

Oleophilic Modification of Poly(vinyl alcohol) Films by Functionalized Soybean Oil Triglycerides

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ABSTRACT: In this study, maleinized (SOMAP) and isocyanated soybean oil (SONCO) triglycerides have been successfully grafted onto one surface of poly(vinyl alcohol)(PVA) films to give films that are hydrophilic on one side and hydrophobic on the other. The surface grafting was accomplished by the reaction of succinic anhydride or isocyanate functionalities of soybean oil derivatives and the hydroxyl groups of PVA films. The reaction was run in toluene, using PVA films on glass slides so that only one side of the film was accessible. After grafting, the films were rinsed with hot toluene to remove ungrafted triglycerides from the surface. The reaction on the surface was confirmed by ATR-FTIR and ¹H-NMR spectroscopic techniques. A series of films were prepared at different concentrations of SOMAP or SONCO in tol-

uene. The increase in hydrophobicity with an increase in SOMAP or SONCO concentrations was observed by water contact angle measurements. The contact angles on the grafted side of the film reach their maximum value of 88° and 94° for 26 and 2.5% SOMAP and SONCO concentrations in toluene, respectively, while the ungrafted side gives contact angle of 48°. Surface morphologies of PVA-g-SOMAP and PVA-g-SONCO films were investigated by atomic force microscopy, whereas optical microscopy and staining was used to determine the homogeneity of the films. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2431–2438, 2011

Key words: films; graft copolymers; modification; renewable resources

INTRODUCTION

Surface modification of polymers enables one to change the surface properties of existing polymers.^{1,2} Functional groups introduced alter the chemical composition and surface properties of the materials resulting in improvements in hydrophilicity, hydrophobicity, biocompatibility, and so on. Many surface modification techniques such as plasma treatment,³ surface blending,⁴ and surface immobilization^{5,6} have been used. Surface reaction that introduces new functionalities on the polymer surface is one of the most reliable methods.

Poly(vinyl alcohol)(PVA) is a highly hydrophilic, nontoxic, and biocompatible polymer with an excellent film-forming property. Because of various characteristics of PVA such as high solvent resistance, high tensile and compressive strength, and superior oxygen barrier properties, its application as films has become attractive. PVA films have also been grafted with various hydrophobic monomers to obtain films with different hydrophilicity on different faces.^{7–9} Although PVA contains a secondary hydroxyl group, it is very reactive and gives typical

reactions of most alcohols. The reactions of PVA with succinic anhydride in the solid state,¹⁰ as a film with hexamethylene diisocyanate¹¹ and various fatty acids¹² have been reported. Thus, we decided to use succinic anhydride and isocyanate-functionalized soybean oil triglycerides to modify the surface of PVA films.

We describe here, a one-step grafting process involving the reaction between SOMAP and SONCO triglycerides onto PVA surface. The synthetic route applied in the synthesis of PVA-g-SOMAP and PVA-g-SONCO films is shown in Figure 1. The choice of triglyceride-based monomers comes from the expected hydrophobicity of the grafted PVA films, the ease of the reactions involving only base catalysts, and the high availability and benign status of triglyceride-based monomers. The grafting reaction was carried out with the PVA film on a glass slide so that only one side of the film was accessible. Toluene, which was demonstrated not to swell the PVA film, was used as a solvent. Such films with different surface properties on different sides may find use as membranes with one-way permeability.¹³ Furthermore, thin films made of two different polymers that have different hydrophilicity on each side are interesting in biomedical applications. Such composite films have found practical use as “one-way” dialysis membranes¹⁴ in wound dressings, biomedical applications¹⁵ such as enzyme purification, and adhesion prevention during surgery.¹⁶

