

방사선 그래프팅에 의한 염화비닐벤질 고분자가 그래프트된 불소필름의 제조

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Preparation of Poly(vinylbenzyl chloride)-grafted Fluoropolymer Films by Using Radiation Grafting Method

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초록: 본 연구에서 염화비닐벤질(vinylbenzyl chloride) 단량체는 동시조사방법을 이용하여 poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) (PFA), poly(ethylene-co-tetrafluoroethylene) (ETFE) 불소고분자 필름에 성공적으로 그래프트되었다. 실험 결과 같은 조사조건을 적용할 경우 다른 불소고분자 필름보다 ETFE 불소필름에 PVBC 고분자가 쉽게 그래프트됨을 확인하였다. 그래프트된 필름들은 FTIR, TGA, SEM-EDS 기기들을 사용하여 분석하였다. 그래프트된 필름의 파단신장률은 그래프트율이 증가할수록 감소되는 것을 확인하였으며 ETFE에 그래프트된 필름은 다른 불소고분자에 그래프트된 필름들과 비교하여 더 좋은 기계특성을 가지고 있음을 확인하였다.

Abstract: In this study, a vinylbenzyl chloride (VBC) monomer was successfully grafted onto the several fluoropolymer films including poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) (PFA), and poly(ethylene-co-tetrafluoroethylene) (ETFE) films by using a simultaneous irradiation method. The results indicated that PVBC graft polymer can be easily grafted onto the ETFE film than other fluorinated films under the same irradiation condition. The grafted films were characterized by using FTIR, TGA, and SEM-EDS instruments. The elongation at the breaking of the grafted films was found to decrease with an increase of degree of grafting (DOG). The PVBC-grafted ETFE films were found to have better mechanical properties than other PVBC-grafted fluorinated films.

Keywords: vinylbenzyl chloride, fluoropolymer, radiation, grafting.

Introduction

Many researchers have put much attention on focusing on the ion-exchange membranes for so many years since they have widely been applied in various industrial fields, including separators in lithium batteries, polymer electrolyte membranes in fuel cells, recovery of noble metals, removals of toxic chemicals, and sensing materials.^{1,2} Among the various ion exchange membrane preparation techniques,

radiation grafting method is considered to be a very convenient and effective way since various functional groups and desirable properties can be easily achieved with proper grafting materials and controlling irradiation conditions.

The radiation grafting can progress via either simultaneous irradiation or pre-irradiation method. Compared with pre-irradiation method, the simultaneous irradiation method is a rather simple one-step process, and the grafting can be achieved under milder conditions (e.g. lower total dose and temperature), while it generates more amount of homopolymer as wastes. The homopolymer formation can be

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minimized by adopting suitable irradiation condition including solvent, total dose, and dose rate.^{3,4}

Vinylbenzyl chloride (VBC) is a very attractive monomer since it contains the polymerizable double bond and a chloromethyl group that can be used for the introduction of new functional group. This VBC monomer has been widely used as a valuable precursor for the preparation of various polymer electrolytes (e.g. ion exchange resins), polymeric supports for solid peptide synthesis, fire-resistant polymers, and photosensitive polymers. The VBC monomer has also been applied for the radiation grafting polymerization onto a commercial film. Usually, a fluoropolymer film with high mechanical and thermal properties, and the resulting PVBC grafted film has been utilized as a precursor for the ion exchange membranes with various functional groups. The PVBC grafted film^{1,5-10} is converted to an anion-exchange membrane after a treatment with amines while less often to a cation-exchange membrane after an introduction of phosphoric acid^{2,9-12} or sulfonic acid group.^{9,10}

Both hydrocarbon and fluoropolymer films have been studied as base films for the preparation of fuel cell membrane by a radiation grafting method. Among the fluoropolymer films, perfluorinated poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) and poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) (PFA) films, and partially fluorinated polymers, polyvinylidene fluoride (PVDF), and poly(ethylene-alt-tetrafluoroethylene) (ETFE) film are often used for the radiation grafting due to its high radiation resistance and efficient grafting yields upon reaction with various monomers and are known to have good mechanical property.¹³

In our previous study, we demonstrated that VBC monomer can be successfully utilized for radiation grafting onto the poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) film to obtain the FEP-g-PVBC film by using a simultaneous irradiation grafting method.^{9,10} In this study, several fluoropolymer films including FEP, PFA, and ETFE films^{14,15} were used as a base film for the preparation of VBC grafted fluoropolymer films by using a simultaneous irradiation method. The several grafted films with the various degrees of grafting were prepared under the same irradiation conditions and characterized using FTIR, TGA and SEM-EDS. The mechanical properties (stress-strain analyses) of the prepared films were also investigated and reported in this paper.

