

Coefficient of Friction Reduction of Ethylene-co-Acrylic Acid Film: Effects of Grafted 12-Aminododecanamide and Solvent Exposure

Ning Luo,¹ Amol V. Janorkar,¹ Douglas E. Hirt,¹ Scott M. Husson,¹ Dwight W. Schwark²

¹Center for Advanced Engineering Fibers and Films and Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina 29634 USA

²Cryovac Division of Sealed Air Corporation, Duncan, South Carolina 29334 USA

Received 18 February 2004; accepted 28 December 2004

DOI 10.1002/app.21884

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of covalently bound 12-aminododecanamide on the surface coefficient of friction (COF) of ethylene-acrylic acid copolymer (EAA) films was investigated. The reaction involved grafting 12-aminododecanoic acid to the inherent carboxylic acid groups on the film, followed by amidation of the grafted amino acid. Conversion of film carboxylic acid groups to primary amide groups was also conducted to compare the impact of direct surface amidation. Subsequent measurements showed that both surface amidation schemes reduced the kinetic COF from 0.30

to 0.15 ~ 0.18. Repetitive COF testing revealed that amide-modified EAA films maintained low COF values that were independent of the number of COF test runs. However, control experiments showed that COF values also depended greatly on simply exposing film to the various reaction solvents, which increased surface roughness. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2242–2248, 2005

Key words: ethylene-acrylic acid copolymer; coefficient of friction; films; modification; surfaces

INTRODUCTION

Polyolefin films typically possess surfaces that are tacky and exhibit a high coefficient of friction (COF).¹ There are many factors that influence the COF of polymer films, including chemical composition, polymer crystallinity, presence of additives, processing conditions, and surface treatments.² For example, using a higher-density resin can lead to a lower COF.^{2,3} Incorporation of migratory additives can also influence the COF of polyolefin films significantly. Primary amides of fatty acids are typically blended into polyolefins prior to extrusion, and, because of the chemical incompatibility between additive and polymer, the fatty amides migrate or “bloom” to the film surface over time and reduce the COF.^{4–9} Commonly used additives include erucamide, oleamide, stearamide, and behenamide. The fatty amides possess an amide head group and a C₁₇ or C₂₁ aliphatic chain.

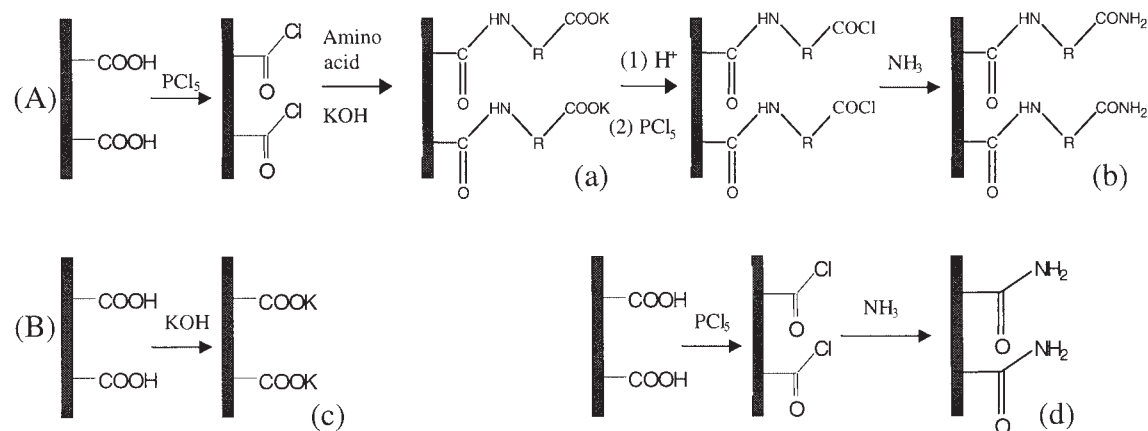
When the additives bloom to the surface, they recrystallize with a variety of morphological structures.⁹ A slip agent, such as erucamide, is normally used at levels of 100 ~ 5,000 ppm to reduce the COF to a

desired value. An excess of additive at a film surface can hinder or interfere with other desired characteristics such as printability and clarity of the film. Another important issue is the potential loss of additive from a film surface because the additive is not chemically bound to the surface. For example, Janorkar et al.¹⁰ reported that surface-segregated erucamide was removed over the course of repeated film-metal contacts, thereby increasing COF. Therefore, to alleviate the problem of additive loss, a more permanent surface modification is critical for many applications.

