVDF-g-PAAc samples determined by titration, Ac_{PVDF} is the acidity of irradiated and washed PVDF powder, and M_{AAc} is the molecular weight of AAc.

2.4.4 Quantitative FT-IR analysis method

The PVDF-g-PS solution dispersed by NMP was prepared into membrane using solvent evaporation method. The membranes were put in a vacuum oven at 60ºC for 24 h. Characterization of the membrane samples was done on a NICOLET AVATAR 370 FTIR. The *DG* of sample was calculated according to Refs.[10-12].

$$DG_{FT\text{-}IR} = 0.12\, Ab^{PS}_{2925}/(Ab^{Sub}_{2985} - 0.05 Ab^{PS}_{2925}) \qquad (6)$$

where $DG_{FT\text{-}IR}$ is degree of grafting calculated by quantitative FT-IR analysis method, Ab^{PS}_{2925} is absorbance of asymmetric stretching vibration peak of -CH$_2$- group in PS at 2925 cm^{-1}, and Ab^{Sub}_{2985} is absorbance of symmetric stretching vibration peaks of -CH$_2$- group in PVDF at 2985 cm^{-1}.

3 Results and discussion

### 3.1 Determination of the *DG* of PVDF-g-PAAc membranes

The FT-IR spectra in ATR mode shown in Fig.1 was the pristine PVDF membrane and PVDF-g-PAAc membranes of different *DG*s. A new absorbance bond could be seen around 1700 cm^{-1} in the spectrum of PVDF-g-PAAc membrane as compared with that of pristine PVDF membrane. This could be attributed to the stretching vibration of carbonyl groups in the PAAc side chains, indicating the existence of the grafted AAc onto PVDF membranes.
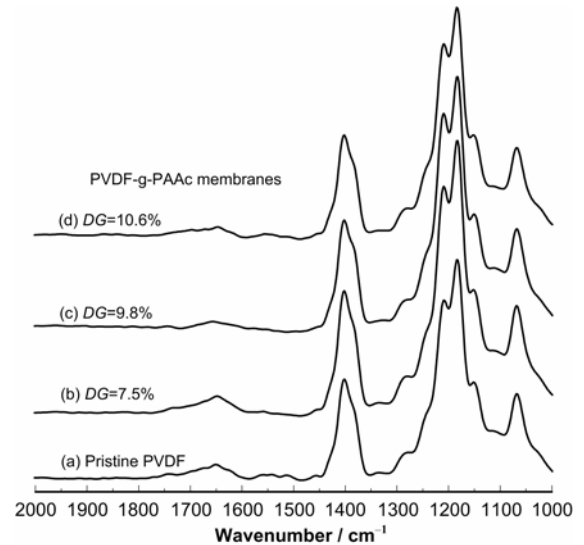
Fig.1 FT-IR spectra of (a) pristine PVDF membrane, (b) PVDF-g-PAAc membrane with DG_{FEA} of 7.5%, (c) 9.8% and (d) 10.6%.

For grafting membrane samples, weighing the mass change before and after graft copolymerization is a convenient and precise method to determine the *DG*, but the *DG* obtained by this way is an averaged *DG* of the whole sample, it does not tell the distribution of grafted chains. With the FEA method, in which only 10-mg sample is needed to determine the *DG*, it is possible to tell the difference in *DG* here and there in the membrane.

In Fig.2, the *DG*s obtained by the weighing (DG_W) and FEA (DG_{FEA}) methods are compared. Theoretically, they should be of the same value, as shown by the straight line. Fig.2 shows that the standard deviation, variance and average deviation of the *DG*s determined by the FEA method, and the differences between the DG_{FEA} and DG_W are small, and the FEA method is accurate and reliable.
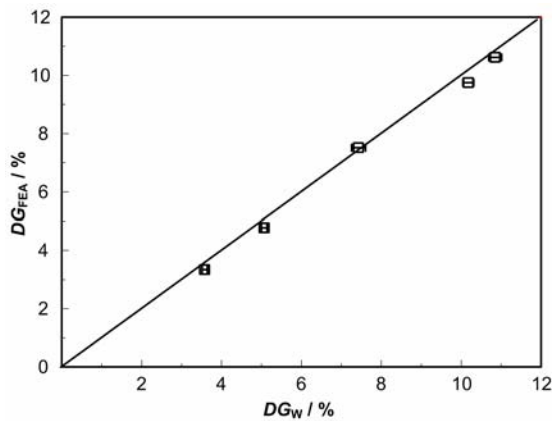
Sample No.	Standard Deviation	Variance	Averaged Deviation
1	0.006572	0.000043	0.00534
2	0.006922	0.000048	0.00600
3	0.017245	0.000297	0.01314
4	0.013605	0.000185	0.01072
5	0.016093	0.000259	0.01302

