Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 46 (2005) 9257–9264
polymer
www.elsevier.com/locate/polymer

Penetration behavior and subsurface grafting of dansyl cadaverine and polyethylene glycol (PEG) derivatives in poly(ethylene-*co*-acrylic acid) (EAA) film

Chun Zhang, Ning Luo[1], Douglas E. Hirt*

Department of Chemical and Biomolecular Engineering, Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634-0909, USA

Received 20 May 2005; received in revised form 18 July 2005; accepted 20 July 2005
Available online 10 August 2005

Abstract

Dansyl cadaverine and polyethylene glycol (PEG) derivatives were grafted on the surface of EAA film and in its subsurface region through formation of amides and esters, respectively. A two-step reaction was conducted. First, EAA film was activated with PCl_5 at room temperature. Second, the acid chloride was reacted with dansyl cadaverine or a PEG derivative to form a modified film. ATR-FTIR spectroscopy and fluorometry were employed to analyze the modified films after each step. It was found that dichloromethane yielded the highest grafting efficiency, with the dansyl cadaverine penetrating throughout the ATR-FTIR analysis region (~400 nm) in a few minutes. As the grafting depth increased with time, so did the amount of fluorescence intensity of grafted dansyl cadaverine. ATR-FTIR spectra for PEG grafting indicated that the acid chloride peak decreased with time, while the ester peak increased. However, hydrolysis occurred at later times, consuming the acid chloride groups within the film. A marked decrease of static water contact angle was observed for EAA grafted with PEG99 (PEG that contains 99 ethylene glycol repeat units), almost 40° lower than that of neat EAA (~99°). For other PEG-grafted films, the surface hydrophilicity was also improved.

Keywords: Poly(ethylene-*co*-acrylic acid) (EAA); Polyethylene glycol (PEG); Grafting

1. Introduction

Poly(ethylene-*co*-acrylic acid) (EAA), a commercially available copolymer, has excellent physical and mechanical properties. It is commonly used as a protective coating because its carboxylic acid groups promote adhesion to metal [1]. EAA has also been investigated to improve the miscibility with polystyrene (PS) as a polymeric emulsifier [2]. However, the low surface energy of EAA limits its biotechnological applications due to its nonspecific adsorption and poor wettability. Therefore, research is being conducted to obtain improved surface properties through controlled surface modification. For example, Chong et al. [3] explored the use of EAA as a surface coating in biosensor applications, where the shielding EAA layer protected the silver coated quartz-crystal microbalance (QCM) and was tethered covalently with DNA oligonucleotides.

Because EAA contains reactive carboxylic acid groups, it can undergo chemical coupling after activation with phosphorus pentachloride [4,5], thionyl chloride [6], or 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) [3,7]. In addition, functional groups exist not only on the outer surface of EAA but also throughout the bulk, and surface rearrangement may result in carboxylic acid groups migrating into the subsurface region of the film [8]. Therefore, it is possible to graft long chain molecular or macromolecular species onto the surface and in the subsurface of EAA.

Currently, much attention is focused on attaching PEG onto surfaces to reduce adsorption of protein, bacteria, and cells. For example, Zhu et al. [9] studied the configuration of PEG molecules on silicon, finding that PEG with low molecular weight exhibits brush like configurations, while

* Corresponding author. Tel.: +1 864 656 0822; fax: +1 864 656 0784.
E-mail address: hirtd@clemson.edu (D.E. Hirt).
[1] Present address: US EPA, National Exposure Research Laboratory, Exposure and Dose Research Branch, Las Vegas, NV 89119, USA.

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.07.070

PEG with higher molecular weight resembles a coil configuration. Some theories suggest that the brush like configuration is more protein resistant because it provides maximum entropic repulsion between the proteins and surfaces [10]. Tajouri et al. [11] compared the behavior of PEG chains grafted on silica both in the presence of and without a solvent, finding that PEG can flatten on the surface or be swollen and spread out depending on the interactions among the chains, the solvent, and the solid surface in a heterogeneous system. In an effort to use polymers as biomaterials and biosensors, grafting techniques have also been employed to immobilize PEG on various polymer surfaces [12–19], including polypropylene, polyethylene, poly(ethylene terephthalate), polyaniline, polyurethane, polysulfone, poly(vinylidene fluoride), and poly(acrylonitrile-*co*-maleic acid).