Ethylene-acrylic acid copolymer (EAA) and its partially neutralized form, EAA ionomer, are important in the packaging industry. They are often used in applications requiring good adhesion to aluminum foil, high clarity and toughness, and contact with products that are high in fat content (e.g., meat).¹¹ Neat EAA film typically has an undesirably high COF, so methods are needed to reduce COF to enhance performance on high-speed packaging equipment. Carboxylic acid groups on the surface of EAA film provide inherent reaction sites for chemical modification. Carboxylic acid groups can also be generated on the surface of polyethylene film by plasma treatment.¹² Therefore, in principle, surface-chemistry approaches developed from EAA could also be transferred to plasma-treated polyethylene. The goal of our study was to investigate the effect of surface amidation on the COF of polyethylene-based packaging

The Supplementary Material referred to in this article can be found at <http://www.interscience.wiley.com/jpages/0021-8995/suppmat>.

Correspondence to: D. E. Hirt (hirt@clermson.edu).



Scheme 1 Chemical approach for the surface amidation of EAA films: (A) reacted with amino acid: (a) EAA-N-K, (b) EAA-N-amide; (B) directly converted to amide: (c) EAA-D-K, (d) EAA-D-amide.

films with an aim of creating a surface modification that is more permanent than that provided by migratory additives. Scheme 1 shows the surface chemistry where 12-aminododecanoic acid is anchored covalently to the surface of EAA film and then converted to an amide.¹³ Scheme 1(B) depicts a more direct method to amidate the surface without the use of the amino acid. In this article, the permanence of the COF of amide-modified EAA film was investigated using repetitive testing. Scanning probe microscopy (SPM) was also used to investigate the changes in surface morphology and roughness of the modified EAA films due to the chemical reactions and COF testing.

EXPERIMENTAL

Materials

EAA (9.5 mol % acrylic acid) films (thickness = 0.06 mm) were used as received from the Cryovac Division of Sealed Air Corp. (Duncan, SC). Phosphorus pentachloride (PCl₅, 95%), 12-aminododecanoic acid, potassium hydroxide (KOH, 85+% ACS reagent), and ammonia (0.5 mol % ammonia solution in dioxane) were purchased from Aldrich (Milwaukee, WI) and used as received. Methylene chloride, dioxane, and ethyl acetate were purchased from Aldrich as ACS reagent grade.

Preparation of acid chloride-modified EAA film [Scheme 1]

A piece of plain EAA film (15 × 25 cm) was put in a PCl₅ bath containing ~ 600 mL of a solution of methylene chloride with 3% (w/v) of PCl₅ to perform the acid chloride surface reaction. The reaction took place for 24 h at room temperature with shaking. After the reaction was finished, the film was removed and washed with methylene chloride and ethyl acetate

sequentially. Residual solvent on the surface was blotted with tissue paper. The dried film was characterized and used in the next reaction step. Films with acid chloride functionality are denoted EAA-Cl.

Preparation of 12-aminododecanamide-modified surfaces [Scheme 1(A)]

Eight grams of amino acid were dissolved in 400 mL of 4% (w/v) KOH aqueous solution at room temperature. 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/v) KOH aqueous solution for 10 min and then washed with a substantial volume of neutral water. The modified film was denoted as EAA-N-K. To convert the carboxylate salt groups to acid groups, the film was treated with 400 mL of 1 N HCl acidic aqueous solution followed by a water rinse. This amino acid-modified EAA film was reimmersed in the PCl₅ solution to convert the carboxyl end groups to acid chloride groups. The reaction and rinsing conditions were the same as those used in the first PCl₅ treatment step. The subsequent film was placed into 400 mL of 0.5 mol % ammonia solution in dioxane for 24 h with shaking to perform the amidation. After the reaction was completed, the film was removed and washed with copious amounts of 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 is denoted as EAA-N-amide.

Preparation of directly amide-modified EAA film [Scheme 1(B)]

The formerly treated EAA-Cl film was put 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 and then dried in air. The final modified EAA film is denoted as EAA-D-amide.

Preparation of surface-neutralized EAA film [Scheme 1(B)]

One piece of plain EAA film was put in 400 mL of 4% (w/v) KOH aqueous solution at room temperature for 24 h to convert carboxylic acid groups to a neutralized salt, potassium carboxylate. After the reaction was completed, the film was removed and then washed with neutral water, then dried in air. The surface modified EAA film was denoted as EAA-D-K.

