Effects of Aging on Radiofrequency-Sputtered Polyethylene Film

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ABSTRACT: The effects of aging on polyethylene film deposited by radiofrequency sputtering on a quartz crystal microbalance were examined by measuring its resonance frequency and conductance, and by measuring the contact angle of the film to distilled water. The film sputtering was observed using *in situ* optical emission spectroscopy. The fabricated film was observed using atomic force microscopy, and analyzed using Fourier transform-infrared and electron spin-resonance spectroscopies. The longer the film was exposed to air, its weight increased and the film became softer. Increase in hydrophilicity of the surface, decrease in spin concentration in the film, and enrichment of the oxygenated moieties in the film were observed. These indicate that the film structure is reconstructed by the reactions between radical sites in the film and reactive species in the air, such as oxygen and water, and by the movement of hydrophilic moieties inside the film towards the surface. When stored in vacuum, the film hardened and oxidation slowered. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1869–1877, 1999

Key words: radiofrequency sputtering; polyethylene; aging

INTRODUCTION

Radiofrequency (RF) sputtering is a common method for modifying polymers and inorganic and organic chemical substances to add functional groups that can provide new physical or chemical characteristics. It modifies the surface of substrates by introducing the atoms of such elements as oxygen, fluorine, and ammonia, at depths of up to a few nanometers, thereby changing the surface characteristics, such as the hydrophilicity and hydrophobicity.[1–5] A variety of substrates and a variety of gases can be used for RF sputtering; the characteristics and thickness of the sputtered film can be controlled by changing the sputtering conditions and sputtering time. Such modified materials have been applied in biological fields[6,7] and to gas separation.[8,9]

Our group has used RF sputtering to fabricate organic films of amino acids, including phenylalanine and glutamic acid.[10] The molecular condition and structure of the surface was examined by using secondary ion mass spectroscopy, X-ray photoelectron spectroscopy, and Fourier-transform infrared (FTIR) spectroscopy. The characteristic sorption of the organic gaseous molecules in these films was measured using a quartz crystal microbalance (QCM).[11] The relation between the type of film and the type of gaseous molecules that are sorbed was determined by examining the physicochemical parameters, i.e., the dipole moment, polarity, hydrogen bonds, and π-electron density.[12,13] We have also fabricated polymer films of polychlorotrifluoroethylene (PCTFE) by RF sputtering.[14] Our group has fabricated a gas-sensing system consisting of several different films sputtered onto QCMs. It works by measuring the characteristics of the dynamic sorption of the gas molecules into the film; these characteristics depend on material of the film.[15,16]

The fabricated organic plasma-deposited films have a lot of molecular grafting and many crosslinks in the rigid backbone. The polymer carbon networks produce reactive unsaturated moieties, such as multiple bonds and radical sites, with high density. Therefore, these materials interact strongly with small organic molecules through π-electrons and unpaired electrons.

However, these plasma films do not have a rigid chemical configuration. The structure of the films can revert to an earlier form in response to the surrounding chemical conditions, resulting in reduced interfacial energy.[17–21] These changes are not necessarily due to a large segment motion, such as a conformation change; they can be due to a relatively small motion, such as a rotation around the backbone or side-group bone or a migration of the segments. This mobility in the polymer chain segment produces the surface reconstruction that prevents an energetically unfavorable situation, such as nonpolar groups locating at the interface with the polar air environment.

We have now fabricated polyethylene (PE) film by using RF sputtering of solid-state polyethylene, a widely used polymer. In this article we report the effects of aging on this PE film. We deposited the film onto QCMs; the relationship between the weight, density, and viscosity of the film was determined from the QCM's frequency and conductance.[22–26] The changes in the physical properties of the film surface caused by exposure to air were examined by measuring the resonance frequency and conductance of the QCMs. The surface hydrophilicity was examined by measuring the contact angle of the surface to distilled water. The films were analyzed using *in situ* optical emission spectroscopy during sputtering. The surface morphology of the film was observed using atomic force microscopy (AFM). The unaged and aged films were analyzed using FTIR spectroscopy and electron spin resonance (ESR) spectroscopy.

