Surface Modification of Ethylene-*co*-Acrylic Acid Copolymer Films: Addition of Amide Groups by Covalently Bonded Amino Acid Intermediates

Ning Luo,[1] Michael J. Stewart,[1] Douglas E. Hirt,[1] Scott M. Husson,[1] Dwight W. Schwark[2]

[1]*Department of Chemical Engineering and Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, South Carolina 29634*
[2]*Cryovac Division of Sealed Air Corporation, Duncan, South Carolina 29334*

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ABSTRACT: Amide groups were anchored covalently on the surface of ethylene-*co*-acrylic acid (EAA) copolymer film by surface grafting of amino acid intermediates. The process consisted of four steps: conversion of carboxylic acid groups on the EAA surface to acid chloride groups, amino acid attachment, conversion of amino acid carboxyl groups to acid chloride groups, and amidation. All steps were carried out at room temperature. ATR-FTIR spectroscopy was used to characterize the film after each step and to measure the kinetics of amino acid attachment. Three amino acids were studied: 12-aminododecanoic acid (12-ADDA), 5-aminophthalic acid (5-APA), and L-aspartic acid (AA). The longer-chain 12-ADDA compound was selected for its chemical similarity to migratory fatty amides that are commonly used to alter the frictional behavior of polyolefin films. The 5-APA and AA compounds were selected because each has two carboxylic acid groups that can be converted to amide groups. After amidation, the modified EAA films were characterized by static water contact angle measurements and scanning probe microscopy. Results showed that the 12-ADDA reacted to the surface much faster than the 5-APA or AA. Several steps of aggressive rinsing confirmed that the 12-aminododecanamide was chemically anchored onto the EAA surface. As a result, both hydrophilicity and surface roughness were increased. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1688–1694, 2004

Key words: amino acid; surface modification; ethylene-*co*-acrylic acid copolymer; amidation; ATR-FTIR

INTRODUCTION

As early as the late 1950s, a series of articles reported results on the grafting of amino acids on polysaccharide polymers (e.g., cellulose).[1–5] By altering the chemistries used, amino acids or their derivatives can be attached to cellulose or other polymeric surfaces through reaction of either their amino or carboxyl functional group(s). Many applications that use surface-grafted amino acids exploit their abilities to selectively and efficiently recognize proteins and thereby resist or encourage surface adsorption of specific proteins. For example, amino acids bonded covalently to the surfaces of conventional polymeric membranes transform them into pseudobiospecific affinity membranes in the purification of a variety of proteins.[6] In this study, we examined a new application: the use of grafted amino acids as intermediates in a process to alter the frictional properties of polymeric films.

The ways in which amino acids are grafted onto polymer surfaces are varied. For polyethylene membranes and films, amino acids can be bonded covalently to the surface by direct Ar^+ irradiation[7] or by reacting with grafted polymer chains in a two-step process. In the latter method, poly(glycidyl methacrylate) is first grafted on polyethylene by electron-beam or γ-ray irradiation. Subsequently, amino acids are attached by sequential ring-opening reactions between amine groups in the amino acids and epoxy groups on the grafted poly(glycidyl methacrylate).[8–11] Polyacrylic acid has also been used as a grafted intermediate layer for subsequent attachment of amino acids on polyethylene membranes.[12] Here, the amine groups of the amino acid are coupled with the carboxylic acid groups of polyacrylic acid. Wu et al.[13] modified the surface of poly(ethylene terephthalate) (PET) film with glycine by a method that involved UV grafting of polyacrylamide and sequential reactions. The glycine-grafted PET film was then reacted with oligopeptides for applications in biomaterials. Amino acids have been attached covalently to the surface of polyurethane by the reaction with sodium sulfonate[14] or hydroxyl[15] groups.