The issue of reactant penetration into the polymer and subsequent reaction in the subsurface or bulk, which can be prevalent in a solution reaction system, is not often addressed. If the reaction occurs deeply within a film, the reaction would result in a bulk modification in addition to a surface modification such that the bulk properties may be affected [20], even though better surface wettability was achieved. Therefore, it is important to know the extent to which reactants penetrate into a polymer film and subsequently react with the reactive groups. ATR-FTIR spectroscopy is a good technique for studying the penetration reaction behavior within depths of tens and hundreds of nanometers [21,22]. The aim of this work was to study the subsurface grafting behavior and penetration reaction of a relatively small biomolecule (dansyl cadaverine) and PEG derivatives (nonoxynol-9 (N9)) [23]. Dansyl cadaverine is normally used as a fluorescent label to quantitatively determine the concentration of carboxyl, hydroxyl, and amino-acid groups on polymer surfaces [24,25]. In this research, it served as a fluorescent molecular label anchored onto the activated EAA surface and subsurface. We also used a series of N9s denoted as PEG4, PEG11, PEG39 and PEG99, where the number corresponds to the number of ethylene glycol repeat units. They were chosen for this reaction for several reasons. First, they are commercially available with monodisperse molecular weights. Second, different chain lengths of the PEG derivatives aid in characterizing the penetration behavior of a series of oligomeric and polymeric chains for comparison with dansyl cadaverine. Third, they serve as well defined materials for PEG grafting on EAA surfaces, which is important for future protein resistance studies.

2. Experimental section

2.1. Materials

Poly(ethylene-*co*-acrylic acid) (EAA, PRIMACOR 1410 from Dow Chemical Co., 9.5% (w/w) acrylic acid) films (thickness ~ 50 μm) were used as received from the Cryovac Division of Sealed Air Corp. (Duncan, SC). Phosphorous pentachloride (PCl_5, 95%), dichloromethane, acetone, methanol, pH7 phosphate buffered saline (PBS) solution, potassium hydroxide (KOH, 85% ACS reagent), dansyl cadaverine, and nonoxynol-9 (N9) (Igepal CO-990, 890, 720, 520) were purchased from Aldrich and used as received. The chemical structures of dansyl cadaverine and the PEG derivatives are shown in Fig. 1.

2.2. Conversion of carboxylic acid groups into acid chlorides

The EAA film was first washed with acetone and then dried at room temperature. To transform the carboxylic acids into acid chlorides, a film specimen was immersed in 20 ml of a 3% (w/w) PCl_5 solution in dichloromethane for 9 h to ensure high conversion. The film was then washed sequentially with dichloromethane and acetone. This film was denoted as EAA-Cl and used for the next reaction after being dried at room temperature.

2.3. Grafting of dansyl cadaverine to the EAA-Cl film

Dansyl cadaverine has a primary amine that can be linked covalently to an acid chloride. The EAA-Cl film was immersed in a 0.1 mg/ml solution of dansyl cadaverine in dichloromethane for 9 h at room temperature. Two other solvents were also used to study the effect of solvent in the grafting reaction, namely, 4% (w/w) aqueous KOH solution (pH12), and a pH7 PBS solution. Modified films were dried at 60 °C for 2 h before characterization. The EAA-Cl film was also immersed in a 1 mg/ml solution of dansyl cadaverine in dichloromethane to obtain higher reaction rates, and the reaction kinetics were studied over a time period of 5 s to 2 min. These EAA-*g*-dansyl films were extracted with dichloromethane in a Soxhlet apparatus for 24 h and then dried at 60 °C for 2 h before characterization.

2.4. Grafting of the PEG derivatives 'onto' the EAA-Cl film

A dried EAA-Cl film was immersed in a 0.01 mol/l solution of PEG derivative in dichloromethane at 60 °C for approximately 24 h. The resulting film was washed sequentially with dichloromethane and acetone, then dried at 60 °C for 2 h. This film was denoted as EAA-*g*-PEG.

The radius of gyration for the PEG derivatives can be estimated using [26]

