

Surface Passivation of Nylon-6,6 Films by Graft Copolymerization for Reduction of Moisture Sorption

JUNFENG ZHANG, K. T. KHONG, E. T. KANG

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 119260

Received 25 August 1999; accepted 3 December 1999

ABSTRACT: To improve the moisture sorption property of nylon-6,6 film, allyl pentafluorobenzene (APFB) was incorporated on the argon plasma-pretreated nylon film by UV or thermally induced surface graft copolymerization. The plasma pretreatment introduced peroxides that were degraded into radicals to initiate the graft copolymerization of APFB on the nylon surface. The modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS) and contact angle measurement. The moisture sorption was assessed by the coulometric test method. The efficiency of surface graft copolymerization was affected by plasma pretreatment time of the nylon substrate, as well as by the UV or thermal graft copolymerization time. The UV graft-copolymerized nylon film exhibited a significantly lower extent of moisture sorption when compared to that of the pristine films, even at low graft concentration. However, the moisture sorption behavior for the thermally graft copolymerized films was similar to that of the pristine films. Contact angle and XPS measurements suggested that the reduction in moisture sorption for the UV graft-copolymerized nylon-6,6 film was attributable to the fact that the hydrophobic polymer layer was formed on the nylon surface, and the hydrophobic layer of an appropriate thickness could serve as an effective barrier to moisture. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1366–1373, 2000

Key words: graft copolymerization; nylon-6,6; plasma; moisture sorption; XPS; fluoromonomer

INTRODUCTION

Nylons are synthetic engineering plastics produced by polycondensation reactions. They are versatile synthetic materials with almost unchallenged utilities in textile, household, and industrial applications. The high tensile strength, toughness, and good processability have led to their acceptance as important engineering materials. However, nylons are known to be sensitive to water or moisture. Moisture causes plasticization and have a profound effect on the mechanical properties of the polymer.¹ The hygroscopic na-

ture of the nylons has limited their applications in many areas. Thus, the water sorption and transport properties in nylons have been extensively studied.^{2–6} These studies showed that the interaction of water with nylon took place at the hydrophilic amide groups in the amorphous phase and reduced the interchain hydrogen bond strength of the N—H groups. Attempts have been made to develop novel techniques for the prevention or reduction of moisture sorption in nylons. A number of reports have dealt with the modification of nylon main chains by the introduction of fluorinated components.^{7,8} Nevertheless, these modifications probably have also affected the bulk properties of the polymers.

Surface graft copolymerization is one of the most versatile means for the molecular design of

Correspondence to: E. T. Kang

Journal of Applied Polymer Science, Vol. 78, 1366–1373 (2000)
© 2000 John Wiley & Sons, Inc.

polymer surfaces to enhance their physical and chemical properties for specific applications. The key advantage of this technique is that the polymer surface can be modified to have different properties through the choice of different monomers,^{9–11} while leaving the bulk properties of the polymer intact. The graft copolymerization approach has been used for the treatment of the nylon surfaces in applications such as the preparation of affinity films for protein sorption,¹² synthesis of microporous membranes, with environment-sensitive permeability,¹³ and incorporation of additional functionalities on nylon fibers.¹⁴

Polymer surfaces have been graft copolymerized using different activation and initiation methods. The most widely used methods basically fall into three major categories: (1) initiation by chemical methods, (2) activation and initiation by irradiation, and (3) activation by discharge treatment followed by UV or thermal initiation. Among these methods, plasma activation and UV or thermal initiation have unique advantages due to their simplicity, cleanliness, and ease of control.^{14–16} Previous works have shown that high graft copolymerization efficiency can be readily achieved by plasma pretreatment and subsequent UV initiation for the various monomer-substrate systems, including the systems involving the chemically inert fluoropolymer substrates.^{17–20}

In the present work, we report on the graft copolymerization of a fluorinated monomer, ally pentafluorobenzene (APFB), onto nylon-6,6 film substrates using both UV and thermal initiation methods. Before graft copolymerization, the nylon-6,6 films are pretreated with argon plasma discharge to introduce active species for the initiation of graft copolymerization. The graft copolymerized nylon surfaces are characterized by X-ray photoelectron spectroscopy (XPS) and contact angle measurements. The surface-modified samples are also evaluated for moisture sorption. The results show that a hydrophobic graft layer has been tethered on the nylon surface to act as an effective barrier to moisture sorption. As the graft chains are covalently tethered on the nylon surface, they should be resistant to most of the leaching and extraction processes.

EXPERIMENTAL

Materials

The nylon-6,6 films, with a thickness of 0.5 mm, were supplied by Goodfellow Inc., Cambridge,

UK. They were cut into strips of 2.5×1.5 cm in area, and were cleaned by extraction with methanol for 1 h before use. Ally pentafluorobenzene (APFB) monomer of 98% purity was purchased from Aldrich Chemical Co., Milwaukee, WI, and was used after purification by distillation under reduced pressure. All other chemicals and solvents were of reagent grade. They were also obtained from Aldrich Chemical Co., and were used as received without further purification.