Preparation of solvent-treated EAA films

Plain EAA films were dipped into various pure solvents to delineate any solvent-induced COF changes versus changes due to grafting. The treatment time and temperature were the same as for the reaction steps but without PCl_5 , KOH, amino acid, or ammonia in the reaction solutions.

Attenuated total reflection infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra of the polymer films were obtained using a Nicolet Avatar 360 FTIR spectrometer 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.

Scanning probe microscopy (SPM)

SPM was performed on a Dimension 3100 (Digital Instruments, Inc.) microscope. Both tapping and phase imaging modes were obtained in ambient air for surface-grafted polymer films. The root-mean-square roughness (RMSR) of the samples was evaluated from SPM images in the tapping mode. Surface roughness is the standard deviation of feature height (Z) values within a scan area.¹⁴

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

where Z_{av} is the average Z value within the scan area, Z_i is the local Z value, and N is the number of points within the scan area.

COF measurements

COF was measured following ASTM 1894D in which the film was taped to a steel sled ($5\text{ cm} \times 5\text{ cm}$ in planar area and 200 g in mass) and pulled across a smooth stainless steel plate ($15\text{ cm} \times 30\text{ cm} \times 1.7\text{ mm}$) by a nylon string that moves over a smooth pulley. The nylon string was attached to a 6.9 N load cell that measured the force required to initiate sliding (from which static COF was calculated) and to maintain sliding over a distance of 20 cm after the static region. The kinetic COF was calculated from the force required for sliding over a distance of 13 cm after the static region. The sliding motion during COF testing coincided with the machine direction of the films. At least three specimens were evaluated after a given reaction step to obtain an average COF and standard deviation. In repetitive testing, the same piece of film was used for all runs without cleaning the metal plate between each successive run.¹⁰

RESULTS AND DISCUSSION

The ATR-FTIR spectral features of interest in the analysis of the amide-modified EAA films are the carbonyl and N-H vibrations. In the present work, the surface of EAA film was functionalized with amide groups both directly and with grafting of an amino acid (Scheme 1). Amidation with or without amino acid grafting differs chemically in the surface layer. Most significantly, amidation after amino acid grafting (EAA-N-amide) yields one secondary amide in the middle of the grafted layer and one primary amide on the periphery of the graft [Scheme 1(A)], whereas direct amidation (EAA-D-amide) yields only a primary amide at the periphery [Scheme 1(B)].

The ATR-FTIR spectrum of amide-modified film with amino acid grafting [EAA-N-amide, Figure 1(c)] is compared with that without amino acid grafting [EAA-D-amide, Figure 1(b)]. The carbonyl stretching vibration of the primary amide occurs in the region of

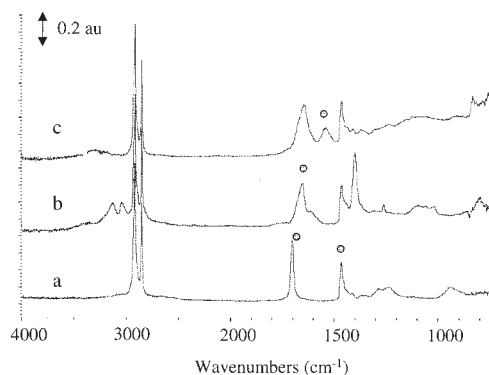


Figure 1 ATR-FTIR spectra of amide-modified EAA film: (a) plain EAA, (b) EAA-D-amide, (c) EAA-N-amide.

1650 cm^{-1} when examined in the solid state; simple, open-chain, secondary amides absorb near 1640 cm^{-1} when examined in the solid state.¹⁵ For the EAA-D-amide in Figure 1(b), only the primary amide, the amide I band at 1653 cm^{-1} , was observed, which is consistent with the literature.¹⁶ For the EAA-N-amide that contained both primary and secondary amides, a combined amide I band was observed at 1647 cm^{-1} [Figure 1(c)]. N–H bending vibration (amide II) bands were also displayed in the spectra. For EAA-D-amide, the N–H bending band was observed as a shoulder at 1614 cm^{-1} with an intensity of one-half to one-third of the amide I band [Figure 1(b)], which is the characteristic of primary amide. For EAA-N-amide, the N–H bending band from the primary amide cannot be seen in the spectrum [Figure 1(c)], which might be overlapped with adjacent bands; the N–H bending band from the secondary amide was displayed at 1543 cm^{-1} . For the plain EAA film in Figure 1(a), characteristic peaks for the polymer (1465 cm^{-1}) and the carbonyl stretch of the acid (1703 cm^{-1}) were observed. However, no peaks corresponding to amide functionality were evident prior to surface grafting. The FTIR spectra confirmed the structural changes in chemical composition and functionalities on the surface of the EAA film.