EXPERIMENTAL

Fabrication and Storage of Samples

The QCMs (AT-cut, 9 MHz, gold electrodes) were purchased from Sogo Yakko, Ltd. The high-density polyethylene used as the sputtering target was obtained from Kaken, Ltd. The sputtered film was deposited on both sides of the QCMs and on one side of a Si wafer at a radio frequency of 13.56 MHz.[10] The sputtering gas (99.995% krypton, Nihon Sanso, Ltd.) had a flow rate of 6 mL/min. The sputtering pressure was 6.7 Pa, and the RF power density was 0.59 W/cm^2. The sputtering time was 30 h for the QCMs and 15 h for the Si wafer; the film thickness was approximately 1200 and 600 nm, respectively. The film thickness was estimated using Sauerbrey's equation:[27]

$$\Delta F/F = -\Delta\ d/d,$$

This equation states that as the thickness of the film increases from d to $d\ +\ \Delta d$, the frequency changes from F to $F\ +\ \Delta F$, assuming that the other film properties do not change.

After sputtering, the samples were taken out and directly measured, moved to a desiccator (with a pressure below 0.01 MPa, achieved using a diaphragm vacuum pump) and kept under vacuum conditions, or taken out and kept under atmospheric conditions. To quickly obtain aged films, some of the QCMs and wafers were dipped into distilled water for a certain interval, then taken out and dried.

Measurements

The *in situ* optical emission spectroscopy during sputtering was done using an Anritsu WAMOS plasma analyzer. The measurements were made through a quartz glass window in the side of the sputtering chamber.

The atomic force microscope (Digital Instrument Nano Scope III) used to observe the surface morphology was used in tapping mode. The PE was sputtered onto Si wafers whose surface was smooth at this scale. To decrease the noise, the measurement scan were done 512 times.

The resonance frequency and conductance of the QCMs were measured using an Advantest R5361A frequency counter; their conductance was measured using a Hewlett-Packard 4195A Network/Spectrum Analyzer with a 16092A impedance-measurement kit. The computer analysis was done using an original program. The maximum conductance was obtained using the least-squares method of QCM Nyquist plots.

The contact angle (CA) of the surface to the water was measured by placing a droplet of distilled water on both unaged and aged samples and by photographically monitoring the change in the angle by using a measuring apparatus (Kyowa Interface Science Co., model CA-X150). The water

Figure 1 AFM image of RF-sputtered polyethylene film on a Si wafer.

was deposited by using a micrometer syringe. The CA was measured at three different points on the same film surface under the same conditions, and the average angle was used.

The FTIR spectroscopy was done using a JASCO FTIR 5M spectroscope with some modification. The PE film deposited on the Au electrodes was examined microscopically using the reflectance method. The resolution was 4 cm^{-1}, and the spectrum was an integration of 256 scans. The background spectrum was obtained using an uncoated Au electrode on QCM. The data was analyzed using the JASCO-FT conversion program.

The ESR spectroscopy was done using a Nikkiso ES-10 spectroscope. Unaged and aged films were examined.

During measurement, the room temperature was 25 ± 2°C, and the relative humidity was 56 ± 10%. The CA measurement and AFM observation were done under a relative humidity of 50 ± 5%.

RESULTS AND DISCUSSION

AFM Image of PE Film

An AFM image of the PE film surface on a Si wafer is shown in Figure 1. As we mentioned, the Si wafer surface was smooth at this scale, so any surface roughness was due to the sputtered PE. The surface was mostly flat but with grains (50–100 nm in diameter) of polyethylene. This roughness is likely related to the hydrophobicity of the surface; the creation of minute protuberances during plasma etching on glass has been shown to create an ultrahydrophobic surface.[28] The RF-

Figure 2 Relation between relative humidity and frequency change in a QCM RF-sputtered with polyethylene (PE) and polychlorotrifluoroethylene (PCTFE).

sputtered films we fabricated could possibly be made ultrahydrophobic by controlling the surface roughness by adjusting the sputtering conditions.

Frequency Change in PE Film

The frequency change in a QCM (ΔF) depends on the film weight (ΔW), density (ρ_f), and viscosity (η_f), as defined in the following equation:

$$\Delta F = -2F_s^2 \Delta W / A (\mu_q \rho_q)^{1/2},$$

where F_s is the basic frequency, μ_q is the QCM viscosity, ρ_q is the QCM density, and A is the electrode surface area of the QCM.