$$R_g = a\left(\frac{N}{6}\right)^{1/2} \quad (1)$$

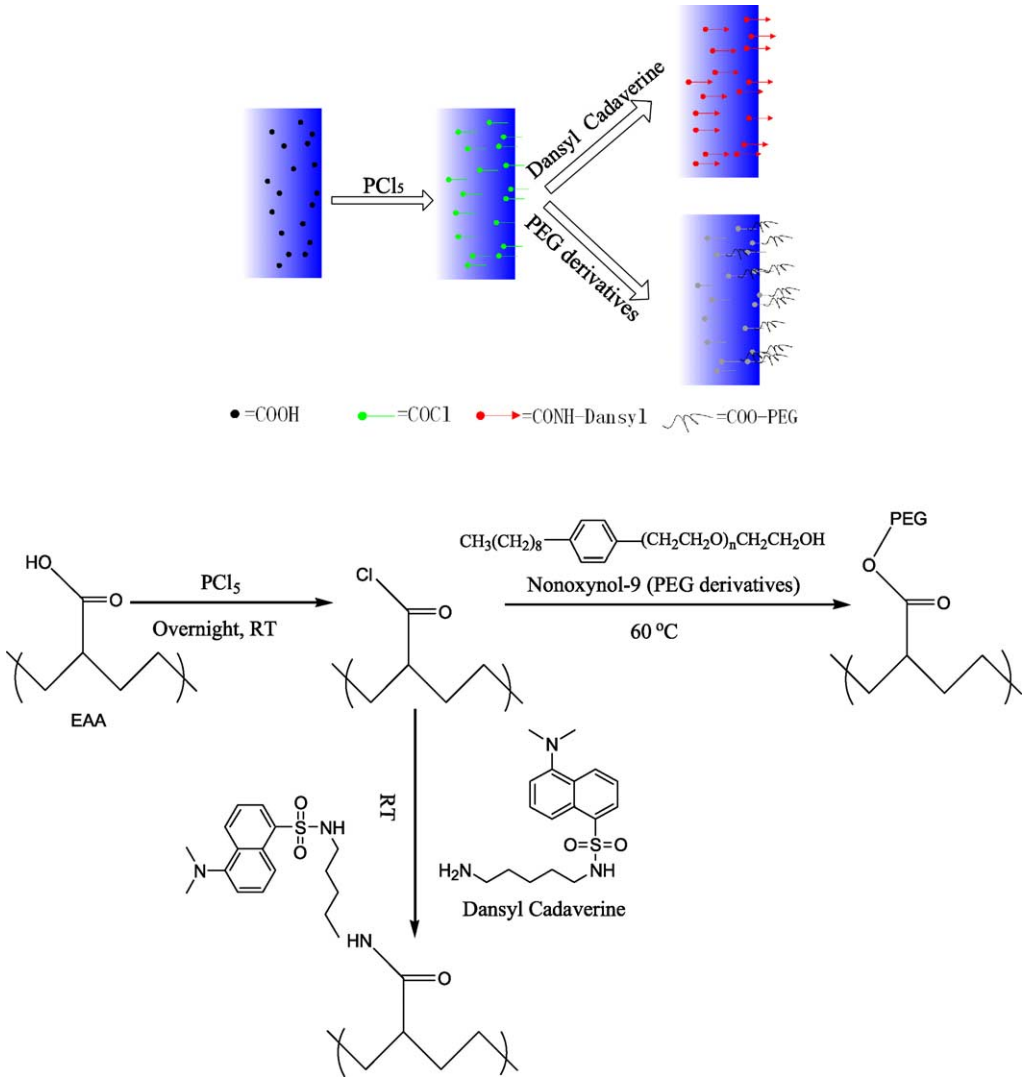

Fig. 1. Reaction scheme for grafting dansyl cadaverine and PEG derivatives on an EAA surface and into the subsurface region.

where a is the segment length for PEG (0.29 nm) and N is the degree of polymerization.

2.5. Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

A Nicolet Avatar 360 FTIR spectrometer equipped with a nitrogen-purged chamber was used to investigate the chemical changes after each reaction step and to provide some evidence concerning the penetration of reactants into the EAA film. The penetration depth d_p of the evanescent wave from the reflected light was calculated knowing the refractive indices of the crystal ($n_1 = 4.0$) and film specimen ($n_2 = 1.5$), the angle of incidence (45°), and the wavelength of interest (λ) [22]. The calculations determined that the average penetration depth of the evanescent wave for the dansyl cadaverine grafted EAA film at $\lambda = 1645\ \mathrm{cm}^{-1}$ was approximately 403 nm, while that for PEG modified EAA film at $\lambda = 1743\ \mathrm{cm}^{-1}$ was approximately 381 nm.

2.6. Fluorometry

Fluorometry measurements were performed using a GENios Multi-Detection Reader (Phenix Research Products). The excitation and emission wavelengths for the dansyl group were 340 and 510 nm, respectively. For each polymer surface, 16 readings were performed at different locations and averaged to report the fluorescence intensity.

2.7. Static contact angle

Static contact angle measurements were conducted using a Kruss G10 instrument. HPLC water was used and the measurement was taken immediately after the drop formed

on the surfaces. The average static contact angle and 95% confidence interval were obtained using at least eight droplets on each specimen.

2.8. Differential scanning calorimetry (DSC)

DSC experiments were performed using TA Instruments MDSC 2920. Five to ten milligrams of film was heated from −50 to 120 °C with heating and cooling rates at 10 °C/min. Crystallinity of the polymers was calculated according to the equation

$$\chi(\%) = \left(\frac{\Delta H}{\Delta H^0}\right) \times 100 \quad (2)$$

where ΔH is the heat of fusion of the film samples and ΔH^0 is the heat of fusion of perfectly crystalline polyethylene (PE).

3. Results and discussion

The carboxylic acid groups in EAA films can be used as reactive sites for surface grafting. In this work, studies focused on grafting dansyl cadaverine and PEG derivatives on the EAA surface and in its subsurface region. The reactions were performed in the two steps shown in Fig. 1. First, EAA film was reacted with PCl_5 for 9 h at room temperature to convert the carboxylic acid groups to acid chlorides, which could occur throughout the film depending on reaction conditions. Second, the acid chlorides were reacted with dansyl cadaverine or PEG derivatives to form a modified film. The penetration rate and reactivity of dansyl cadaverine in EAA film was studied initially as a function of solution concentration and immersion time.