To evaluate the permanence of the covalently bound amide, the modified films were tested repetitively for COF. Unmodified EAA films were also tested for comparative purposes. Figure 2 shows static and kinetic COFs for the directly amide-modified EAA films. For unmodified film (circles), both static and kinetic COF were relatively high and the values were scattered during the first eight runs but then became more consistent after that point [the y -axis scale in Figure 2(b) is less than that in Figure 2(a), so the kinetic COF data show less scatter than the static COF, which is typical of COF measurements on polymer films]. When the inherent carboxylic acid groups were neutralized to the potassium salt (EAA-D-K), the kinetic COF and static COF were similar to nonneutralized EAA. Once reacted with ammonia to convert the acid chloride to the amide, the static and kinetic COFs decreased significantly to values less than 0.2, and the COFs remained unchanged for up to 15 repeated film–metal COF runs.

Similar trends were observed in Figure 3 for the amino acid–modified films, although two differences were noted between the results in Figures 2 and 3. In the latter results, the potassium salt–neutralized, amino acid–modified films showed a COF reduction compared to the unmodified films, perhaps due to the secondary amide group that results from grafting the C_{12} amino acid to the surface [see Scheme 1(A)]. Additionally, the static COFs for the EAA-D-amide [Figure 2(a)] were less than those for the EAA-N-amide [Figure 3(a)]. Specifically, static $\text{COF}_{\text{EAA-D-amide}} \sim 0.18$

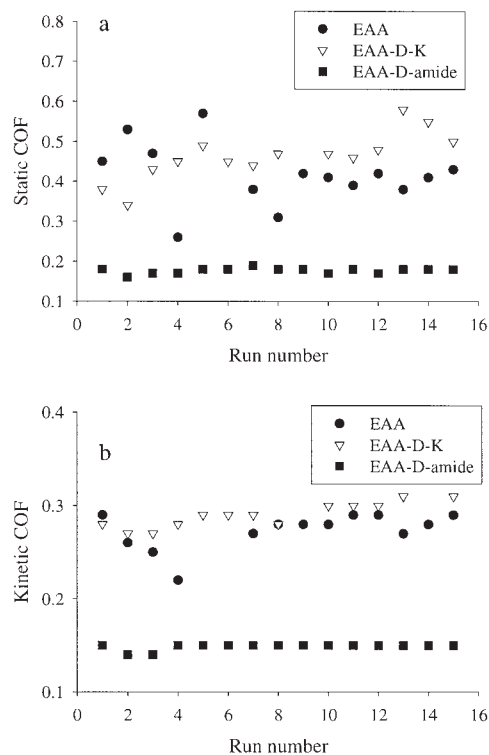


Figure 2 COF as a function of the number of repetitive COF tests for directly amide-modified EAA films. (a) Static COF; (b) kinetic COF.

and $\text{COF}_{\text{EAA-N-amide}} \sim 0.23$. However, more importantly for film processing, the kinetic COFs for EAA-D-amide and EAA-N-amide were approximately the same at 0.15–0.18. By way of comparison, erucamide-containing polyolefin films have shown a more significant change in COF as a function of the number of COF runs with the same piece of film. Janorkar et al.¹⁰ reported results for trilayer cast films with erucamide and SiO_2 (an antiblocking agent) blended into one of the skin layers. When the skin layer was LLDPE with an erucamide loading of 1,200 ppm, the kinetic COF increased from 0.17 to 0.22 from the 1st to the 15th run; a polyolefin plastomer skin layer containing 2,500 ppm erucamide exhibited a kinetic COF change from 0.28 to 0.51 over 15 runs. It was believed that the COF increase was due to the removal of erucamide from the film surfaces during repetitive testing. Therefore, the films with covalently bound amides, EAA-D-amide and EAA-N-amide, provided a more consistent COF over the course of repetitive testing.