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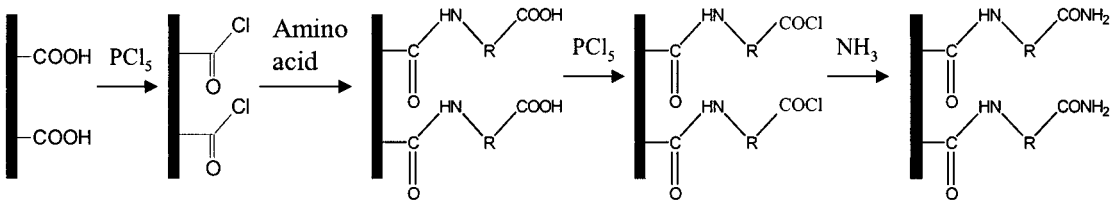

Scheme 1 Chemical approach to anchor an amide on the surface of EAA film using an amino acid intermediate.

As mentioned, the present study was motivated by issues related to the processing of polyolefin films, which, in their neat form, typically possess surfaces that are tacky and exhibit a high coefficient of friction (COF).[16,17] Commercial films travel over metal rollers in high-speed packaging lines where the performance of the film in contact with the rollers depends on the frictional characteristics of the film. To reduce the COF and make the films easier to process, fatty-amide additives, for example, erucamide (C_{22}) or stearamide (C_{18}), are blended into a polyolefin before extrusion.[17–20] Once the film solidifies, the additives (referred to as slip agents) migrate to the surface over time, thereby reducing the COF. In a recent study, Janorkar et al.[21] reported that surface-segregated erucamide was removed during repetitive COF testing, resulting in a process-dependent COF that increased with an increasing number of film–metal contacts. This COF increase can occur because the slip agent is not covalently bound to the polyolefin film surface. By anchoring the slip agent or a chemically analogous compound to the polyolefin surface, it might be possible to reduce the deleterious COF changes. Therefore, the focus of the present study was to develop the protocol for covalent attachment of relatively long-chain amides to polyethylene-based films. Subsequently, we will investigate the effect of these surface-bound amides on film COF.

The approach is to first graft amino acid intermediates to the film surface, followed by amidation of the carboxylic acid group(s) of the amino acid. For this study, ethylene–acrylic acid copolymer (EAA) film was selected. EAA and its partially neutralized form, EAA ionomer, are important products in the packaging industry. They are often used for applications that require good adhesion to aluminum foil, for products that are high in fat content (e.g., meat), and for applications that require high film clarity and toughness.[22] Carboxylic acid groups on the surface of EAA film provide the reaction sites to attach amino acid molecules. We chose to anchor amino acid intermediates rather than to amidate the surface directly because the former approach results in amide functionality that more closely resembles the C_{18} or C_{22} migratory amide additives used in practice. In principle, carboxylic acid groups can be generated on the surface of polyethylene film by plasma treatments.[23] Therefore, it will be possible to extend the present technique to polyethylene, the most commonly used packaging-film material. In the present contribution, we describe the reaction conditions used to covalently bond amino acids to EAA and the conditions for subsequent amidation. We present characterization data that illustrate the changes that occur to the chemical and physical properties of the modified films. The effect of amino acid grafting on film COF will be discussed in a subsequent article.

EXPERIMENTAL

Materials

EAA (9.5 mol % acrylic acid) films (thickness = 0.06 mm) were used as received from Cryovac Division of Sealed Air Corp. (Duncan, SC). Phosphorus pentachloride (PCl_5, 95%), 12-aminododecanoic acid (95%), potassium hydroxide (KOH, 85+% ACS reagent), 5-aminophthalic acid (94%), and ammonia (0.5 mol % ammonia in dioxane solution) were purchased from Aldrich (Milwaukee, WI) and used as received. L-Aspartic acid (>99%) was purchased from Sigma (Milwaukee, WI). Methylene chloride, dioxane, methyl ethyl ketone, and ethyl acetate were purchased from Aldrich as ACS reagent grade.

Preparation of acid chloride–modified film surface

Referring to Scheme 1, a piece of EAA film (15 × 25 cm) was immersed in 600 mL of a 3% (w/w) PCl_5 solution in methylene chloride to perform the surface reaction. The reaction took place 24 h at room temperature with shaking. After the reaction was finished, the film was removed and washed sequentially with methylene chloride and ethyl acetate. Residual solvent on the surface was blotted off with tissue paper. For a sample subjected to characterization, the film was allowed to air dry for at least 24 h. All other samples were used immediately in the next reaction step. Hereafter, the surface-modified EAA film is denoted as EAA-Cl.