Low-Frequency (LF) Plasma Treatment and Graft Copolymerization

The plasma treatment of the nylon films was performed between two parallel plate electrodes in a glow discharge quartz reactor (Model SP100 Plasma System), manufactured by Anatech Co. Ltd., Illinois. The plasma power supply was set at 32 W at a frequency of 40 kHz. The nylon films were placed on the ground electrode and exposed to the glow discharge at an argon pressure of about 0.58 Torr for a predetermined period of time. The plasma-pretreated nylon films were subsequently exposed to the atmosphere for about 30 min to allow the formation of surface peroxide and hydroperoxides for the subsequent surface graft copolymerization experiment.¹⁰ As the glow discharge chamber was purged thoroughly with a continuous argon stream before ignition, the contribution of residual air or water vapor in the chamber would be negligible, if at all.

The monomer, APFB, was purged with argon before use. In the UV-induced graft copolymerization experiment, a drop of pure APFB of about 50 μL was introduced onto the surface of the plasma pretreated nylon film. The film was subsequently sandwiched between two quartz plates, and the assembly was introduced into a Pyrex[®] tube. The graft copolymerization was performed by subjecting the side of the nylon film, which had been directly exposed to the glow discharge, to UV illumination in a Riko Rotary (Model RH 400-10W) photochemical reactor, manufactured by Riko Denki Kogyo, Chiba, Japan. The reactor was equipped with a 1000-W high-pressure mercury lamp and a constant temperature water bath. All the UV-induced graft copolymerization experiments were carried out at a constant temperature of 30°C. The UV source of wavelength (λ) below 290 nm was effectively cut off by the wall of the Pyrex[®] tube, and the transmitted light source ($\lambda > 290$ nm) passed readily through the quartz plate to initiate the graft copolymerization.

In the thermally induced graft copolymerization experiment, the monomer was similarly introduced onto the Ar plasma pretreated nylon films, which were then sandwiched between two quartz plates as described above. The assembly was subjected to thermal graft copolymerization at 140°C for a predetermined period of time in a constant temperature oven. After the grafting experiment, all samples were washed thoroughly with acetone to remove the residual monomer and homopolymers.

Surface Characterization

Static water contact angles were measured at 25°C and 60% relative humidity by the sessile drop method, using a 3- μ L water droplet in a telescopic goniometer (Ramé-Hart, Pennsylvania, Model 100-0-230). The telescope with a magnification power of 23 \times was equipped with a protractor of 1° graduation. For each sample, at least five measurements on different surface locations were averaged.

The chemical compositions of the polymer surfaces were determined by X-ray photoelectron spectroscopy (XPS) analysis. The XPS measurements were performed on a VG Scientific (East Sussex, UK) ESCALAB MkII spectrometer with a nonmonochromatized Mg K α X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The films were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron take-off angle (α , with respect to the sample surface) of 75°. The X-ray source was run at a reduced powder of 120 W (12 kV and 10 mA). The pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during each measurement. All binding energies (BEs) were referenced to the C1s neutral carbon peak at 284.6 eV. Surface elemental stoichiometries were determined from XPS peak area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to $\pm 10\%$. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

Moisture Sorption Analysis

The moisture sorption for all samples was carried out at 25°C, 100% relative humidity for a predetermined period of time. To provide a same baseline for comparing the kinetics of moisture sorp-

tion, the trace amount of moisture present initially in each sample was removed by exhaustive pumping under reduced pressure for 24 h in a 70°C vacuum oven. For the surface modified films, to prevent the moisture from penetrating into the nylon matrix through the edges, paraffin wax was used to seal the edges before the sorption experiments. The moisture uptake was measured using a Mitsubishi CA/VA-06 Coulometric Moisture Meter. The apparatus was first primed at 180°C with nitrogen as a carrier gas to remove background water content. When the meter indicated a steady reading, the film sample after the moisture sorption was cut into small pieces and introduced into the 180°C heating chamber to release the adsorbed water. The vapor was swept by the carrier gas into an electrolytic cell where it reacted with P₂O₅ to produce H₃PO₄. Electrolysis of the H₃PO₄ then occurred to regenerate the P₂O₅, O₂, and H₂ species. This reaction was measured coulometrically, and the measurement was related directly to the moisture content in the sample. For the coulometric method, about 2 g of samples was used each time and the moisture content could be measured down to an accuracy of 0.1 wt %.