A 0.1 mg/ml solution of dansyl cadaverine was prepared in three different solvents, namely, dichloromethane, 4% (w/w) KOH aqueous solution (pH12), and pH7 buffer solution. When dansyl cadaverine reacts with an acid chloride in the EAA-Cl film, an amide bond should form as evidenced by an IR absorption peak at 1645 cm^{-1}. Fig. 2 shows the ATR-FTIR spectra for neat EAA (spectrum 1), EAA-Cl (spectrum 2), and EAA-Cl immersed in the various dansyl cadaverine solutions for 9 h (spectra 3–5). The neat EAA showed a peak at 1705 cm^{-1}, which is characteristic of the carbonyl stretching of the acid portion of EAA. For the EAA-Cl, the 1705 cm^{-1} peak was not observed as the carboxylic acids were converted to acid chlorides, indicated by the peak at 1793 cm^{-1}. Spectrum 3, corresponding to the reaction in the KOH solution, showed evidence of amide formation with a peak around 1645 cm^{-1}; the KOH solution was the only case where this was observed. Reactions did not appear to occur in the aqueous pH7 or CH_2Cl_2 dansyl cadaverine solutions. Although it is generally considered that the acid chlorides will hydrolyze rapidly in aqueous solution, it was interesting to note that the ATR-FTIR spectra did not show any hydrolysis. But there was still a large amount of acid chlorides in the film for both of the aqueous solutions, even after a 9 h reaction time. A control experiment was conducted in which a piece of EAA-Cl film was immersed in water for 2 days, but no acid peak was observed in the ATR-FTIR spectrum, indicating that a large amount of acid chlorides in the subsurface were not hydrolyzed. By neutralizing hydrochlorides produced in the reaction, KOH solution promoted the anchoring reaction of dansyl cadaverine at the surface, but the aqueous solution still could not reach the acid chlorides in the subsurface region.

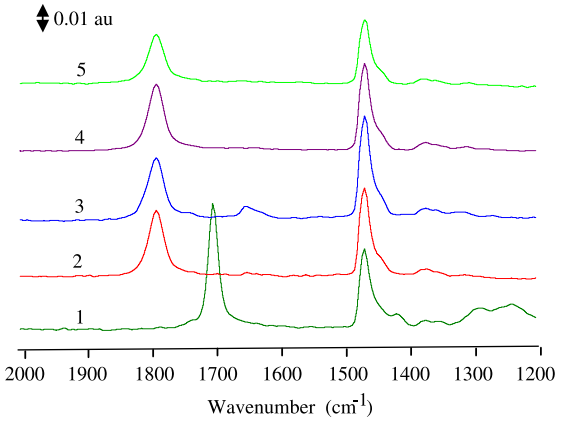

Fig. 2. ATR-FTIR spectra for EAA activation and dansyl cadaverine grafting (1) neat EAA, (2) EAA-Cl, (3) EAA-Cl reacted in dansyl cadaverine/KOH solution, (4) EAA-Cl reacted in dansyl cadaverine/pH7 solution, (5) EAA-Cl reacted in dansyl cadaverine/CH_2Cl_2 solution. Solution concentrations were 0.1 mg/ml and reaction time was 9 h.

The static water contact angles for the unmodified and modified EAA films were measured and it was found that the majority of the contact angles were approximately 98–101°, not only because of the low coverage of carboxylic acids on the surface but also because of the hydrophobic nature of the two-member rings on dansyl cadaverine. In fact, the high contact angle values provided some hint of the surface density of carboxylic acids. As estimated by Holmes-Farley [24], the contact angles for polyethylene (PE), PE–COOH (treated by chromic acid), and acid-terminated monolayers are 103, 55, and 0°, respectively. For our EAA film, the contact angle was approximately 99°, indicating that the acrylic acid surface coverage on EAA film was low. This is reasonable since the weight percentage of acrylic acid in this EAA was 9.5%, which means that the polymer consisted of approximately 25 ethylene units for every acrylic acid. Therefore, the acid content is only 4% on a molar basis, and the Cassie equation [27] would then predict only a small deviation from the contact angle of neat polyethylene.