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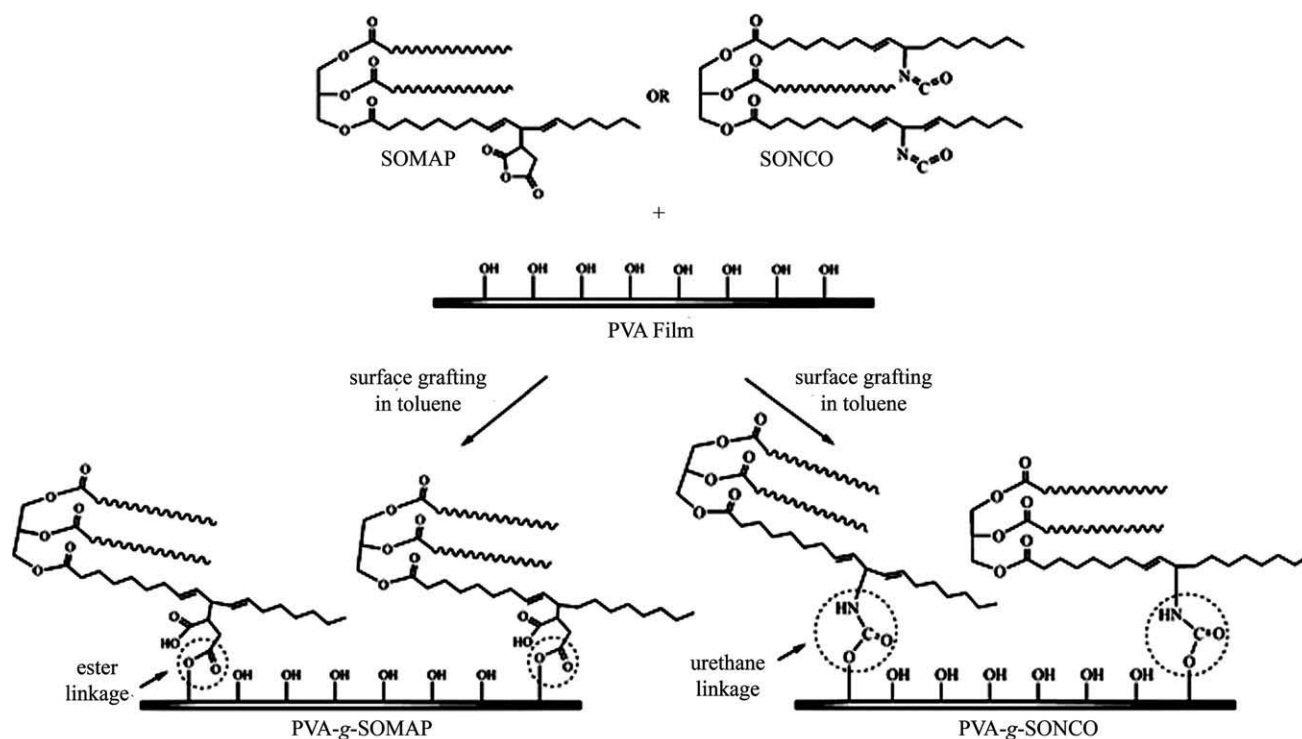


Figure 1 Synthesis of PVA-g-SOMAP and PVA-g-SONCO films.

EXPERIMENTAL

Reagents and instruments

PVA was procured from the Aldrich Chemical Co. (Milwaukee, WI). The molecular weight was $88,000 \text{ g mol}^{-1}$ and it was 98% hydrolyzed. Dimethylaminopyridine (DMAP) and toluene were purchased from Merck (Hohenbrunn and Darmstadt, Germany, respectively). The SOMAP containing 0.8 mol succinic anhydride and SONCO having 2.1 isocyanate functionalities per mole of triglyceride were synthesized by the procedures described in our earlier publications.^{17,18} DMSO- d_6 was purchased from BDH Chemicals (Poole, England). All reagents were used without further purification. The attenuated total reflectance Fourier-transform infrared (ATR-FTIR) analysis was performed on a Nicolet 380 FT-IR spectrometer with Smart Diamond ATR. All the $^1\text{H-NMR}$ spectra were recorded on a Varian 400-MHz instrument operating at a frequency of 399.986 MHz for proton. The spectra were recorded as ppm (δ) with Tetramethylsilane (TMS) as an internal standard. Contact angle measurements were performed by using KSV Instruments CAM 101 instrument. Contact angles were measured by the sessile drop method using water at room temperature. Each contact angle reported was the mean value of at least five measurements taken at different positions on the film and averaged. For each grafted film, the contact angles were always ± 3 suggesting a uniform grafting of SOMAP or SONCO onto PVA surface.

Atomic force microscopy (AFM) was performed by using Quesant-Ambios universal scanning probe microscope (USPM, Ambios Technology, Santa Cruz, CA). Phase mode imaging was performed using a silicon nitride cantilever probe with a nominal resonance frequency around 170 kHz and a nominal tip radius of 5–10 nm. Optical Microscopy was performed by Olympus BX51-polarized microscope equipped with Camedia C7070 7.1 MP camera. Differential Scanning Calorimetry (DSC) characterization was performed by "thermal analysis" Q200 instrument using a $10^\circ\text{C min}^{-1}$ heating rate.

Preparation of PVA films

A 10% PVA solution was prepared by dissolving 4.03 g polymer in 36 mL deionized water at 90°C with continuous stirring for 3 h. This solution was cooled to room temperature and cast onto microscope slides. Extreme care was taken in drying to ensure complete dryness. After 2 days of open air drying, films were kept at 60°C in a vacuum oven for 2 days. The film thickness was about $60 \mu\text{m}$. IR showed that the water peak at 1650 cm^{-1} , which was apparent before drying, was completely eliminated.