Experimental

Materials. VBC (a mixture of 3- and 4-isomers, 97% purity) was purchased from Aldrich, and used as received.

Table 1. Fluoropolymer Base Films Used for VBC Grafting

Name	Structure	Manufactory
ETFE	$-(CF_2CF_2)_m-(CF_2CF(CF_3))_n-$	ASAHI GLASS Co., Ltd (Japan)
PFA	$-(CF_2CF_2)_m-(CF_2CF(OC_aF_{2a-1}))_n-$	Universal Co. Ltd. (Japan)
FEP	$-(CF_2CF_2)_m-(CH_2CH_2)_n-$	Universal Co. Ltd. (Japan)

Poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA), and poly(ethylene-co-tetrafluoroethylene) (ETFE) films having thickness of 25 μm , were used as the base films for the radiation grafting of VBC. The structures, manufacturers, and crystallinities of these fluoropolymer films are summarized in Table 1. Other chemicals including the solvents were of reagent or higher grade, and used without further purification.

Grafting Procedure. The grafted films were prepared by our previously reported methods. Fluoropolymer films (FEP, PFA, and ETFE) were cut into 5 cm \times 5 cm, washed with acetone, and then dried in a vacuum oven at 60 $^\circ\text{C}$ for 6 h. The dried film was then placed in a glass ampoule containing mixtures of VBC and chloroform (40:60 volume ratio). The mixtures were flushed with nitrogen gas for 10 min to remove the oxygen and then subjected to a γ -ray irradiation from a ⁶⁰Co source at a total dose of 20~80 kGy at dose rates of 2 kGy/h for the grafting of VBC onto the fluoropolymer films. The grafted films were washed with dichloromethane and dried in a vacuum oven at 60 $^\circ\text{C}$ overnight. The degree of grafting (DOG) was calculated using the following equation:

$$\text{DOG}(\%) = [(W_g - W_0) / W_0] \times 100$$

Where, W_0 and W_g are the film weights before and after the grafting process, respectively.

Characterization of the PVBC Grafted Films. IR spectra of the grafted films were obtained by using the FTIR spectrometer Tensor-37 (Bruker, Germany) at ambient conditions in the transmittance mode. The spectra were measured in a wavenumber range of 400~4000 cm^{-1} . The thermal properties of the grafted films were investigated by using a thermogravimetric analysis (TGA). The samples (about 5 mg) were heated from 40 to 650 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C min}^{-1}$ under a dry nitrogen atmosphere. SEM-EDS (7200-H, HORIBA Company) instrument was utilized to investigate the distribution of the PVBC grafting polymer on the cross-section of the grafted films. A tensile strength test was conducted with an Instron model 4400 universal testing machine at room

temperature.

Results and Discussion

Radiation Grafting of VBC onto Fluoropolymer Films. The grafted films were obtained by grafting VBC onto FEP, PFA and ETFE films using the simultaneous irradiation process. The degree of grafting as a function of irradiation dose is plotted in Figure 1. As shown in the figure, the degree of grafting of each film linearly increased with increasing irradiation dose and the grafting ability of the fluoropolymer film was found to be observed as following order: ETFE > PFA > FEP. The highest grafting ability of ETFE can be attributed to the fact that the radicals that initiate the grafting process are known to be easily formed on the partially fluorinated film (ETFE) than on the perfluorinated films (FEP and PFA) during the simultaneous irradiation process due to the low bond dissociation energy of C-H bond (98 kcal/mol) compared to that of C-F bond (117 kcal/mol).¹⁶⁻¹⁸

Characterization of the PVBC Grafted Films. In the Figure 2(a), the FTIR-ATR spectrum of the original FEP, PFA, and ETFE films showed strong bands at 1150~1250 cm^{-1} and a sharp band at around 980 cm^{-1} arising from the C-F stretching vibration. Compared with FEP and PFA films, the ETFE film showed aliphatic absorption bands at 2800~2900 cm^{-1} (C-H stretching vibration). After the grafting procedure (in the Figure 2(b)), the PVBC-grafted FEP, PFA, and ETFE films (with DOG 71%, DOG 75%, and DOG 81%, respectively) showed the new absorption bands arising from the grafted PVBC components combined with each original base film bands,¹⁰ indicating that the successful grafting of VBC monomer onto the fluoropolymer films. The aromatic absorption bands of the grafted PVBC appeared at 3050 (C-H stretching vibration) and 1450~1600 cm^{-1} (C=C stretching vibrations), respectively. The aliphatic absorption bands were observed at 2800~2900 cm^{-1} (C-H stretching