Friction between a film and a metal plate is a complex process that can be influenced by many factors. In general, friction acting at the surfaces of two bodies is believed to be associated with deformation processes as well as adhesion caused by atomic, molecular, and intermolecular interactions between the contacting substrates.^{17–21} We examined the aspect of deformation by evaluating changes in surface roughness. Fig-

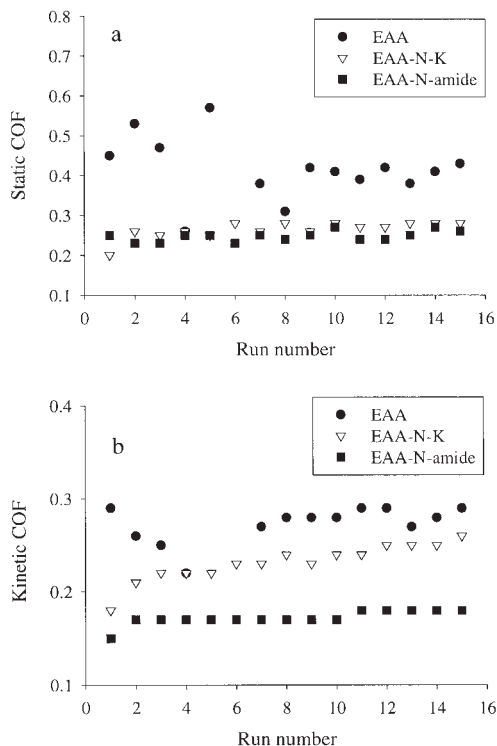


Figure 3 COF as a function of the number of repetitive COF tests for amino acid-modified EAA films. (a) Static COF; (b) kinetic COF.

Figure 4 summarizes data for kinetic COF as a function of surface roughness, which is characterized by RMSR as measured by scanning probe microscopy. The filled symbols represent COF data obtained from the first run in a series of repetitive tests while the open symbols represent data from the 15th run. To examine the effect that roughness may have on the slip properties, EAA films were soaked in various reaction solvents (water, methylene chloride, dioxane), which may af-

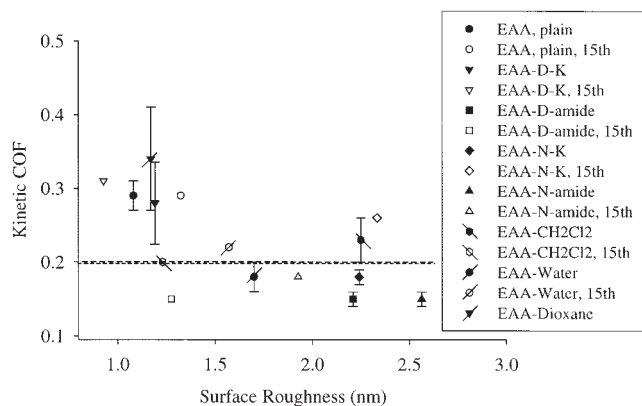


Figure 4 Kinetic COF correlated with surface roughness of EAA films with different surface functionalities and solvent exposures (the error bars represent 95% confidence intervals).

fect the COF by altering the surface roughness or surface morphology (e.g., accentuating amorphous acid-rich domains versus semicrystalline polyethylene domains²²). No changes in surface chemistry should be expected since no reactants were added to the solvents. As seen in Figure 4, plain EAA film had a kinetic COF of about 0.3 and an RMSR of about 1.1 nm. When exposed to the various solvents the RMSR increased and the kinetic COF decreased, with the water and methylene chloride eliciting the lowest COF values and greatest increase in RMSR values. After 15 repetitive tests for the water- and methylene chloride-treated specimens, the RMSR decreased and the kinetic COF changed only slightly (the COF results from films that were tested repetitively after being soaked for 24 h and then dried by blotting the surface with tissue paper are shown in Figure 5).

The results for the surface reacted films are also shown in Figure 4 and exhibit a similar trend, that is, the kinetic COF decreased as the RMSR increased as demonstrated by the filled symbols. Focusing on the amidated films [EAA-D-amide (squares) and EAA-N-amide (triangles)], repetitive testing reduced the RMSR while the kinetic COF remained approximately the same, analogous to the solvent-treated films. It is likely that at least a portion of the COF reduction for the amidated films was due to solvent exposure, and therefore increased RMSR, during the reaction steps. Further COF reduction may be due to the grafting of