We were curious as to why there was no reaction using dichloromethane as the solvent, so we conducted another series of experiments by immersing EAA and EAA-Cl film specimens in a more concentrated (1 mg/ml) dansyl cadaverine dichloromethane solution for a shorter time

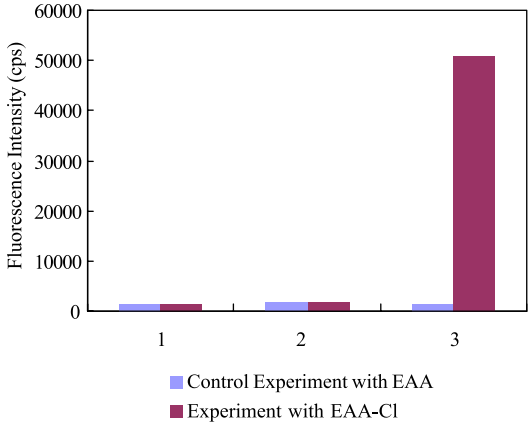

Fig. 3. Fluorescence intensities: (1) Neat EAA and EAA-Cl; (2) EAA and EAA-Cl films after immersion in 0.1 mg/ml dansyl cadaverine/CH_2Cl_2 solution at room temperature for 9 h; (3) EAA and EAA-Cl films after immersion in 1 mg/ml dansyl cadaverine/CH_2Cl_2 solution at room temperature for 10 s. Soxhlet extraction was then performed for one day in dichloromethane to remove unreacted material from the film.

(10 s). Fluorescence intensities for those samples are shown in Fig. 3 and the height of each bar denotes the fluorescence intensity for each specimen. It was observed that there was no significant difference between neat EAA film, EAA-Cl film, and EAA and EAA-Cl films attempted to be modified in dilute solution of dansyl cadaverine, but a dramatic increase occurred for EAA-Cl film reacted in the more concentrated solution. The control experiment in which unmodified EAA film was immersed in the concentrated solution showed a fluorescence intensity equivalent to that of neat EAA, as expected. The dramatic increase of fluorescence intensity could be explained by the higher penetration rate of dansyl cadaverine from concentrated solution than from dilute solution, so that a large amount of dansyl cadaverine was rapidly absorbed into the film and grafted over a period of 10 s. In the concentrated-solution case, the increased intensity was due to dansyl cadaverine grafted to the film since the fluorescence measurement was conducted after 24 h of Soxlet extraction in dichloromethane.

To estimate the speed of the dansyl-cadaverine-attaching reaction in a 1 mg/ml dansyl cadaverine solution with dichloromethane, a series of reactions was conducted for different immersion times from 1 s to 2 min. Fig. 4 summarizes the ATR-FTIR results. The amide peak at 1645 cm^{-1} increased while the acid chloride peak at 1793 cm^{-1} decreased as the reaction proceeded. The intensity of the amide peak was used to study the time-dependence of the amide formation within the analysis depth of the ATR-FTIR. The grafting depth can be estimated as

$$d = \frac{A}{A_\infty} d_p \tag{3}$$

where A is the peak area at 1645 cm^{-1} at any given time, A_∞ represents the peak area at 24 h when all of the acid chloride

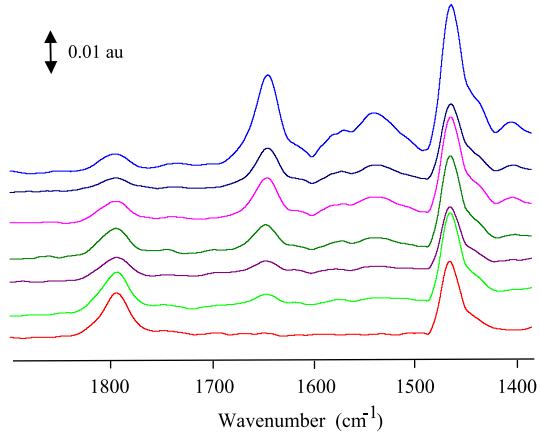

Fig. 4. ATR-FTIR spectra as a function of grafting time in 1 mg/ml dansyl cadaverine solution in dichloromethane. From bottom to top, the spectra correspond to immersion times of the film after 1, 5, 10, 20, 40, 60 and 120 s at room temperature.

groups were converted into amides ($A_\infty \sim 0.5$), and d_p is the analysis penetration depth of ATR-FTIR ($d_p = 403$ nm at $\lambda = 1645$ cm^{-1} [22]). Results obtained using the ATR-FTIR data and Eq. (3) are shown in Fig. 5. Also shown are the fluorescence intensities at $\lambda_{emision} = 510$ nm measured directly using $\lambda_{excitation} = 340$ nm for all samples. As expected, the rate of amide formation within the subsurface region of the film indicated a gradual decrease with time, faster at the beginning and then slowing down. The fluorescence data indicated the same trend. The ATR-FTIR and fluorescence results in Fig. 5 appear nearly superimposed, only because of the y-axis scale chosen for the fluorescence data (a different scale would have separated the data). However, the intent is not to superimpose the data, but to demonstrate that the two sets of data can be correlated.