Preparation of amino acid–modified film surface

Three different amino acids were used in this study: 12-aminododecanoic acid, 5-aminophthalic acid, and

L-aspartic acid. The latter two compounds have two carboxylic acid groups, which potentially allow the final concentration of amide groups to exceed the concentration of surface carboxylic acid groups on the starting EAA film. Amino acid (8 g) was dissolved in 400 mL of 4% (w/w) KOH aqueous solution at room temperature. One piece of the EAA-Cl film was placed in the amino acid solution to perform the reaction at room temperature for 24 h. After the reaction was completed, the film was removed and washed with a 4% (w/w) KOH aqueous solution for 10 min, and then washed with substantial volumes of neutral water. To convert the carboxylate salt groups to acid groups, the films were treated with 400 mL of 1*N* HCl acidic aqueous solution. Tissue paper was used to absorb the residual solvent on the surface after acidification. The amino acid–modified EAA film in the salt form was denoted as EAA-*N*-K; in the acid form, it was denoted as EAA-*N*-acid.

Preparation of acid chloride–modified, amino acid–modified film surface

EAA-*N*-acid film was reimmersed in the PCl_5 solution to convert the carboxyl end groups to acid chloride groups. The reaction conditions were the same as those used in the first reaction step. After this step, the EAA film was denoted as EAA-*N*-Cl.

Preparation of amide-modified film surface

EAA-*N*-Cl film was placed into 400 mL of 0.5 mol % ammonia solution in dioxane. The amidation reaction took place for 24 h with shaking. After the reaction was completed, the film was removed and washed with water. Tissue paper was used to absorb the residual solvent on the surface, and the film was dried in air. The final modified EAA film was denoted as EAA-*N*-amide.

Characterization

Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra of the polymer films were obtained using a Nicolet Avatar 360 FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI) equipped with a nitrogen-purged chamber. ATR-FTIR spectroscopy was conducted with a horizontal multibounce attachment using a germanium crystal and a 45° angle of incidence. All spectra were taken at 4 cm^{-1} resolution and reported as an average of 540 scans.

Static contact angle measurement

Static contact angle measurements were conducted using a Krüss G10 instrument (Krüss, Hamburg, Germany) with a digital photoanalyzer. With a 1-mL syringe, a water drop (volume ≅ 1.4 μL) was carefully placed onto the film specimen of interest. At least nine drops were evaluated for each specimen to obtain an average contact angle and 95% confidence interval.

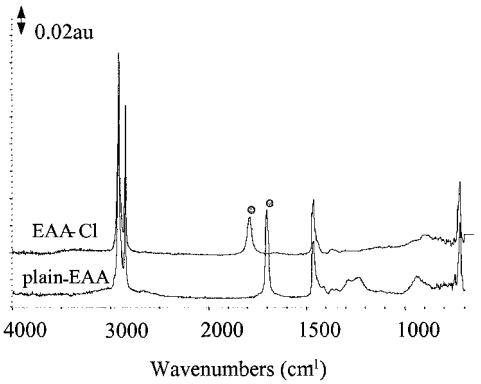

Figure 1 Conversion of carboxylic acid groups to acid chloride groups evaluated by ATR-FTIR spectroscopy.

Scanning probe microscopy (SPM)

SPM characterization was done using a Dimension 3100 (Digital Instruments, Santa Barbara, CA) microscope. Both tapping and phase-imaging modes were used to characterize the modified EAA films in ambient air. The root-mean-square roughness of the samples was evaluated from AFM images in the tapping mode. Surface roughness is the standard deviation of feature height (Z) values within a given area[24]:

$$\text{Roughness} = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{av})^2}{N}} \qquad (1)$$

where Z_{av} is the average Z-value within the given area, Z_i is a point feature height, and N is the number of points within a given area.