Grafting of SOMAP onto PVA film surface

In a typical procedure, $2 \times 2 \text{ cm}^2$ PVA film samples, which were still attached to the microscope slides, were placed in a round-bottom flask equipped with

TABLE I
The Assignment of ATR-FTIR Peaks of PVA-g-SOMAP Film

| ATR-FTIR peaks, $\nu(\text{cm}^{-1})$ | Assignment |
|---------------------------------------|--|
| 3287 | O—H, stretching of PVA |
| 2927, 2857 | C—H, stretching of SOMAP |
| 1774 | succinic anhydride stretching of SOMAP |
| 1740 | ester group stretching of SOMAP |
| 1714 | newly formed ester group stretching |
| 1654 | C=C, stretching of SOMAP |
| 1088 | C—O, stretching of PVA |
| 846 | C—H, bending of PVA |

a reflux condenser, N₂ inlet, magnetic stirrer, and containing a solution of known concentration of SOMAP in dry toluene. One percent of DMAP catalyst by weight based on SOMAP was dissolved in the solution, and the temperature was raised to the desired level. The mixture was kept at these temperatures under N₂ for 24 h. The grafted PVA films were then rinsed with hot toluene several times to remove ungrafted SOMAP and finally dried at 60°C under vacuum for 2 days. SOMAP concentrations of 6, 12, 22, 26, and 33% and temperatures of 60, 75, and 90°C were separately tested. The film surfaces were characterized by ATR-FTIR and ¹H-NMR after peeling them from microscope slides. A control film was also prepared without catalyst. The assignment of ATR-FTIR peaks of PVA-g-SOMAP is shown in Table I.

¹H-NMR (DMSO-*d*₆) δ : In addition to the PVA peaks, extra peaks appear at 0.95 and 1.2 ppm corresponding to CH₃ and CH₂— protons of SOMAP.

Grafting of SONCO onto PVA film surface

The procedure applied for the synthesis of PVA-g-SOMAP films was repeated with 1, 1.5, 2, 2.5, and 6% SONCO concentrations in toluene. The reaction was carried out at 60 or 75°C under N₂ for 18 h. The films were characterized by ATR-FTIR and ¹H-NMR. The assignment of ATR-FTIR peaks of PVA-g-SONCO is listed in Table II.

¹H-NMR (DMSO-*d*₆) δ : Except PVA peaks, extra peaks appear at 0.95 and 1.2 ppm corresponding to —CH₃ and —CH₂— protons of SONCO.

RESULTS AND DISCUSSION

Synthesis and characterization of PVA-g-SOMAP films

The surface grafting reaction between succinic anhydride functional groups on SOMAP and the secondary hydroxyl groups of PVA was facilitated in the presence of a base catalyst, DMAP. As the interac-

TABLE II
The Assignment of ATR-FTIR Peaks of PVA-g-SONCO Film

| ATR-FTIR peaks, $\nu(\text{cm}^{-1})$ | Assignment |
|---------------------------------------|--------------------------|
| 3299 | OH, stretching of PVA |
| 2939, 2907 | C—H, stretching of SONCO |
| 1758 | C(=O)—O—, stretching |
| 1711 | O—C(=O)—NH, stretching |
| 1644 | C(=O)—NH—, stretching |
| 1564 | N—H bending |
| 1088 | C—O, stretching of PVA |
| 846 | C—H, bending of PVA |

tion between toluene and PVA film is very weak (the swelling degree with toluene is less than 1% after 48 h), this reaction occurs only on the film surface.¹⁹ The characterization of PVA-g-SOMAP films was done by ATR-FTIR and ¹H-NMR spectroscopic techniques. The ATR-FTIR spectra of PVA, PVA reacted with SOMAP without catalyst, and PVA-g-SOMAP synthesized in the presence of catalyst are shown in Figure 2. There is a need to prove that SOMAP actually reacts with the PVA surface, and the observations above are not caused by some physical adsorption phenomena. Thus, the same reaction was repeated without catalyst. SOMAP-reacted surface was carefully extracted with hot toluene in a soxhlet's apparatus, and it was observed that the ATR-FTIR spectrum of the film prepared without catalyst is identical to that of PVA. This shows that the reaction between SOMAP and PVA film does not occur without DMAP, but the reaction does take place in the presence of DMAP and the unreacted SOMAP could be effectively removed after the rinsing process with hot toluene. Because the common peaks of SOMAP overlap with PVA, only carbonyl and alkyl regions are available to confirm the reaction on the surface. The PVA-g-SOMAP film shows a distinct band at 1740 cm⁻¹ corresponding to the ester peak of soybean oil. A new band at 1714 cm⁻¹ is attributed to the new ester peak. The peaks

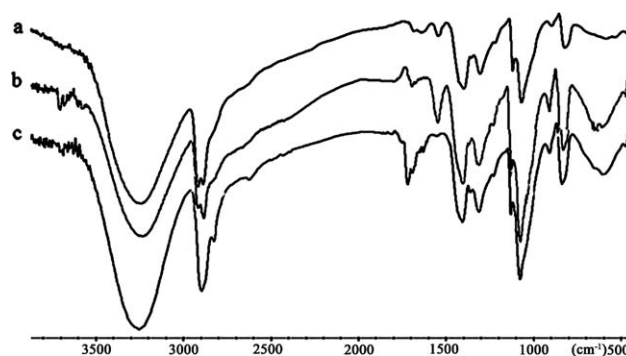


Figure 2 ATR-FTIR spectra of (a) PVA, (b) PVA reacted with SOMAP without catalyst, and (c) PVA-g-SOMAP in the presence of catalyst.