Fig.2 A comparison between the *DG*s determined by the FEA (*DG*$_{FEA}$) and weighing (*DG*$_W$) methods for PVDF-g-PAAc membrane samples. The standard deviation, variance, and average deviation of *DG* determined by FEA method are given in the table under the figure.
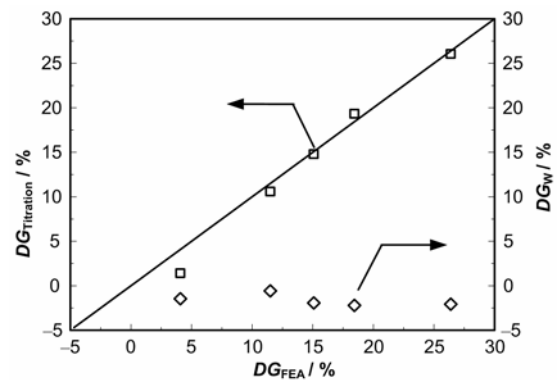
3.2 Determining the *DG* of PVDF-g-PAAc powder

Figure 3 is FT-IR spectra of the pristine PVDF powder, and the PVDF-g-PAAc powders of different *DG*s, where a new absorption band could be seen at about 1712 cm^{-1}, attributing to the stretching vibration of carbonyl groups of the AAc grafted PVDF chains.
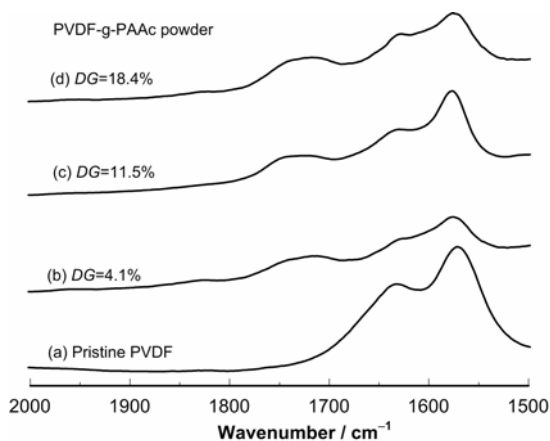
Fig.3 FT-IR spectra of the pristine PVDF powder (a), and PVDF-g-PAAc powders with *DG*$_{FEA}$ of 4.1% (b), 11.5% (c), and 18.4% (d).

The *DG*s of PVDF-g-PAAc powders *via* acid-base back titration method, FEA method, and weighing method were compared in Fig.4. The

determination of *DG* of PVDF-g-PAAc powder *via* acid-base back titration method has been reported[8]. Although it was suitable for the samples containing acid or base groups, despite its complicated process, the acid-base back titration method agreed well with that obtained by FEA method for *DG*. However, *DG*$_W$ of PVDF-g-PAAc powder *via* weighing method differed strikingly from the other results, due to the unavoidable mass loss of the grafted PVDF powder during experimental procedures of filtration and extraction. Therefore, weighing method is not suitable for determining the *DG* of powder samples.
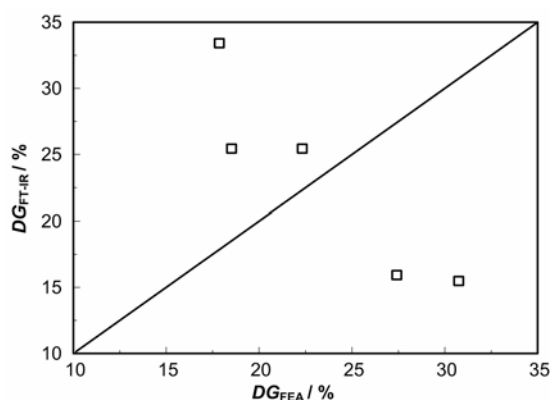

Fig.4 A comparison between the *DG*s determined by acid-base back titration (*DG*$_T$), weighing (*DG*$_W$), and FEA (*DG*$_{FEA}$) methods for PVDF-g-PAAc powder samples.