RESULTS AND DISCUSSION

Scheme 1 shows the four-step approach to bond amide groups covalently to EAA film. ATR-FTIR spectroscopy was used to characterize the chemical changes to the film after each step. Figure 1 shows the ATR-FTIR data after the first reaction step. Plain (unmodified) EAA showed a hydrogen-bonded carbonyl stretching vibration at 1703 cm^{-1}. After reacting EAA with PCl_5, the carbonyl band shifted to 1793 cm^{-1}, consistent with the transformation of the carboxylic acid groups to acid chloride groups.

For step 2, 12-aminododecanoic acid or one of the other two amino acids was dissolved in a basic aque-

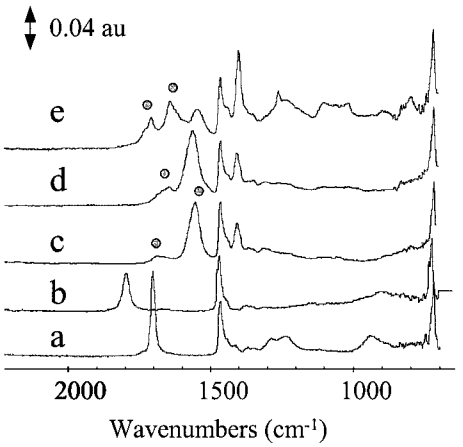

Figure 2 Attachment of 12-aminododecanoic acid on EAA film evaluated by ATR-FTIR spectroscopy: (a) plain EAA; (b) EAA-Cl; (c) EAA reacted with KOH aqueous solution directly; (d) EAA-*N*-K; (e) EAA-*N*-acid.

ous solution. After this reaction step, the surface-anchored amino acid was in its salt form (EAA-*N*-K). The ATR-FTIR spectrum of EAA-*N*-K [Fig. 2(d)] shows a weak vibration at 1641 cm^{-1} associated with the amide group that is formed and a strong peak located at 1554 cm^{-1}. The strong band is assigned to the asymmetrical stretching vibration of a carboxylate anion.[25] To confirm the property of this 1554 cm^{-1} band, plain EAA was neutralized directly with KOH aqueous solution. The ATR-FTIR spectrum [Fig. 2(c)] shows a strong 1554 cm^{-1} band and a weak band at 1689 cm^{-1}, which verified that the 1554 cm^{-1} band is associated with the carboxylate anion. Next, the carboxylate salt was converted to COOH by treating the EAA-*N*-K film with HCl aqueous solution. The ATR-FTIR spectrum [Fig. 2(e)] shows the existence of a hydrogen-bonded carbonyl band of COOH (1709 cm^{-1}), an amide carbonyl band (1641 cm^{-1}), and a band at 1545 cm^{-1}. The 1545 cm^{-1} band was attributed to the N—H bending vibration (amide II band).[26,27]

The reaction between EAA-Cl and amino acid consumes acid chloride groups on the EAA film. As a result, the 1793 cm^{-1} band [seen in Fig. 2(b)] disappeared in the ATR-FTIR spectra after complete reaction conversion. Thus, the intensity of 1793 cm^{-1} band can be used to measure reaction kinetics for conversion of EAA-Cl to EAA-*N*-acid. Reaction conversion χ is defined and measured as

$$\chi = 1 - \frac{\left(A_{1793}/A_{1465}\right)_t}{\left(A_{1793}/A_{1465}\right)_0} \qquad (2)$$