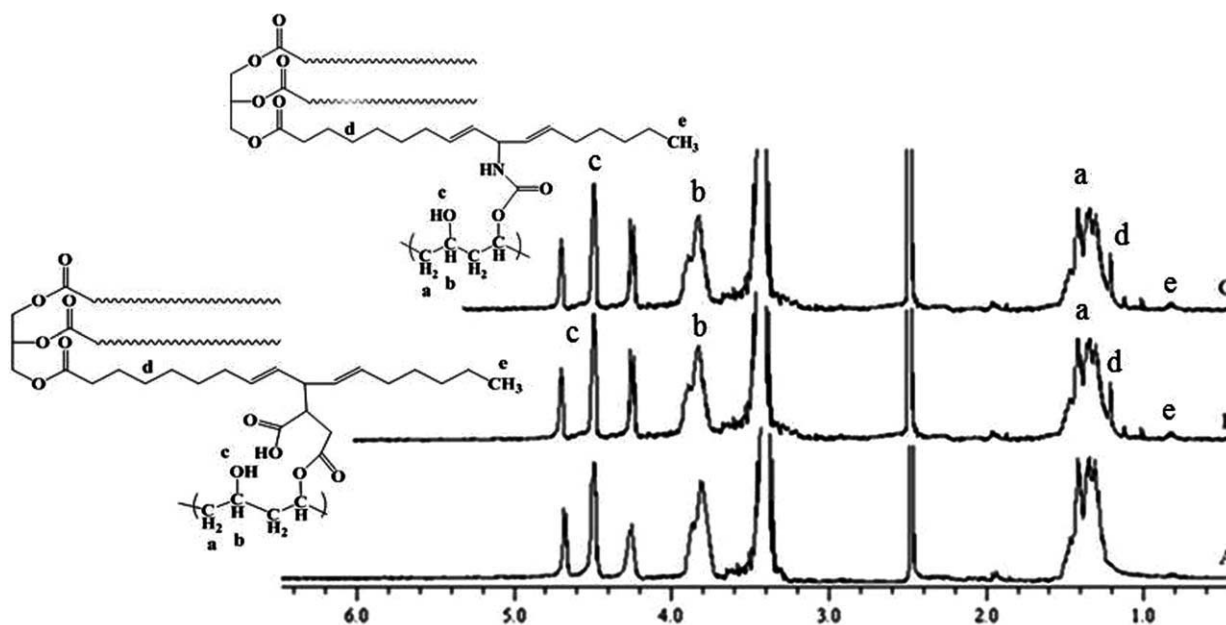


Figure 3 $^1\text{H-NMR}$ spectra of (A) PVA, (B) PVA-g-SOMAP, and (C) PVA-g-SONCO films.

at 2927 and 2857 cm^{-1} correspond to the C—H stretching of SOMAP indicating that large fatty methylene groups exist on the surface of the film. The O—H stretching vibrations of the remaining acid group on anhydride cannot be distinguished as they overlap with the O—H stretching vibrations of PVA. When the grafted film was lifted from the microscope slide and the ungrafted side was placed on the ATR-FTIR instrument, the spectrum obtained was identical to PVA. This technique proved to be a simple method for the oleophilic surface modification of PVA films on one surface only. Such films may find applications as membranes or tubes with one-way permeability.

PVA-g-SOMAP film for $^1\text{H-NMR}$ characterization was prepared by dissolving a sample scraped from the grafted side of the film with hot $\text{DMSO-}d_6$. This method gives a sample that is much enriched in PVA-g-SOMAP. However, an unknown amount of PVA is also dissolved from the lower layers. The comparison between the $^1\text{H-NMR}$ spectra of PVA and PVA-g-SOMAP film in $\text{DMSO-}d_6$ is shown in Figure 3. Methylene protons of the PVA backbone appear at 1.3–1.5 ppm, and the methine protons attached to —OH and residual acetate appear at 3.8 and 3.9 ppm, respectively. The — CH_3 protons of the unhydrolyzed acetate groups of PVA give a characteristic peak at 1.95 ppm. The hydroxyl protons (—OH) of the PVA are separated into triads at 4.2, 4.5, and 4.7 ppm due to the H bonding between —OH groups of the polymer and DMSO. The solvent peak appears at 2.5 ppm while the water peak due to DMSO appears at 3.4 ppm. All the peaks, which appear in PVA, also appear in the grafted film with

a very little change in the chemical shift values. However, the extra peak that appears at 1.2 ppm corresponds to the — CH_2 — protons of soybean oil triglycerides, indicating that grafting took place.