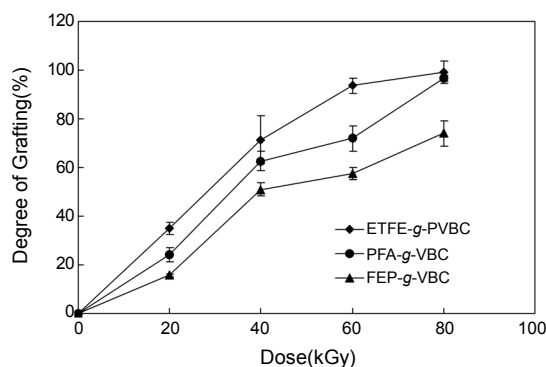


Figure 1. The degree of grafting of the PVBC grafted films as a function of irradiation dose.

vibration) and a characteristic band of the chloromethyl group (C-Cl stretching vibration) of the grafted PVBC was observed at 820 cm^{-1} .^{10,19}

The TGA thermograms of the PVBC-grafted FEP, PFA, and ETFE films (with DOG 71%, DOG 75%, and DOG 81%, respectively) are shown in Figure 3. Each of the films showed a two-step degradation process. The first degradation temperatures observed from 360 to 400 $^{\circ}\text{C}$ were considered due to the decomposition of the PVBC graft chains incorporated in the fluoropolymer films. The second degradations observed above 450 $^{\circ}\text{C}$ were considered due to the decomposition of the FEP, PFA, and ETFE base matrix films, respectively. These TGA results indicate that the radiation grafting processes proceeded smoothly without significant alteration of the fluoropolymer base films.

To observe the distributions of PVBC grafts in the cross-

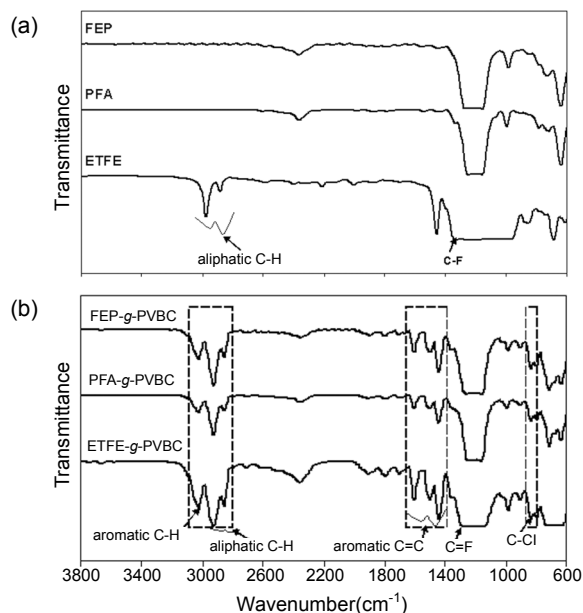


Figure 2. The FTIR-ATR spectra of (a) the original fluoropolymer film (FEP, PFA and ETFE base films); (b) the PVBC grafted films.

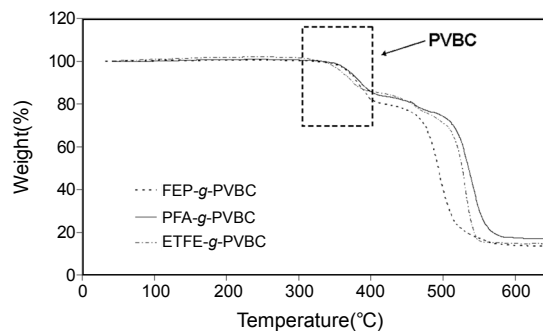


Figure 3. TGA thermograms of the PVBC grafted fluoropolymer films.

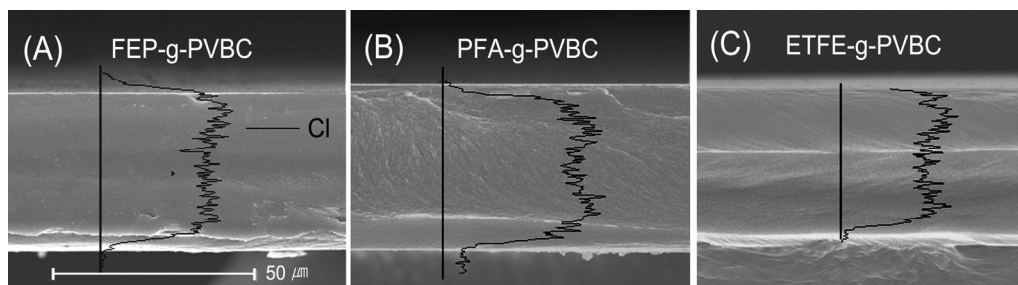


Figure 4. Cross-sectional SEM micrograph image and EDS profiles of chlorine atom of the PVBC grafted: (A) FEP–; (B) PFA–; (C) ETFE–based films.