where A_{1793} and A_{1465} represent the absorption intensities at 1793 and 1465 cm^{-1}, respectively; subscripts 0 and t represent initial time and reaction time, respectively. The band at 1465 cm^{-1} is the C—H bending vibration that results primarily from the polyethylene segments of EAA film; as such, it is used as an internal reference. Figure 3 shows that the reaction conducted with 12-aminododecanoic acid (12-ADDA) occurs much faster than that with 5-aminophthalic acid (5-APA) or L-aspartic acid (AA). To obtain about 80% reaction conversion, 12-ADDA required about 3 min, whereas both 5-APA and AA took more than 10 h. Given that the reaction between acid chloride and amine is a nucleophilic substitution, the observed differences in reaction rates are likely attributable to differences in the nucleophilicities of the lone electron pair of the amine nucleophiles. For 5-APA, the amine group is attached directly to an aromatic ring that contains two electron-withdrawing carboxylic acid groups. For this compound, the nucleophilicity of the amine group is reduced from donating electrons to the aromatic ring and the two carboxylic acid groups. Therefore, the reactivity of the aromatic amine group in 5-APA is lower compared to that of the isolated aliphatic amine group in 12-ADDA. L-Aspartic acid is an aliphatic α-amino acid with its amine group positioned on the same carbon atom as the carboxylic acid group. Here again, the proximity of the carboxylic group reduces the nucleophilicity of the amine in AA. As an example, lysine can be used to illustrate the relative basicities of α- and ω-amine groups in an aliphatic amino acid. Much stronger basicity was reported for the ω-amine group (pK_a = 10.53 ω-NH_3^+) than for the α-amine group (pK_a = 8.95 α-NH_3^+) in lysine.[28] The reduced basicity (similar trend of nucleophilicity in the present case) of the α-amine group in AA makes it less reactive toward nucleophilic substitution than the amine group of 12-ADDA.

Figure 4 shows the ATR-FTIR spectra in all reaction steps intermediated with 12-aminododecanoic acid. After the amino acid was attached to the EAA surface,

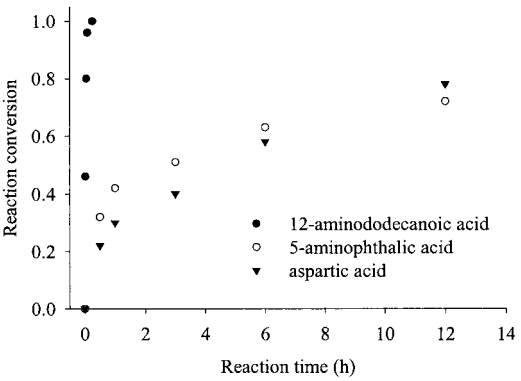

Figure 3 Reaction kinetics of amino acid coupling with acid chloride groups on EAA film. Data were collected from ATR-FTIR measurements and processed using eq. (2).

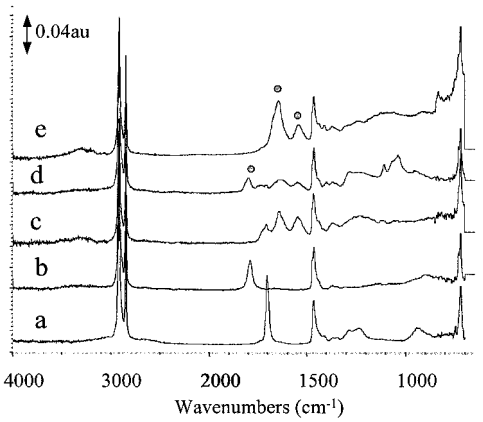

Figure 4 ATR-FTIR data tracking the formation of longer-chain amide groups on EAA film by surface grafting of 12-aminododecanoic acid: (a) EAA plain; (b) EAA-Cl; (c) EAA-*N*-COOH; (d) EAA-*N*-Cl; (e) EAA-*N*-amide.

its carboxylic acid group was converted to an acid chloride group. A band at 1793 cm^{-1} in the spectrum [Fig. 4(d)] supports the conversion of the amino acid to the acid chloride functionality. In a final step, ammonia was reacted with the acid chloride groups to generate primary amide groups at the grafted-layer periphery. The ATR-FTIR spectrum of the EAA-*N*-amide film [Fig. 4(e)] shows a strong amide I absorption band at 1645 cm^{-1} and an amide II absorption band at 1545 cm^{-1}, and supports the successful grafting of amino acids to EAA film and subsequent amidation.