Synthesis and characterization of PVA-g-SONCO films

Reactivity of isocyanate groups with secondary hydroxyl groups is known to be very small unless a catalyst is used.²⁰ DMAP also catalyzes the formation of polyurethanes from isocyanates and alcohols. Because of the fact that SONCO prepared by the method referred to has 2.1 isocyanate functionalities per mole of triglyceride and that the isocyanate groups are more reactive with hydroxyl groups than succinic anhydride, the surface grafting reaction was faster and gave higher grafting ratios despite low amounts of SONCO used.

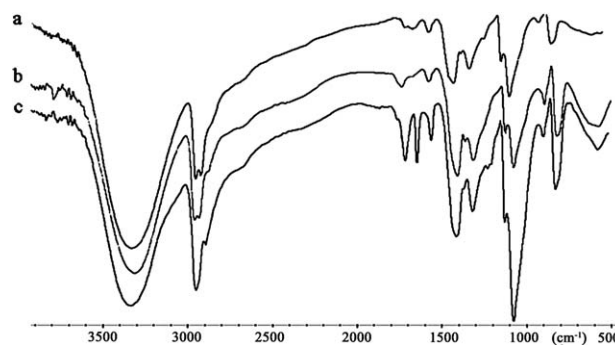


Figure 4 ATR-FTIR spectra of (a) PVA, (b) PVA reacted with SONCO without catalyst, and (c) PVA-g-SONCO film in the presence of catalyst.

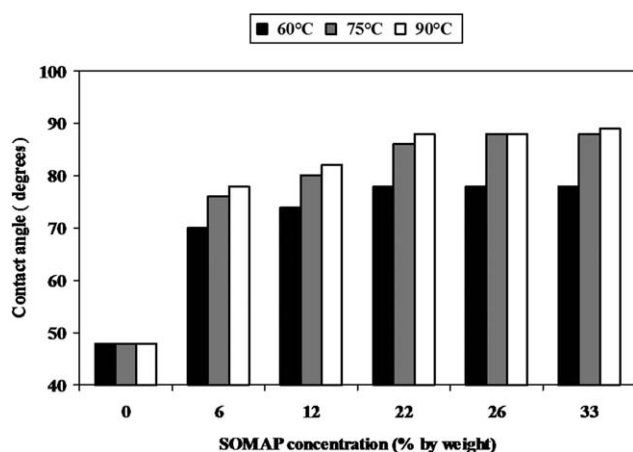


Figure 5 The variation of contact angles with SOMAP concentration and reaction temperature.

The PVA-g-SONCO films were studied by ATR-FTIR and $^1\text{H-NMR}$ spectroscopy. ATR-FTIR spectra of PVA, PVA reacted with SONCO without catalyst, and PVA-g-SONCO film in the presence of catalyst are shown in Figure 4. The loss of isocyanate peak at 2259 cm^{-1} is observed. The broad peak at 1711 cm^{-1} is unique for polyurethane linkages. The peaks at 1644 and 1564 cm^{-1} correspond to $\text{C}=\text{O}$ stretching of the amide group and N-H bending, respectively. However, the N-H stretching vibrations of the amide group around 3500 cm^{-1} cannot be distinguished because it overlaps with O-H stretching vibrations. The peaks at 2939 and 2907 cm^{-1} correspond to the C-H stretchings of SOMAP indicating that large fatty methylene groups exist on the surface of the film.

$^1\text{H-NMR}$ spectrum of PVA-g-SONCO film is shown in Figure 3. The sample was obtained by scraping the surface of the sample in DMSO. The peak at 1.2 ppm corresponds to $-\text{CH}_2-$ protons of soybean oil triglycerides and clearly confirms the reaction of SONCO with PVA film.

Contact angle measurements

Measuring the contact angle (Θ) between water and a given surface provides information about the hydrophilicity and hydrophobicity of the surface.²¹ Dried PVA films treated with SOMAP solutions of various concentrations (6–33% by weight) at different temperatures were studied by water contact angle measurements. The variations of contact angles with SOMAP concentration in the grafting reagent and the reaction temperature are shown in Figure 5. For a given concentration, contact angle increases considerably when the reaction temperature is increased from 60 to 75°C , but remains almost the same when the temperature is increased to 90°C . Therefore, 75°C was found as the best tem-

perature for the grafting reaction and contact angle of the grafted surface reached its maximum value of $\Theta = 88^\circ$ for 26% SOMAP concentration at this temperature. Unmodified PVA film has a contact angle of $\Theta = 48^\circ$.