It was evident that the relatively small dansyl cadaverine penetrated into the EAA film. To assess the depth of penetration as a function of molecular size, a subsequent grafting study was performed using a series of PEGs with various molecular weights. The hypothesis was that the grafting would occur first on the surface and then polymer

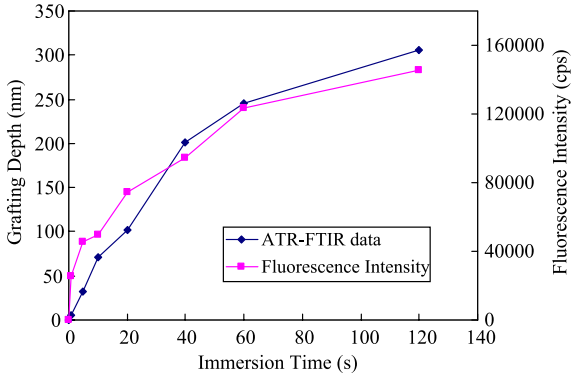

Fig. 5. Relationship of reaction depth (obtained from the peak area from ATR-FTIR data) and fluorescence intensity with immersion time for 1 mg/ml dansyl cadaverine solution in dichloromethane.

chains would have to overcome a potential barrier to penetrate into the film. Initially, a control experiment was conducted in which a reaction was attempted between PEG99 and EAA-Cl film in dichloromethane at room temperature. Comparing ATR-FTIR spectra for EAA-Cl film and EAA-Cl film reacted with PEG99, no grafting was evident over a 1-day reaction period. However, at 60 °C in dichloromethane, the acid chloride peak decreased while an ester peak at 1743 cm^{-1} and a 1110 cm^{-1} peak (corresponding to the ether groups in the grafted PEG) appeared. The contact angle also showed a large decrease of approximately 40° for EAA-*g*-PEG99. However, as reaction time increased, hydrolysis occurred with the appearance of a peak at 1705 cm^{-1}, and there was still a large amount of acid chloride groups left in the film, suggesting that after the outermost PEG layer formed, it was more difficult for other PEG chains of that size to penetrate and react. As the grafting rate is affected by temperature, 60 °C was used for all subsequent PEG grafting. A higher temperature was avoided so that any crystallinity changes in EAA, a semi-crystalline polymer with a melting point of 95 °C, would be minimized. To demonstrate that the 60 °C was not altering the EAA crystallinity during grafting, DSC experiments were conducted. DSC data of neat EAA, EAA-Cl, and PEG39 grafted films showed crystallinities of 18, 17, and 20%, respectively, based on the measured enthalpies of crystallization and a value of $\Delta H^0 = 286$ J/g [28], the heat of fusion of perfectly crystalline polyethylene.

The extent of the grafting reaction as a function of immersion time in dichloromethane was first studied. Fig. 6 presents the FTIR spectra of the film grafted with PEG39. It can be observed that the acid chloride peak at 1793 cm^{-1} decreased with time, while the ester peak at 1743 cm^{-1} increased. However, hydrolysis occurred at later times, as evidenced by the increase in the 1705 cm^{-1} peak, also consuming acid chloride groups within the analysis depth. When the reaction time was extended to 120 h, it was found that the acid chloride peak at 1793 cm^{-1} disappeared with the appearance of a large carboxylic acid peak at 1705 cm^{-1}, suggesting that all of the acid chlorides not grafted with PEG were hydrolyzed to acids.

When a control experiment was conducted using neat EAA films immersed in the same reaction solution at the same temperature, no peaks appeared at 1743 and 1110 cm^{-1} and the contact angles of those samples were similar to neat EAA and EAA-Cl within $\pm 5°$. Therefore, no PEG grafting occurred on neat EAA without activation. It also suggested that covalent bonding played an important role in the penetration reaction process. A depiction of the penetration reaction process is shown in Fig. 7. Moving from top to bottom, the figure has three regions within 400 nm, the grafted, hydrolyzed, and activated regions. Hydrolysis occurred beneath the grafted region, extending inside the film over time, because a small amount of water was taken up into the film by the grafted hydrophilic PEG chains. Based on the acid peaks, the hydrolysis increased with PEG size at a give time, since, on a molar basis, more water was associated with larger PEG chains.

The accessibility and reactivity of a PEG's hydroxyl group to the acid chloride should limit the esterification reaction rates. Therefore, PEGs with different molecular weight should have different subsurface grafting behavior because larger molecules cannot penetrate as deeply into the film, resulting in a relatively low grafting efficiency but potentially improved surface hydrophilicity. The grafting process was performed under the same conditions as the earlier experiments, the only difference being the use of four PEGs (radii of gyration of 1.2, 0.7, 0.4 and 0.3 nm for PEG99, 39, 11, and 4). Eq. (3) was used to estimate the grafting depths for the PEGs, where the peak area of interest was the ester peak at 1743 cm^{-1}. To determine A_∞ for this case, methanol was used as a small molecule that would penetrate into the film and convert all of the acid chlorides to esters (analogous to hydroxyl-terminated PEGs reacting with acid chlorides). All of the acid chlorides were converted to esters within 24 h of immersion in methanol to yield $A_\infty \sim 0.18$. The grafting depth as a function of reaction time for different PEG derivatives is shown in