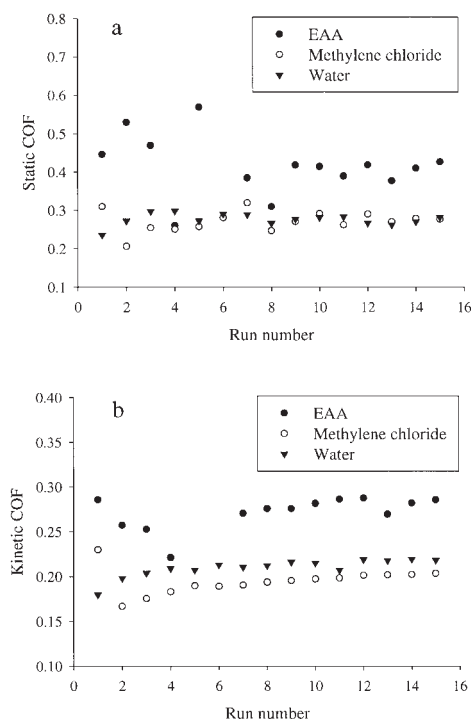


Figure 5 COF as a function of the number of repetitive COF tests for EAA films exposed to two solvents. (a) Static COF; (b) kinetic COF.

the amide functionality on the surface, but that is more difficult to prove with certainty. As a reference point, a dashed line has been drawn on Figure 4 at an arbitrarily selected kinetic COF value of 0.2. The dioxane results fall above this line, the water and methylene chloride results fall slightly below and above this line, and the amidated film results fall further below this line. The error bars for the water and methylene chloride results (filled circles and hexagons with the slashes) do not overlap those for the amidated films (filled square and triangle), so the surface chemistry may provide a slight COF reduction beyond that provided by solvent exposure alone. This behavior may be due to the fact that the amide groups would have less intermolecular interaction with the steel plate than would the carboxylic acid groups at the EAA surface. Hackerman and Roebuck²³ provided evidence of lower strength of interaction between the amide and steel in their work on adsorption of polar organic compounds on steel. Comparing adsorption of long-chain carboxylic acids and corresponding amides, they found that the acids had greater reactivity toward the steel sorbent than did the amides. Further evidence to suggest that surface chemistry provides COF reduction is that the kinetic COF of the water-treated film increased above 0.2 after the RMSR decreased from repeated testing. By contrast, both direct (EAA-D-amide) and amino-acid (EAA-N-amide) amidation treatments resulted in a surface that maintained a low kinetic COF (below 0.2) even after the RMSR decreased from repetitive testing.

With a few exceptions, the RMSR decreased upon repetitive testing, which may be due to the softer amorphous regions of the EAA being smeared as the film was moved repeatedly over the metal plate during COF testing. This phenomenon is borne out in SPM phase images of film specimens that show a more homogeneous (and typically less rough) surface after repetitive testing (an example is shown in Figure 6; see additional SPM images²⁴).

CONCLUSIONS

Ethylene-acrylic acid copolymer films were modified chemically to produce surface amide functionalities. Surface amidation was achieved by direct conversion of EAA carboxylic acid groups and via grafting of the amino acid intermediate, 12-aminododecanoic acid, followed by amidation of its acid group. Despite the structural similarity between the amino acid amide and conventional, blended fatty amide slip agents, the former offered no advantage to reduced COF relative to direct amidation of surface carboxylic acid groups on EAA. Both amidated films showed low kinetic COF values of 0.15–0.18 compared to plain EAA with a COF value of ~ 0.30 . However, based on SPM measurements, the majority of the COF reduction appeared to be due to changes in surface roughness of the films upon solvent exposure, with only a slight COF reduction that could potentially be attributed to the surface amide grafting.