As mentioned previously, by covalently anchoring a longer-chain amide compound to the EAA surface, we expect to overcome the problems associated with loss of slip additives from the surface. To ensure that no surface modifying agents were physically adsorbed to the surface, aggressive washing experiments were conducted on the final films. These washing experiments were done in addition to wash steps that were carried out after each reaction step. Because water was used as the final wash step before ATR-FTIR characterization, we did not expect PCl_5 or ammonia as a surface contaminant. Also, after the amino acid grafting step, the film was washed with 4% (w/w) KOH solution, so we did not expect residual amino acid. Nevertheless, in the event that residual amino acid was present after the base wash, it might be possible for the film to hold physically adsorbed 12-aminododecanamide or even its oligomer. Therefore, our aggressive washing focused on solvent selection to remove any physically adsorbed 12-aminododecanamide that might be present.

The molar volume of 12-aminododecanamide was calculated based on a group contribution method given by Fedors in Van Krevelen.[29] A solubility parameter was calculated for this molecule based on a group contribution method given by Hoftyzer-Van Krevelen in Van Krevelen.[29] The contributions of dispersion forces, polar forces, and hydrogen bonding to the solubility parameter of 12-aminododecanamide were calculated to be 17.9, 3.6, and 7.0 $J^{1/2}/cm^{3/2}$, respectively. According to these calculations, methyl ethyl ketone (MEK) and methylene chloride should be good solvents for this compound. The contributions of dispersion forces, polar forces, and hydrogen bonding to the solubility parameters of MEK and methylene chloride are 15.9, 9.0, and 5.1; and 16.6–17.3, 1.0, and 1.0 $J^{1/2}/cm^{3/2}$, respectively.[29] Figure 5 shows the result of aggressive washing with these two solvents. The spectrum in Figure 5(a) represents a film with amide grafting without subsequent aggressive washing. Figure 5(b) is for a film washed with MEK at room temperature for 1 h and then oven dried at 110°C for 17 h. Figure 5(c) is for a film washed in methylene chloride for 1 h. No significant differences were observed between the spectra of the EAA-*N*-amide film

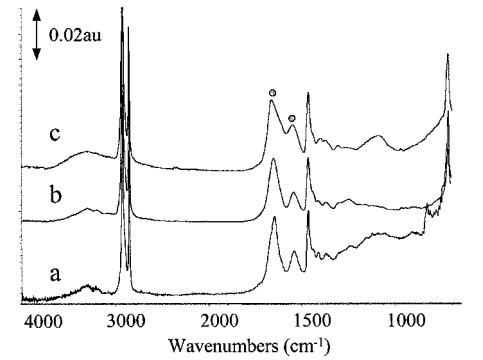

Figure 5 Comparison of ATR-FTIR spectra of 12-aminododecanamide–modified EAA film after different postmodification solvent washes: (a) EAA-*N*-amide, without aggressive wash; (b) EAA-*N*-amide, after MEK RT wash for 1 h and oven drying at 110°C for 17 h; (c) EAA-*N*-amide, after CH_2Cl_2 wash for 1 h.

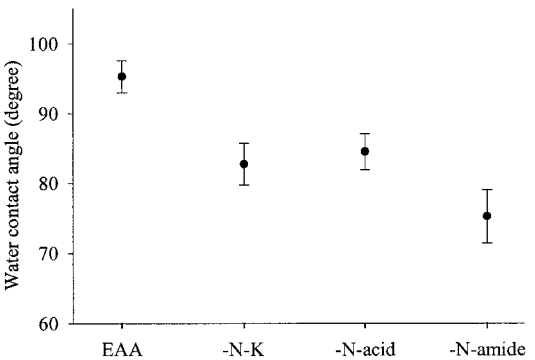

Figure 6 Static water contact angle data for EAA film and modified EAA film. The –*N*-acid and –*N*-amide films were prepared with 12-aminododecanoic acid. The error bars represent 95% confidence intervals.