The frequency change of PE- and PCTFE-sputtered QCMs against the relative humidity in the atmosphere as obtained from QCMs exposed in air is shown in Figure 2. The frequency change in the PE-sputtered QCMs decreased linearly as the relative humidity increased, while that of the PCTFE-sputtered ones showed virtually no change.

The frequency change over time of QCMs exposed in air at a constant relative humidity of 53% is shown in Figure 3. The humidity was not

Figure 3 Frequency change in a QCM sputtered with PE and PCTFE, taken at a relative humidity of 53%.

Figure 4 Frequency and conductance changes in PE-coated QCMs over time. (A) (filled circles): exposed in air; (B) (triangles): dipped in water and exposed in air; (C) (open circles): stored in vacuum; (D) (crosses): stored in air for 3 h, then in vacuum.

actually constant; instead, we converted the frequencies to what they would be at a relative humidity of 53%. Once again, the PE-sputtered samples shown a significant frequency change, while the PCTFE-sputtered ones showed virtually no change. This indicates that the effect of the substances in the air depends on the humidity only for PE-coated QCMs. Considering that fluorine-containing moieties in plasma perfluorocarbons have a high hydrophobicity and that the surface configuration is dynamically stable even after immersion in distilled water,[21] the frequency change in the PE-sputtered film was due to the hydrophilicity of the film or to a configuration change in the polymer chain.

Conductance Change in PE Film

To examine the changes in the physical properties of the PE film due to aging in more detail, we measured the conductance of the QCMs. The change in conductance is strongly related to the density (ρ_f) and viscosity (η_f) of the film from the electric equivalent equation,[29,30] and $1/G_{max}$ is linear to $(\rho_f \eta_f)^{1/2}$, where G_{max} is the maximum conductance.

The changes in both the maximum conductance and frequency of films kept under different conditions are shown in Figure 4. Under all conditions, the frequency decreased. The conductance decreased only in the film stored in vacuum. The film exposed in air after dipping in distilled water showed the largest decrease in frequency and the largest increase in conductance.

These results show that exposure in room atmosphere decreases the frequency and increases the conductance, and this is accelerated by immersion in distilled water. This should increase

the film weight and decrease the $\rho_f \eta_f$, which suggests the possibility of softening and dampening the film. Even the film exposed to air for only 3 h showed a conductance increase, indicating that a change in film viscosity can occur within only a few hours. The film stored in vacuum showed both a frequency and a conductance decrease, suggesting the increase in film weight and the hardening of the film.

The change in film viscosity even in only a few hours is assumed to be caused by reconstruction of the hydrophilic interface due to the active substances in the air, including water vapor. The hardening of film stored in vacuum may be caused by a reaction to a trace amount of hydrocarbons in the vacuum.

Contact Angle Measurement of the Surface

Contact angle (CA) measurement is one of the simplest ways to evaluate the physical and chemical properties of a surface. For example, it can be used to measure the free energy in the interface between the surface and the contacting medium.

The CA of the PE film surface to distilled water is shown in Figure 5. The film exposed in air for 15 days (B) was the smaller in the CA than the film stored in vacuum (A), and the film exposed in air for 15 days, dipped in distilled water for 5 min, and dried for 1 min (C), was the smallest.

When the film is nonpolar, the critical surface tension (CTS) of the film, γ_S^d, can be deduced from the CA as follows:

$$1 + \cos \theta = 2(\gamma_S^d / \gamma_L^d)^{1/2}$$

where θ is the CA, γ_S^d is the CTS of the film, and γ_L^d is the CTS of the water. Based on a γ_L^d of 72.6

Figure 5 Contact angle of RF-sputtered PE film on Si wafer: (A) stored in vacuum for 15 days; (B) exposed in air for 15 days; and (C) exposed in air for 15 days, immersed in distilled water for 5 min, and dried for 1 min.

Figure 6 Change in contact angle of RF-sputtered PE film after water immersion for 7 min followed by drying: (A) (filled circles): stored in vacuum for 15 days; and (B) (open circles): exposed in air for 15 days.

dyn/cm,[6] the γ_S^d for films A, B, and C in Figure 5 were 29.8, 41.3, and 46.6 dyn/cm, respectively. Considering that the CTS of polyethylene itself is 31.4 dyn/cm,[6] and considering that Ar plasma treatment decreases the CA of polypropylene and polyethylene,[1,2,6,31] our results indicate that the of RF-sputtered PE film stored in vacuum had large hydrophobicity, and it decreased when it is stored in air then immersed in water.