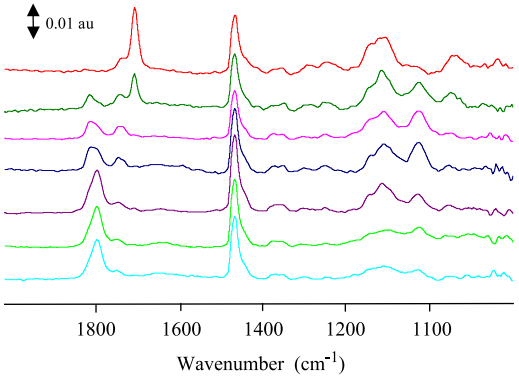

Fig. 6. ATR-FTIR data showing the penetration reaction process of PEG39 in EAA-Cl film at 60 °C in 0.01 mol/l dichloromethane solution. From bottom to top, the spectra represent immersion times of 2, 4, 6, 12, 24, 72 and 120 h.

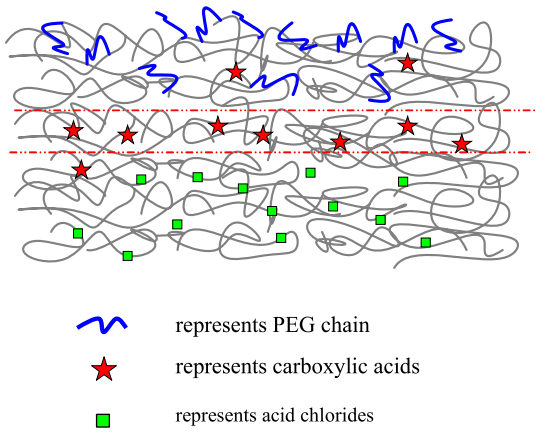

Fig. 7. Simplified schematic of the penetration reaction process inside of EAA-Cl film.

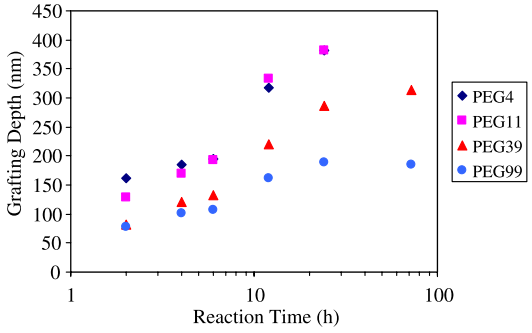

Fig. 8. Grafting depth versus reaction time for PEG4, PEG11, PEG39 and PEG99 (0.01 mol/l in dichloromethane at 60 °C). The figure does not show the grafting depth for PEG4 and PEG11 at 72 h, because they reached the analysis depth of ATR-FTIR at 24 h.

Fig. 8. The grafting depth for PEG4 and PEG11 increased continuously but the rate of increase slowed beyond 6 h. The larger PEG39 and PEG99 chains achieved less grafting depth to confine the grafting nearer to the surface. Therefore, the grafting depth can be controlled either by grafting time or molecular size.

The measurement of static water contact angles can be used to assess the wettability of the outermost few angstroms of the modified films. Fig. 9 showed that the static water contact angle of neat EAA was approximately 99°. After grafting with different PEG derivatives, the contact angle decreased continuously to approximately 60° for EAA-*g*-PEG99. This decrease is reasonable because larger PEG molecules will cover more surface area with hydrophilic ethylene glycol repeat units.

4. Conclusions

Dansyl cadaverine and PEG derivatives were successfully grafted on EAA surfaces and in its subsurface region. For dansyl cadaverine grafting, ATR-FTIR spectra and fluorescence intensities indicated that the acid chloride groups of EAA-Cl were not hydrolyzed in aqueous solution because the moisture could not reach the acid chlorides in the subsurface regions, thus protecting those reactive functional groups.

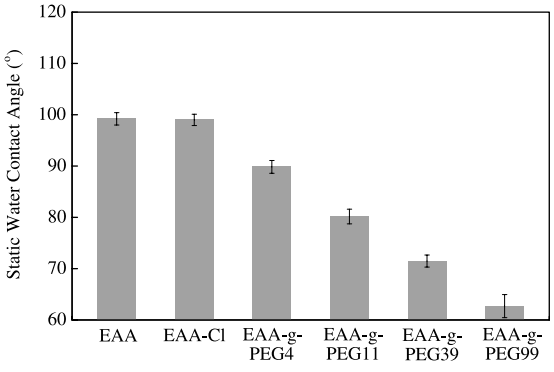

Fig. 9. Static water contact angle results for PEG-grafted films after 2 h drying at 60 °C (error bars represent 95% confidence intervals).