3.3 Determining the *DG* of PVDF-g-PS powder

Figure 5 shows the spectra of PVDF-g-PS powder. The 698 cm^{-1} peak is attributed to the -C-H bond of phenyl rings, while the peak at 1490 cm^{-1} are due to skeletal -C=C- in plate-stretching vibrations of phenyl rings[11-13]. These characteristic peaks for phenyl rings indicate polystyrene was successfully grafted onto the PVDF powder.
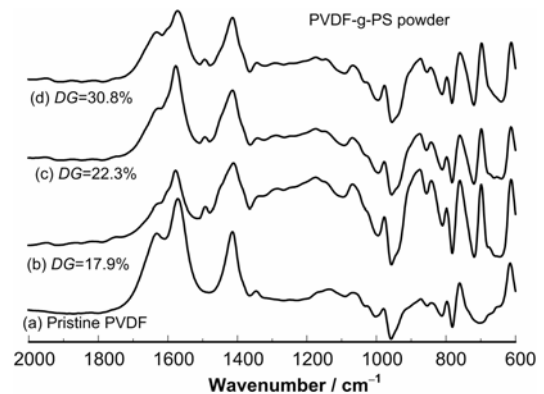
Fig.5 FT-IR spectra of the pristine PVDF powder(a), and PVDF-g-PS powders with *DG*$_{FEA}$ of 17.9% (b), 22.3%(c) and 30.8%(d).

Fig.6 A comparison between the *DG*s determined by FT-IR (*DG* FT-IR) and FEA (*DG* FEA) methods for PVDF-g-PS powder samples.

For the St-grafted powder samples, we used quantitative FT-IR calculation method in Refs.[12-14] to determine the DG_{FT-IR}, which was compared with DG_{FEA} (Fig.6). As mentioned in Section 3.1, FEA could be a standard method to determine the *DG* of the grafted powders. The striking differences between the two data sets indicated that the FT-IR method was not suitable for determining the *DG* of the grafted powder samples.

A number of factors might contribute to the big deviations of the DG_{FT-IR}. During the procedures for FT-IR measurement, for example, in pressing the sample powder into pellets with KBr, it would be difficult to control the mass ratio of KBr to the sample powder, and thickness of the sample pallet.

4 Conclusion

The fluorine elemental analysis method is used to determine the *DG* of AAc or St grafted PVDF membrane and powder samples. The *DG*s obtained by the FEA method is compared with the weighing method, the acid-base back titration method and the quantitative FT-IR calculation method. It can be seen that the FEA method is a reliable and accurate for both powder and membrane samples. The FEA method is advantageous for it needs only 10 mg sample to determine the *DG* of polymeric materials in different forms (e.g. film, powder, fiber, etc), and this is of special significance for large-area industrial membranes, where homogeneity of graft copolymerization needs to be determined.

References

1 Souzy R, Ameduri B. Prog Polym Sci, 2005, **30:** 644–687.

2 Cardona F, George G A, Hill D J T, *et al.* Macromolecules, 2002, **35:** 355–364.

3 Deng B, Yang X, Xie L, *et al.* J Membr Sci, 2009, **330:** 363–368.

4 Li J, Muto F, Miura T, *et al.* Eur Polym J, 2006, **42:** 1222–1228.

5 Geng W, Nakajima T, Takanashi H, *et al.* Fuel, 2007, **86:** 715–721.

6 Geng W, Nakajima T, Takanashi H, *et al.* Fuel, 2008, **87:** 559–564.

7 Li L, Deng B, Ji Y, *et al.* J Membr Sci, 2010, **346:** 113–120.

8 Deng B, Li J, Hou Z, *et al.* Radiat Phys Chem, 2008, **77:** 898–906.

9 Yang X, Deng B, Liu Z, *et al.* J Membr Sci, 2010, **362:** 298–305.

10 Shi Z, Holdcroft S. Macromolecules, 2005, **38:** 4193–4201.

11 Qiu J, Zhang J, Chen J, *et al.* J Membr Sci, 2009, **334:** 9–15.

12 Aymes-Chodur C, Betz N, Porte-Durrieu M C, *et al.* Nucl Instrum Methods Phys Res B, 1999, **151:** 377–385.

13 Ducouret C, Petersohn E, Betz N, *et al.* Spectrochim Acta A, 1995, **51:** 567–572.

14 Porte-Durrieu M C, Aymes-Chodur C, Betz N, *et al.* Nucl Instrum Methods Phys Res B, 1997, **131:** 364–375.