The change over time of the CA after the PE films were immersed in distilled water and dried is shown in Figure 6. Both films were dipped in distilled water for 5 min and dried immediately before measurement. Both of the PE films stored in vacuum and the one exposed in air showed a decreased CA, with the latter showing the larger decrease. Even after drying for 40 min, the CA of neither films returned to its initial level.

These results confirm that storing the film in air increases the surface hydrophilicity, and that this change is accelerated by immersing the film in distilled water. This increase in hydrophilicity might be due to water molecules being adsorbed into the film surface, to hydrophilic groups on the film surface created by a reaction between molecules in the film and molecules of water or oxygen, or to the rotational mobility, i.e., "overturn," of the hydrophilic moieties of the film molecules in the surface, which rearranges the film orientation so as to produce a stable interface under environmental conditions.[17] Storing the film in vacuum might cause the hydrophobic moieties to return to the surface, which would increase the surface hydrophobicity.

Optical Emission Spectra

The optical emission spectrum during sputtering are shown in Figure 7. The intensive peak at 5570

Å was due to krypton, the sputtering gas. The complicated multiple peaks around 4300 Å were due to CH, and the peaks around 3400–3700 Å were due to CH^+. These peaks indicate that the polymer chain in PE is scissored by sputtering and that the hydrocarbons of smaller molecules can be deposited. Similar decomposition and degradation of the polymer chain has been observed in the plasma treatment of PE surfaces.[1,2]

The peaks around 3600–3700 Å were due to CH_2O (3642 Å) or O_2 (3671 Å), the peak at 3650 Å was due to CO^+, the peaks at 3370, 3517, 3671, and 3743 Å were due to O_2, and the peaks at 4510, 4835, 5198, and 5610 Å were due to CO. These peaks indicate the existence of oxygen in the sputtering chamber. Because the sputtering chamber always contains small residues of O_2, CO, and H_2 gases, it is likely that O_2 and H_2 are incorporated into the deposited film, affecting the film characteristics. Furthermore, oxygen in the plasma state is assumed to create smaller molecules from hydrocarbon polymers[32]; therefore, the small hydrocarbon molecules found in the sputtering process might due to krypton and oxygen in the plasma state.

FTIR Spectra of PE Film

We investigated the chemical film structure for four storage conditions by using IR spectroscopy. As shown in Figure 8, one of the predominant peaks observed in each spectrum was at 2900 cm^{-1}, which is a characteristic of C—H asymmetric stretching of aliphatic CH. The intensive peak observed at 3500 cm^{-1} was assigned to the stretching vibration of the hydroxyl group (—OH), and that of 1700 cm^{-1} was assigned to stretching of the carbonyl group (C=O). The peak

Figure 7 *In situ* optical emission spectrum during PE sputtering with Kr.

Figure 8 IR spectra of RF-sputtered PE film on Au electrodes: (A) 30 min after sputtering; (B) stored for 7 days in air; (C) stored for 60 days in vacuum; and (D) stored for 60 days in air.

at 1380 cm^{-1} was due to symmetric deformation of aliphatic CH_3 (sp^3—CH_3), and that at 1200 cm^{-1} was due to asymmetrical stretching of C—O in an ether group (—C—O—C—). The bands at 900–1100 cm^{-1} were due to rocking vibrations of the methyl group (CH_3—rocking).

All four spectra showed peaks at 1200 and 1700 cm^{-1}, indicating the existence of oxygen atoms in the film; these peaks were expected from the optical emission spectrum obtained during sputtering (Fig. 7). The existence of oxygen was also confirmed in Ar-sputtered polyaniline film by using glow discharge after air exposure.[33]

To determine the change in the film configuration, we compared the ratio of the FTIR peak areas to the aliphatic CH stretching (2900 cm^{-1}). As shown in Table I, the film stored in air (B) showed an increase in the relative areas of the peak due to —OH, —C=O, and CH_3—rocking. The films stored in vacuum (C), showed an increase in the sp^3—CH_3 peak, while the —OH peak did not increase as much as that of the film

stored in the air (B) did. For the film with long air exposure (D), the peaks due to —OH, —C—O—C—, and CH_3—rocking were higher and that of —C=O were lower compared to those for the film with a short exposure (A).