section of the FEP, PFA, and ETFE films, the grafted samples were subjected to the scanning electron microscope connected with an energy dispersive X-ray spectroscopy (SEM–EDS). Figure 4 showed the cross-sectional SEM images of the films and the EDS profiles of chlorine atom distributed over cross-sections of the PVBC-grafted FEP, PFA, and ETFE films (with DOG 71%, DOG 75%, and DOG 81%, respectively). Since the fluoropolymer films have very low swellability in most organic solvents including VBC monomer, the radiation grafting is known to initially occur on the surface and then proceed into the inner part of the film by diffusing of the monomer through the grafted region.^{20–22} The EDS profiles in Figure 4 show that the PVBC grafts are uniformly distributed into the fluoropolymer films (FEP, PFA, and ETFE), indicating that the VBC monomer diffuses well into the inner side of the films during the radiation grafting process. In our previous work,²⁰ the distribution profiles of the PVBC grafts were found to be largely dependent on the radiation grafting conditions and the uniform distribution could be achieved by optimizing the degree of grafting and other grafting parameters such as solvent and monomer concentration.^{20,23} The uniform distribution of grafts in the film plays a key role, especially in a fuel cell application, since it affects ion transfer through the membrane during the fuel cell operation.^{6,8,10,23,24}

The stress–strain diagrams of the PVBC grafted fluoropolymer films with various DOG (about 30~90%) were shown in Figure 5. The results showed that the tensile strength of each PVBC grafted film increased and the elongation at the breaking of the graft films decreased as the DOG values increased. These results indicated that the DOG value, namely PVBC grafts content in the grafted films was an important factor that determines the mechanical properties of the films. Compared with the grafted films, the PVBC grafted onto the partially fluorinated ETFE films obviously showed the higher elongations than the PVBC grafted onto the perfluorinated FEP and PFA films. This result can be attributed to the fact that the ETFE film composed of alternating units of ethylene

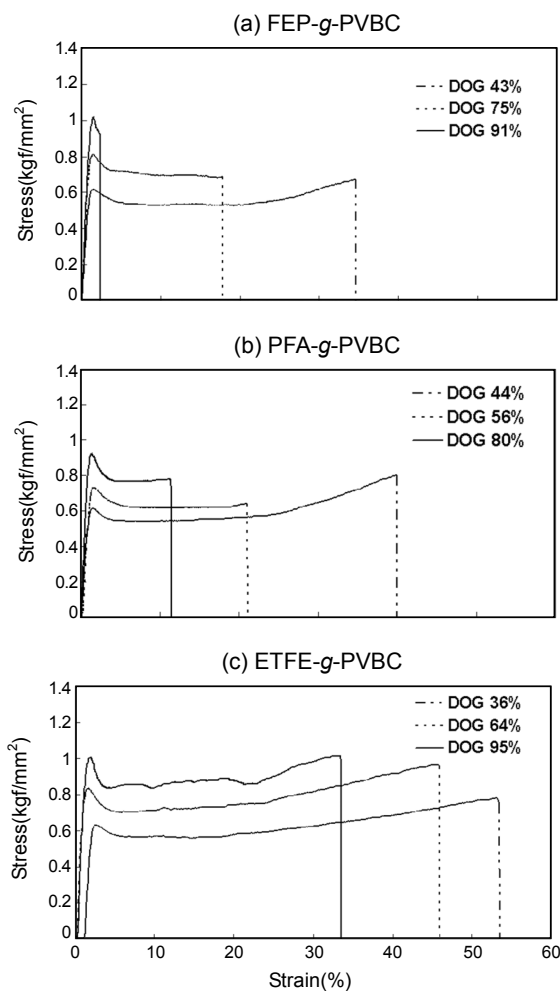


Figure 5. Stress–strain curves for the PVBC grafted: (a) FEP–; (b) PFA–; (c) ETFE–based films as function of the degree of grafting.

and tetrafluoroethylene has excellent tensile strength and elongation compared to other fluoropolymer films (such as PTFE, FEP, and PFA films).^{16,25–27} The similar results were also observed from the poly(styrene sulfonic acid)–grafted fluoropolymer membranes.^{25,28,29}

Conclusions

In this paper, the VBC monomer was successfully grafted into the fluoropolymer base film and the grafted films were characterized by using FTIR, TGA, SEM-EDS, and a mechanical strength test. The results indicated that partially fluorinated ETFE films were found to have the higher grafting ability than the perfluorinated FEP and PFA films. And also, the grafted ETFE films were found to have better mechanical property than the other perfluorinated films. The radiolytically prepared PVBC grafted fluoropolymer films are expected to be applied in a number of broad industrial fields, such as separator, polymer electrolytes, medical application, as well as fuel cells.

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