The reaction of SOMAP with PVA requires that a new $-\text{COOH}$ group is formed for every graft reaction. The presence of this polar and hydrogen bonding group makes the surface more hydrophilic and detracts from the overall aim of our work. Efforts were made to see if this newly formed $-\text{COOH}$ group could be esterified with another available $-\text{OH}$ group on the PVA surface. Extended heating of the grafted films at 100°C for 24 h did not show any further increase in contact angles. It is generally known that further esterification of the second acid group of an anhydride requires very high temperatures. However, such high temperatures could not be applied to the reactions on PVA films due to the danger of degrading the PVA film. Thus, we conclude that further esterification did not take place under our reaction conditions.

The change in water contact angles with the concentration of SONCO in the grafting reagent (1–6% by weight) and with temperature were also investigated (Fig. 6). It can be noted that the contact angles increases rapidly and reaches its maximum value of 94° for a 2.5% SONCO concentration at 75°C . The higher contact angle obtained from the SONCO-grafted films is probably due to the absence of the $-\text{COOH}$ group that is present on the SOMAP-grafted surfaces and the formation of a more homogeneous monolayer with SONCO. Again, the water contact angle of the unmodified side of PVA film does not change and remains at $\Theta = 48^\circ$ after the grafting process.

The water contact angles obtained after the grafting reactions are consistent with other references.

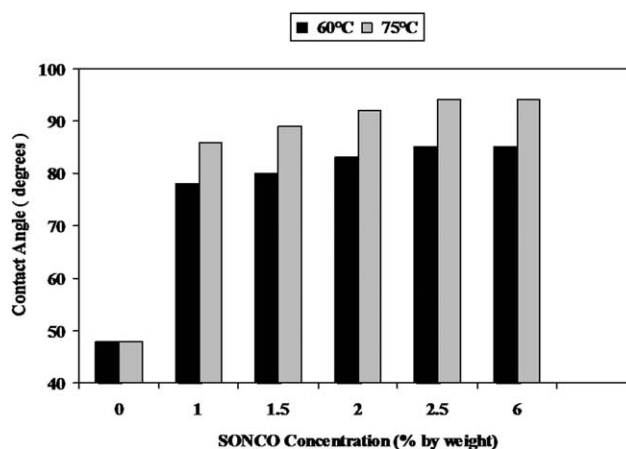


Figure 6 The variation of contact angles with SONCO concentration and reaction temperature.