The enhancement of the —OH peak suggests the sorption of water molecules from the air or formation of —OH bonds by the oxygen or water. From the decrease in —C=O with a long air exposure, the change from —C=O to —C—OH might occur due to the reaction;

$$R—C=O \rightarrow R—C—O—OH \rightarrow R'—OH.$$

The increase in —C—O—C— indicates the formation of new dangling bonds by the oxygen molecules in the air; however, this reaction is assumed to be fairly slow. This increase in the oxygen content with aging has been observed in PE films fabricated using plasma polymerization.[34] Increase in oxygen-containing moieties may increase the hydrophilicity of the film. This accords with our result that the CA to water decreased when a sample is exposed to air, which is also observed in high-density polyethylene film sputtered by an Ar glow discharge.[31] A higher concentration of oxygen-containing moieties increases the interaction between water molecules and the surface.[21] This might cause the dampening of the film when it is exposed to air.

The increase in the rocking vibrations of the methyl group observed in the film stored in air indicates that the mobility of the moieties in the film increased, which may be caused by the coordination of water molecules trapped from the air, causing a repulsive force between the hydrophobic moieties in the film and the water molecules.

The increase in sp^3—CH_3 in the film stored in vacuum may indicate the reconstruction of the molecular chain; i.e., grafting of the polymer chain in the film caused by trace amounts of hydrocarbons in the vacuum desiccator. This might cause the hardening of the film shown by the

Table I   Ratio of FTIR Peak Area Obtained from Figure 8

Sample	—OH/C—H	C=O/C—H	sp^3—CH_3/C—H	C—O—C/C—H	CH_3—rocking/C—H
A	0.72	0.95	<0.005	0.013	0.015
B	1.15	1.31	<0.005	0.014	0.057
C	0.83	1.14	0.043	0.017	0.053
D	2.89	0.99	0.027	0.370	0.160

Figure 9 IR spectra of RF-sputtered PE film on Au electrodes: (A) stored in air for 30 days; (B) stored in air for 30 days, immersed in distilled water for 7 min, and dried for 1 min; and (C) stored in air for 30 days, immersed in distilled water for 7 min, and dried for 30 min.

Figure 10 Spin concentrations in RF-sputtered PE film: (A) stored in vacuum for 3 days; and (B) exposed to air for 20 days.

conductance measurement. The slow increase in the sp^3—CH_3 observed in the film exposed in air may be due to trace amounts of hydrocarbons in the air. However, the reaction is assumed to be slow compared to the reaction to O_2 and water molecules for the film stored in the air.

The FTIR spectra of PE films immersed in distilled water and dried in air are shown in Figure 9. Table II shows the relative peak areas from Figure 9. The film stored in air for 30 days, immersed in water for 7 min, and dried for 1 min (B) showed an increase in —OH, C=O, and CH_3—rocking. However, after drying, the relative peak area at —OH and C=O decreased almost to the nonimmersion state (A). This means that dipping in water for 7 min did not cause a reaction producing —OH or C=O, but did increase the mobility of the methyl groups due to the coordination of water to the film. The increase in the mobilities agrees with the conductance change

observed after only 3 h of exposure and with the decrease in CA after air exposure and water immersion.

ESR Spectra of PE Film

Using ESR, we obtained the spin concentrations shown in Figure 10. The film exposed in air for 20 days (B) had a smaller concentration than the one stored in vacuum for 3 days (A).

The existence of radical sites in the plasma film results from the excessive rate of free radical formation during the plasma process,

$$R—R' \rightarrow R\bullet + R'\bullet,$$

compared to the dissipation rate due to recombination.

The decrease in the spin concentration may be caused by substances in the air becoming trapped at the radical sites in the film. If so, a film with a higher spin concentration is more likely to uptake the radical molecules. A decrease in the spin concentration was also observed in plasma-polymerized acetylene film after nitrogen exposure; this decrease is more apparent when the film is exposed to water vapor.[34]

Unreacted free radicals in the film tend to combine with the oxygen and water in the air. In the presence of oxygen, a large majority of the free