Concentrated dansyl cadaverine solution in dichloromethane promoted subsurface grafting with a higher penetration rate than in dilute solution. In a few minutes, the dansyl cadaverine penetrated throughout the analysis region (~400 nm) afforded by ATR-FTIR spectroscopy. In a subsequent study, four PEGs, PEG99, 39, 11, and 4 with different radii of gyration of 1.2, 0.7, 0.4, and 0.3 nm, were grafted on the EAA surface and in the subsurface region. Three regions were proposed to explain the penetration behavior of PEG chains, including the grafted, hydrolyzed, and activated regions. It was found that the two larger PEGs achieved less grafting depth to confine the grafting nearer to the surface. For PEG99, the grafting depth was about 180 nm after 24 h of reaction time. However, after grafting with different PEG derivatives, the static water contact angle decreased to approximately 60° for EAA-*g*-PEG99, almost 40° lower than that of neat EAA.

Acknowledgements

This work was supported by the Engineering Research Centers Program of the National Science Foundation under NSF Award Number EEC-9731680. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect those of the National Science Foundation.

References

[1] VanderKam SK, Bocarsly AB, Schwartz J. Chem Mater 1998;10(3):685–7.
[2] Shin JS, Cheong IW, Lee DY, Kim JI, Kim JH. Colloids Surf, A 2002;207(1–3):155–60.
[3] Chong KT, Su XD, Lee EJD, O'Shea SJ. Langmuir 2002;18(25):9932–6.
[4] Luo N, Stewart MJ, Hirt DE, Husson SM, Schwark DW. J Appl Polym Sci 2004;92(3):1688–94.
[5] Luo N, Husson SM, Hirt DE, Schward DW. J Appl Polym Sci 2004;92(3):1589–95.
[6] Zhang R, He CB, Craven RD, Evans JA, Fawcett NC, Wu YL, et al. Macromolecules 1999;32(7):2149–55.
[7] Zhang P, Fawcett NC, Evans JA, Hurt T, Harvey KG, Craven RC. Anal Biochem 2000;282(2):218–26.
[8] Gagnon DR, McCarthy TJ. J Appl Polym Sci 1984;29(12):4335–40.
[9] Zhu XY, Jun Y, Staarup DR, Major RC, Danielson S, Boiadjiev V, et al. Langmuir 2001;17(25):7798–803.
[10] Prime KL, Whitesides GM. J Am Chem Soc 1993;115(23):10714–21.
[11] Tajouri T, Bouchriha H, Hommel H. Polymer 2003;44(22):6825–33.
[12] Oh SJ, Jung JC, Zin WC. J Colloid Interface Sci 2001;238(1):43–7.
[13] Kiss E, Samu J, Toth A, Bertoti I. Langmuir 1996;12(6):1651–7.
[14] Kingshott P, Wei J, Bagge-Ravn D, Gadegaard N, Gram L. Langmuir 2003;19(17):6912–21.
[15] Li ZF, Ruckenstein E. J Colloid Interface Sci 2004;269(1):62–71.
[16] Park KD, Kim YS, Han DK, Kim YH, Lee EHB, Suh H, et al. Biomaterials 1998;19(7–9):851–9.
[17] Song YQ, Sheng J, Wei M, Yuan XB. J Appl Polym Sci 2000;78(5):979–85.
[18] Ademovic Z, Klee D, Kingshott P, Kaufman R, Hocker H. Biomol Eng 2002;19(2–6):177–82.

[19] Nie FQ, Xu ZK, Qian Y, Jian W, Wan LS. J Membr Sci 2004; 235(1–2):147–55.
[20] Luo N, Zhang C, Husson SM, Hirt DE. Adsorption of fluorescently labeled protein residues on poly(ethylene-*co*-acrylic acid) films modified with affinity functionalities. In preparation.
[21] Tatsumi D, Yamauchi T. J Appl Polym Sci 1998;69(3):461–8.
[22] Luo N, Husson SM, Hirt DE, Schwark DW. Advances in controlled/Living Radical Polymerization. vol. 854. Washington, DC, USA: ACS Books; 2003. p. 352–65.
[23] Owen DH, Dunmire EN, Planys AM, Katz DF. J Controlled Release 1999;60(1):23–34.
[24] Holmes-Farley SR, Whitesides GM. Langmuir 1986;2(3):266–81.
[25] Ivanov VB, Behnisch J, Hollander A, Mehdorn F, Zimmermann H. Surf Interface Anal 1996;24(4):257–62.
[26] Zdyrko B, Varshney SK, Luzinov I. Langmuir 2004;20(16):6727–35.
[27] Cassie ABD, Baxter S. Trans Faraday Soc 1944;40:546–51.
[28] Liu SS, Yu GQ, Huang BT. J Appl Polym Sci 1997;66(9):1715–20.