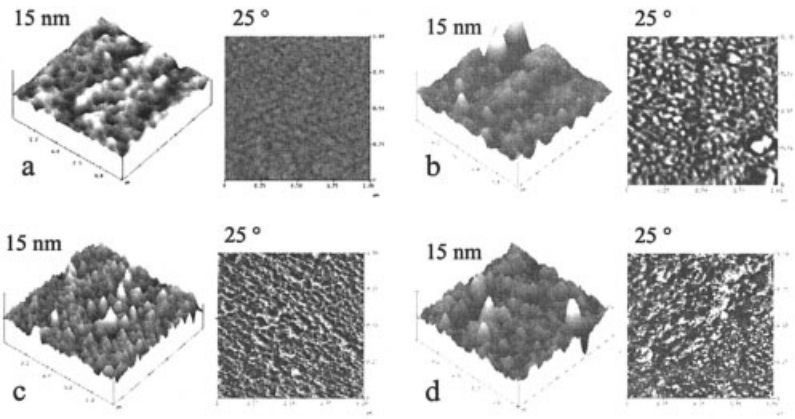

Figure 7 Surface topography (3-D images) and phase (2-D images) of modified EAA film followed by SPM. The vertical scale is 15 nm and 25° for topographical and phase images, respectively: (a) plain EAA, roughness = 1.1 nm; (b) EAA-*N*-K, roughness = 2.2 nm; (c) EAA-*N*-acid, roughness = 1.5 nm; (d) EAA-*N*-amide, roughness = 2.6 nm.

taken before and after aggressive wash steps. This result further supports covalent bonding of amide groups on the surface of EAA film by surface grafting of 12-aminododecanoic acid.

The covalently bonded amide groups affected the surface wettability of EAA measurably. Figure 6 shows that the static water contact angle decreased by about 20° from about 95° for plain EAA to about 75° for EAA-*N*-amide. This decrease in contact angle seems reasonable given that amide groups are hydrophilic. For example, static water contact angle measurements on the surface of polyacrylamide give values $\cong 25°$.[30] The net effect of surface modification is to replace each carboxylic acid group on the EAA surface with one secondary amide (at the amino acid anchor point) and one primary amide (at the chain end). It also seems reasonable that the contact angle should remain relatively high given that the EAA in the current study contains only 9.5 mol % acrylic acid. Thus, water in contact with the surface primarily sees polyethylene chains.

Structurally, bonding the longer-chain amide to the EAA surface affected the surface morphology. Figure 7 shows topographic and phase images of plain EAA and modified EAA measured by SPM. Phase images map surface composition differences based on differences in local mechanical or adhesive properties of the sample. The SPM results show that surface roughness increased from 1.1 nm for plain EAA film to 2.6 nm for EAA-*N*-amide, based on topographical analysis. Phase images show that the amino acid–grafted film [Fig. 7(c)] and amide-modified film [Fig. 7(d)] were more heterogeneous than the plain EAA film. This result is consistent with the findings of McEvoy et al.,[31] who demonstrated that the molar concentration of acrylic acid at the surface of EAA is higher than the bulk concentration, likely because of the rejection of acrylic acid segments from polyethylene crystallites. Thus, the surface heterogeneity of plain EAA film is likely attributable to formation of ethylene-rich regions and acrylic acid–rich regions. Surface modification reactions were conducted selectively on acrylic acid–rich regions, thereby increasing the differences in mechanical/adhesive properties of the two types of regions. Postmodification phase imaging highlighted these differences.

CONCLUSIONS

Amides were anchored covalently to the surface of EAA film by surface grafting of amino acid intermediates. ATR-FTIR spectroscopy indicated that 12-aminododecanoic acid was much more reactive with surface acid chloride groups of modified EAA than were 5-aminophthalic acid and L-aspartic acid. The 12-aminododecanoic acid required about 3 min for 80% conversion to occur. Amide modification resulted in a 20° decrease in static water contact angle relative to that of unmodified EAA film. Scanning probe microscopy indicated that the surface reactions occurred selectively on acrylic acid–rich regions on the surface of EAA film. This conclusion was based on an increased surface roughness from 1.1 nm for unmodified EAA film to 2.6 nm for amide-modified EAA film, along with measurable differences in the phase images, indicating that the surface became more heterogeneous.