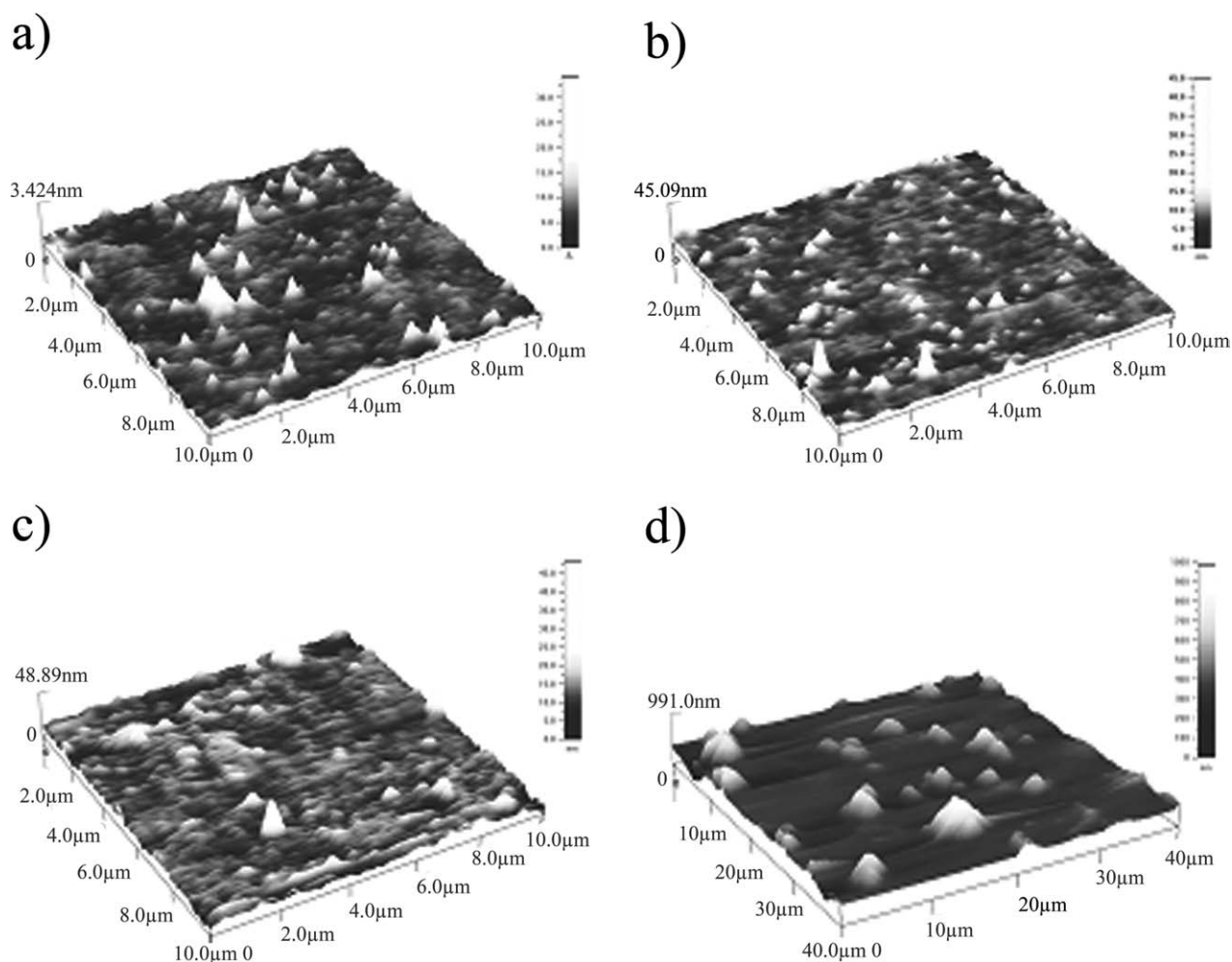


Figure 7 3D AFM images of (a) PVA film, (b) PVA film kept in toluene, (c) PVA-g-SOMAP film, and (d) PVA-g-SONCO film.

PVA films have also been grafted with various non-polar monomers to obtain films with differing hydrophilicity on different faces.^{7,8}

Atomic force microscopy

The AFM is a well-established and powerful tool for probing surface topography and roughness of various materials. Because of the fact that the air contact surface of the solution-cast PVA film was rough, an aqueous PVA solution was spin coated on a 2×2 cm² microscope slide to get a smooth surface for AFM measurement. Three-dimensional AFM images of PVA film, PVA film kept in toluene without reagents under the same conditions with the grafting reaction, PVA-g-SOMAP film prepared from 26% SOMAP solution, and PVA-g-SONCO film from 2.5% SONCO solution are depicted in Figure 7. From AFM image of PVA film, the irregular rolling peaks and troughs with different sizes were observed over the surface [Fig. 7(a)]. The same peaks can also be seen with PVA film kept in toluene [Fig. 7(b)] showing that toluene has very little effect on

the surface morphology of the PVA film. After grafting reaction of SOMAP in toluene, most of the rolling peaks disappeared [Fig. 7(c)]. AFM image of PVA-g-SONCO film depicted in [Fig. 7(d)] shows the distribution of SONCO over the surface of PVA. The area scale investigated is higher than that of the PVA-g-SOMAP film to see the overall distribution of SONCO. SONCO in addition to a more complete coverage of the PVA surface also gave thick and large clusters at some localities. The succinic

TABLE III
RMS and Mean Surface Roughness Values of PVA Film, PVA Film in Toluene, PVA-g-SOMAP Film, and PVA-g-SONCO Film

| | RMS deviation, Sq (nm) | Mean deviation, Sa (nm) |
|-------------------------------|------------------------|-------------------------|
| Pure PVA film | 0.25 | 0.17 |
| Pure PVA film in toluene | 2.15 | 1.36 |
| PVA-g-SOMAP film ^a | 3.16 | 2.16 |
| PVA-g-SONCO film ^b | 68.07 | 42.13 |

^a Grafted in the presence of 26% SOMAP solution.

^b Grafted in the presence of 2.5% SOMAP solution.