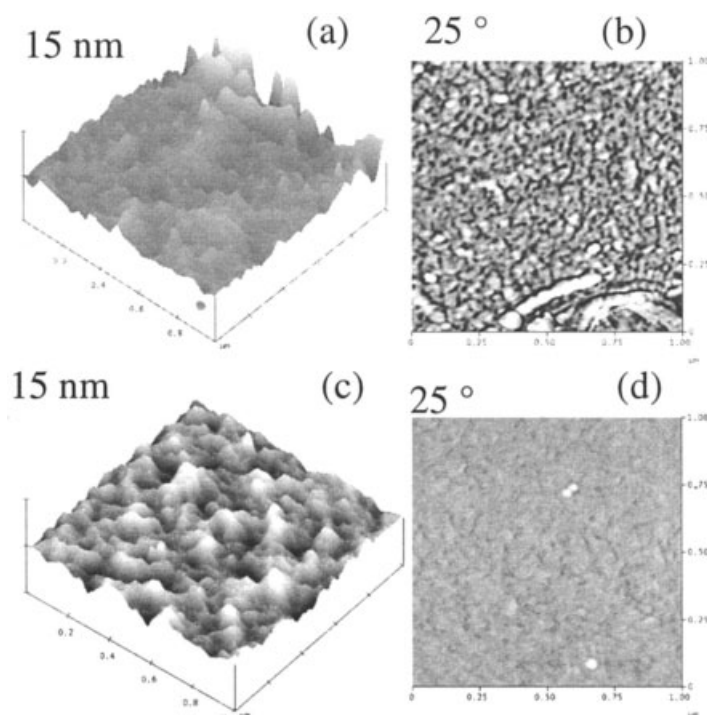


Figure 6 Topography (3D) and phase (2D) images of directly amide-modified EAA: (a and b) EAA-D-amide with RMSR ~ 2.2 nm; (c and d) EAA-D-amide tested 15 times for COF with RMSR ~ 1.3 nm. Images are $1 \times 1 \mu\text{m}$.

We gratefully acknowledge the financial support of this research from the Cryovac Division of Sealed Air Corp. and the National Science Foundation under Grant EEC-9731680. We also thank Dr. Igor Luziov, Dr. Viktor Klep, Bogdan Zdyrko, and K. Swaminathan Iyer at Clemson University for obtaining the SPM data.

References

1. Wooster, J. J.; Simmons, B. E. *J Plastic Film Sheeting* 1996, 12, 50.
2. Thompson, K. I. *Tappi J* 1988, 71, 157.
3. Constant, D. R. SPE ANTEC, San Francisco, May 5-9 2002.
4. Molnar, N. M. *J Am Oil Chem Soc* 1974, 51, 84.
5. Rawls, A. S.; Hirt, D. E.; Havens, M. R.; Roberts, W. P. *J Vinyl Additive Technol* 2002, 8, 130.
6. Schuhmann, B. H.; Wooster, J. J. SPE ANTEC, New York City, May 2-6 1999.
7. Coupland, K.; Maltby, A. *J Plastic Film Sheeting* 1997, 13, 142.
8. Swanson, C. L.; Burg, D. A.; Kleiman, R. *J Appl Polym Sci* 1993, 49, 1619.
9. Ramirez, M. X.; Hirt, D. E.; Wright, L. L. *Nano Lett* 2002, 2, 9.
10. Janorkar, A. V.; Hirt, D. E.; Wooster, J. J. *Polym Eng Sci* 2004, 44, 34.
11. Jenkins, W. A.; Harrington, J. P. *Packaging Foods with Plastics*; Technomic Publishing Co. Inc., Basel, 1991.
12. Bergbreiter, D. E. *Prog Polym Sci* 1994, 19, 529.
13. Luo, N.; Stewart, M. J.; Hirt, D. E.; Husson, S. M.; Schwark, D. W. *J Appl Polym Sci* 2004, 92, p 1688.
14. Iyer, K. S.; Luzinov, I. *Langmuir* 2002, 19, 118.
15. Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons, Inc., New York, 1998.
16. Luo, N.; Husson, S. M.; Hirt, D. E.; Schwark, D. W. In *Controlled/Living Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 854, Washington, D.C., 2003; p 352.
17. Gemant, A. *Frictional Phenomena*; Chemical Publishing Co., New York, 1950.
18. Bely, V. A.; Sviridenok, A. I.; Petrokovets, M. I.; Savkin, V. G. *Friction and Wear in Polymer-Based Materials*; Pergamon Press, New York, 1982.
19. Persson, B. N. J. *Sliding Friction Physical Principles and Applications*; Springer, New York, 2000.
20. Kragelsky, I. V.; Dobychn, M. N.; Combalov, V. S. *Friction and Wear: Calculation Methods*; Pergamon Press, New York, 1982.
21. Sarkar, A. D. *Friction and Wear*; Academic Press, New York, 1980.
22. McEvoy, R. L.; Krause, S.; Wu, P. *Polymer* 1998, 39, 5223.
23. Hackerman, N.; Roebuck, A. H. *Ind Eng Chem* 1954, 46, 1481.
24. http://www.ces.clemson.edu/chemeng/faculty/hirt/research_group/COF_paper_Supplemental_figures.htm.