Table II   Ratio of FTIR Peak Area Obtained from Figure 9

Sample	—OH/C—H	C=O/C—H	C—O—C/C—H	CH_3—rocking/C—H
A	1.45	1.05	0.046	0.012
B	3.84	1.65	0.069	0.035
C	1.70	1.06	0.049	0.034

radicals on the surface will react to form peroxides and hydroperoxides.[1] These reactions can be written as

$$R\bullet + H_2O \rightarrow R\text{—}OH,$$

$$R\bullet + O_2 \rightarrow R\text{—}O\text{—}O\bullet \rightarrow$$
$$R\text{—}O\text{—}OH \rightarrow R\text{—}OH,$$

$$R\bullet + O_2 \rightarrow R\text{—}O\text{—}O\bullet \rightarrow R\text{—}O\text{—}OH \rightarrow$$
$$RR'\text{—}C\text{=}O,$$

$$R\bullet + O_2 \rightarrow R\text{—}O\text{—}O\bullet \rightarrow R\text{—}O\text{—}OH \rightarrow$$
$$RH\text{—}C\text{=}O,$$

and

$$R\text{—}O\text{—}O\bullet + R'\text{—}C\text{=}O \rightarrow$$
$$R\text{—}O\text{—}O\text{—}O\text{—}R' \rightarrow R\text{—}O\text{—}R' + O_2.$$

These reactions cause hydroxyl, carbonyl, and ether groups to form, as shown by our FTIR results. These reactions were also suggested in a study that showed a CA decrease is prevented and the surface energy is stabilized by using free radical inhibitors and antihydrides.[4]

These oxygen uptakes can be attributed to the addition of diffusing atmospheric O_2 to the radical sites created by the plasma. According to Gengenbach, this initial process is very fast. The second process is oxidative degradation of polyolefins related to radical reactions, such as the formation of —C—O—C—, which is a long-term oxidation.[20] This slow formation of —C—O—C— was confirmed by our FTIR results. Our finding that immersion in distilled water accelerates the reaction indicates that water molecules might be involved in the consuming of radical sites.

The decrease in the spin concentration can be assumed to be also cause by the reaction between the radical sites:

$$R\bullet + R'\bullet \rightarrow R\text{—}R'.$$

Moreover, small hydrocarbon molecules can become trapped at the radical sites:

$$R\bullet + R' \rightarrow R\text{—}R'\bullet.$$

These reactions may harden the film. The decrease in the spin concentration of the PE film stored in vacuum may be caused by these reactions because the oxygen concentration is low, meaning the oxygen uptake is slow.

These surface restructurings and oxidations are assumed to take place simultaneously until the radical site or active species in the ambient air completely depleted.

CONCLUSION

We have examined the effects of aging on polyethylene films deposited on a quartz crystal microbalance. The film deposition was observed using *in situ* optical emission spectroscopy. The fabricated film was observed using atomic force microscopy and analyzed using infrared and electron spin-resonance spectroscopies.

Exposing the film to air increased its weight and softened it. The critical surface tension of the film increased after exposure in air. This indicates that the surface hydrophilicity is increased by exposing the film in air. Optical emission and Fourier transform-infrared spectroscopy revealed the existence of oxygen atoms in the sputtered films. Aging of the films in the air caused an uptake of oxygen and water molecules, leading to the formation of oxygenated bonds. Electron spin-resonance spectroscopy showed the spin concentration decreased over time, indicating that the radical sites might react to water or oxygen molecules.

In contrast, exposure in vacuum hardened the film and the oxidation was slowered. This may be due to a reaction between the radical sites in the film, a reaction between the film and small hydrocarbon molecules in the vacuum chamber, and a reconstruction of the molecular chain.

Unlike other studies of the aging effect and the molecular-configuration change in films fabricated using plasma,[17,18,20,35] the PE films we used were deposited by RF sputtering. However, our films were similar in that they did not have a rigid configuration; instead the moieties in the polymer chains enabled mobility, depending on the surrounding conditions. The interaction between the film molecules and the contacting medium, such as water or oxygen, is a major force in the change of the surface configuration that is needed to minimize the interfacial tension. Therefore, when PE film is immersed in water, its surface configuration changes.

Our study has shown that the surface properties of PE-sputtered film depend on the environmental conditions. The properties can change due to 1) sorption and reaction with oxygen, 2) sorption and reaction with water molecules, 3) sorption and reaction with hydrocarbons, 4) overturn or migration of the hydrophilic moieties in the film, and 5) polymerization due to reactions between radical sites.

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