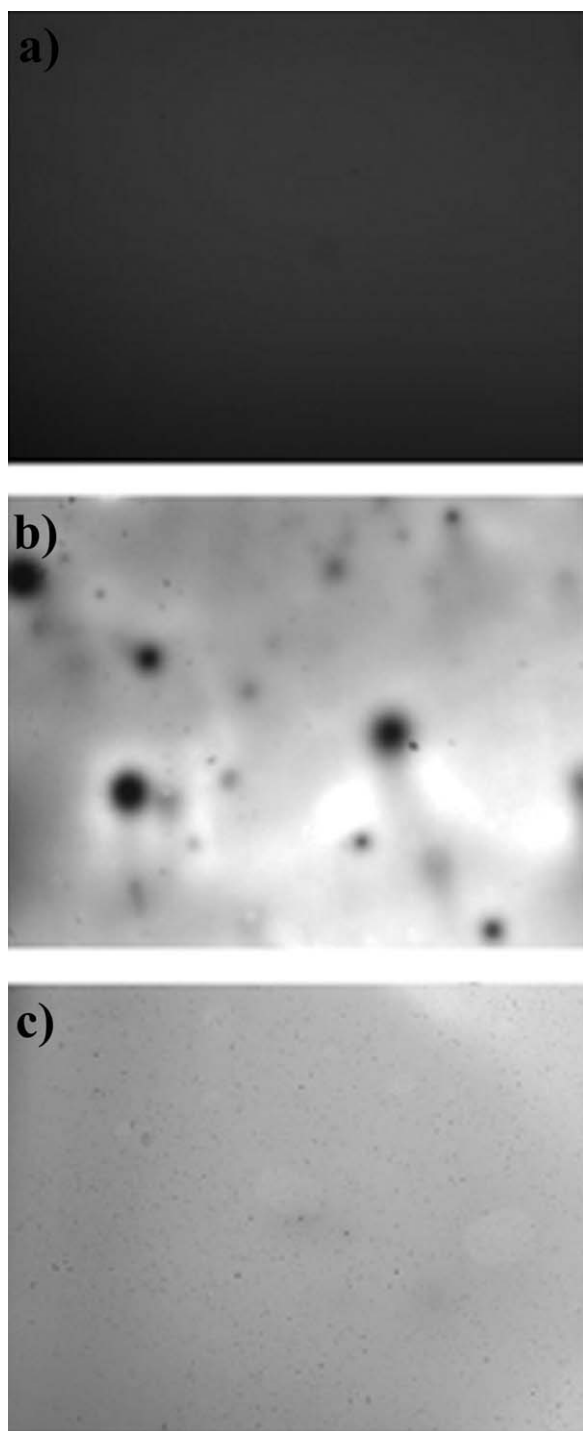


Figure 8 The optical microscopy images of the (a) PVA, (b) PVA-g-SOMAP, and (c) PVA-g-SONCO film surfaces after color reaction.

anhydride group on SOMAP can react with hydroxyl groups but not with itself. The isocyanate groups on SONCO, however, can react both with hydroxyl groups and with itself. Dimerization and trimerization of isocyanate groups to give isocyanurate are known.²² Thicker region observed in the AFM images of SONCO-grafted films are probably

such regions of stacked-up layers of SONCO trimers and oligomers. Such behavior is not possible with SOMAP.

The RMS and mean surface roughness values of PVA, PVA film kept in toluene, PVA-g-SOMAP, and PVA-g-SONCO films are listed in Table III. The surface becomes much rougher with the surface grafting of SOMAP or SONCO onto PVA film and roughness increases from 0.25 to 3.16 nm for SOMAP and 68.07 nm for SONCO. It can be seen that toluene is also responsible for some roughness of the PVA film. However, the PVA-g-SOMAP and PVA-g-SONCO films have higher RMS values than that of the film kept in toluene, which proves that the surface grafting reaction took place.

Homogeneity of grafted films

A simple method to determine the presence of PVA in a chemical formulation qualitatively is to run a well-known color reaction of PVA. In the presence of one drop of iodine and a few drops of boric acid solution, PVA gives a dark blue color.²³ This procedure was applied onto grafted PVA films to get qualitative information about the homogeneity of grafting. Figure 8(a–c) shows, respectively, the optical microscopy images of the PVA, PVA-g-SOMAP, and PVA-g-SONCO film surfaces after the color reaction. PVA film was completely dyed blue. However, only the unreacted regions of PVA-g-SOMAP film were dyed blue, whereas the grafted regions remained undyed. Staining experiments show that SOMAP grafted PVA surfaces show regions of unmodified PVA. PVA-g-SONCO film was not dyed at all indicating that essentially all PVA surface was grafted successfully with SONCO. Lower contact angles observed for SOMAP-grafted film can be attributed to the regions of unmodified PVA as well as the presence of the newly formed polar $-\text{COOH}$ group.

DSC results

In this study, the T_g values of PVA, PVA-g-SOMAP, and PVA-g-SONCO film samples were determined. Temperature scans were run at a heating rate of $10^\circ\text{C min}^{-1}$. For each sample, two runs were done and approximately the same T_g values were observed in both runs. No crystalline melting was observed in any of the samples. The T_g values of PVA, PVA-g-SOMAP, and PVA-g-SONCO films were found as 76.2, 72.9, and 74.0°C , respectively. The samples used were small pieces cut from the grafted films having a very thin grafted region on one surface only. Therefore, the actual concentration of the grafted molecules in the sample is very low.

CONCLUSIONS

PVA films were hydrophobically modified by the grafting reaction of SOMAP or SONCO triglycerides in the presence of DMAP catalyst. The hydrophobicity of the surfaces was studied by water contact angle measurements. The surfaces obtained were further characterized by AFM. The grafting homogeneity of the surfaces was examined from the images taken from optical microscopy after a color reaction. AFM images show that the triglycerides cover the PVA surface in clusters. SONCO due to its ability to react with itself gives larger and higher clusters than SOMAP. Grafting SOMAP and SONCO onto PVA fibers is now in progress. Our hope is that such materials can one day be used as selective and one-way membranes for biomedical use and for plant-oil refining.

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