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References

1. Sun, T. U.; Derevitskaya, V. A.; Rogovin, Z. A. Vysokomol Soedin 1960, 2, 1768; CAN 1755: 147109.
2. Sun, T.; Derevitskaya, V. A.; Rogovin, Z. A. Vysokomol Soedin 1959, 1, 1178; CAN 1154: 106078.
3. T'ung, S.; Derevitskaya, V. A.; Rogovin, Z. A. Vysokomol Soedin 1960, 2, 785; CAN 755: 48406.
4. Polyakov, A. I.; Derevitskaya, V. A.; Rogovin, Z. A. Vysokomol Soedin 1961, 3, 1027; CAN 1056: 13683.
5. Avny, Y.; Migdal, S.; Zilkha, A. Eur Polym J 1966, 2, 355.
6. Klein, E. J Membr Sci 2000, 179, 1.
7. Svorcik, V.; Hnatowicz, V.; Stopka, P.; Bacakova, L.; Heitz, J.; Ochsner, R.; Ryssel, H. Radiat Phys Chem 2001, 60, 89.
8. Kim, M.; Saito, K.; Furusaki, S.; Sato, T.; Sugo, T.; Ishigaki, I. J Chromatogr 1991, 585, 45.
9. Kim, M.; Saito, K.; Furusaki, S.; Sugo, T.; Ishigaki, I. J Chromatogr 1991, 586, 27.
10. Kiyohara, S.; Sasaki, M.; Saito, K.; Sugita, K.; Sugo, T. J Membr Sci 1996, 109, 87.
11. Choi, S.-H.; Lee, K.-P.; Lee, J.-G. Microchem J 2001, 68, 205.
12. Kiyohara, S.; Kim, M.; Toida, Y.; Saito, K.; Sugita, K.; Sugo, T. J Chromatogr A 1997, 758, 209.
13. Wu, G.; Wang, C.; Zhao, Q.; Liu, J; Li, T. Sichuan Daxue Xuebao Ziran Kexueban 2000, 37, 568; CAN 134: 344502.
14. Ji, J.; Ji, R.-T.; Qiu, Y.-X.; Chen, B.-L.; Feng, L.-X. Gaoden Xuexiao Huaxue Xuebao 1999, 20, 814; CAN 131: 204550.
15. Anderheiden, D.; Klee, D.; Hocker, H.; Heller, B.; Kirkpatrick, C. J.; Mittermayer, C. J Mater Sci Mater Med 1992, 3, 1.
16. Ramirez, M. X.; Hirt, D. E.; Wright, L. L. Nano Lett 2002, 2, 9.
17. Coupland, K.; Maltby, A. J Plast Film Sheet 1997, 13, 142.
18. Swanson, C. L.; Burg, D. A.; Kleiman, R. J Appl Polym Sci 1993, 49, 1619.
19. Briscoe, B. J.; Mustafaev, V.; Tabor, D. Wear 1972, 19, 399.
20. Molnar, N. M. J Am Oil Chem Soc 1974, 51, 84.
21. Janorkar, A.; Hirt, D. E.; Wooster, J. J. In: Proceedings of SPE ANTEC, San Francisco, CA, 2001.
22. Jenkins, W. A.; Harrington, J. P. Packaging Foods with Plastics; Technomic Publishing: Lancaster, PA, 1991.
23. Bergbreiter, D. E. Prog Polym Sci 1994, 19, 529.
24. Iyer, K. S.; Luzinov, I. Langmuir 2002, 19, 118.
25. Sukhishvili, S. A.; Granick, S. Macromolecules 2002, 35, 301.
26. Reddy, P. S.; Kobayashi, T.; Abe, M.; Fujii, N. Eur Polym J 2002, 38, 521.
27. Kailani, M. H.; Sung, C. S. P. Macromolecules 1998, 31, 5779.
28. White, A.; Handler, P.; Smith, E. L. Principles of Biochemistry, 5th ed.; McGraw-Hill: New York, 1973; pp. 88–108.
29. Van Krevelen, D. W. Properties of Polymers; Elsevier Scientific: Amsterdam, 1990; pp 196–197, 211–214.
30. Hamilton, L. M.; Green, A.; Edge, S.; Badyal, J. P. S.; Feast, W. J.; Facynko, W. F. J Appl Polym Sci 1994, 52, 413.
31. McEvoy, R. L.; Krause, S.; Wu, P. Polymer 1998, 39, 5223.