RESULTS AND DISCUSSION

The processes of Ar plasma pretreatment of the nylon-6,6 film and the subsequent UV or thermally induced surface graft copolymerization are shown schematically in Figure 1. The changes in the surface O/N atomic ratio and water contact angle of the nylon-6,6 film as a function of the Ar plasma treatment time under the present glow discharge conditions are shown in Figure 2. The O/N ratios were determined from the sensitivity factors-corrected O1s and N1s core-level peak area ratios obtained at the photoelectron take-off angle (α) of 75°. The O/N ratio of the pristine film surface is about 0.94, which is in good agreement with the theoretical of 1.0, dictated by the chemical structure of nylon-6,6. An increase in the O/N ratio and a decrease in the water contact angle were observed upon increasing the Ar plasma treatment time. These results agree with the common observation that the oxygen concentration of a polymer surface increases with Ar plasma treatment time, due to the increasing concentration of the activated species on the surface which can interact with oxygen when exposed to the air.^{21,22} The O/N ratio increases rapidly with Ar plasma

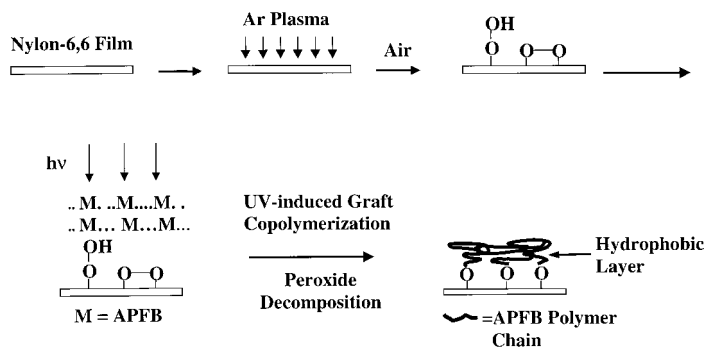


Figure 1 Schematic diagram for the process of surface modification of nylon-6,6 film by Ar plasma pretreatment and graft copolymerization.

treatment time up to a treatment time of about 10 s. After that, the ratio approaches an asymptotic value of about 1.32. It has been reported previously that prolonged plasma or corona treatment of polymer surfaces does not result in the introduction of a larger amount of oxygen atoms or peroxides during the subsequent atmospheric exposure.^{10,23} The fact that prolonged Ar plasma treatment does not result in an increase in oxygen content can probably be attributed to the onset of etching, which removes the activated species. Although the amide groups in nylon molecules are hydrophilic, the pristine nylon surface exhibits only limited hydrophilicity, owing to the presence of other hydrophobic components. The static water contact angle for the pristine nylon-6,6 surface is about 55°. The plasma treatment introduces polar groups, such as peroxides and other oxygenated species, onto the C—C bonds.

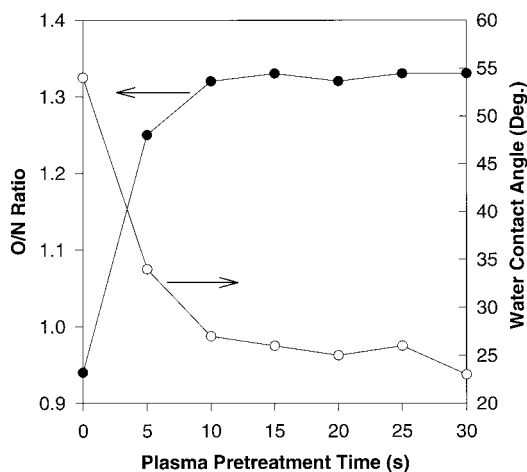


Figure 2 Dependence of the surface O/N ratio and the water contact angle on the argon plasma treatment time.

The polar groups, in turn, gives rise to a more wettable surface, as indicated by the contact angle data in Figure 2. The water contact angle decreases to below 30° after 10 s of plasma treatment.

As indicated above, argon plasma pretreatment under the present glow discharge conditions, followed by atmosphere exposure, causes a rapid increase in the concentration of the oxygen species on the nylon-6,6 surface. Figure 3(a)–(d) shows, respectively, the XPS wide scan spectra, obtained at α of 75°, for the pristine nylon-6,6 film, a 30-s argon plasma-treated nylon-6,6 surface, the 30-s plasma pretreated surface after UV-induced graft copolymerization with APFB, and the 30-s plasma pretreated surface after thermal graft copolymerization with APFB. Pristine nylon-6,6 surface shows three main peak components, associated with the carbon, nitrogen, and oxygen species. After 30 s of argon plasma treatment and subsequent exposure to air, the intensity of the oxygen component increases significantly. The phenomenon is consistent with the plasma-induced surface oxidation process.²⁴ The argon plasma causes the breakage of C—H bonds at the surface of nylon. The abstraction of hydrogen atoms from the surface results in the formation of free radicals on the polymer chains. The subsequent exposure of the activated surface to air causes oxygen to be incorporated onto the polymer surface, leading to surface oxidation and the formation of peroxides and hydroperoxides species. The peroxides species formed will subsequently initiate the surface free radical polymerization generally proposed for the UV or thermally induced graft copolymerization of vinyl monomers.¹⁰ When the plasma-pretreated nylon film is subjected to further modification by UV-

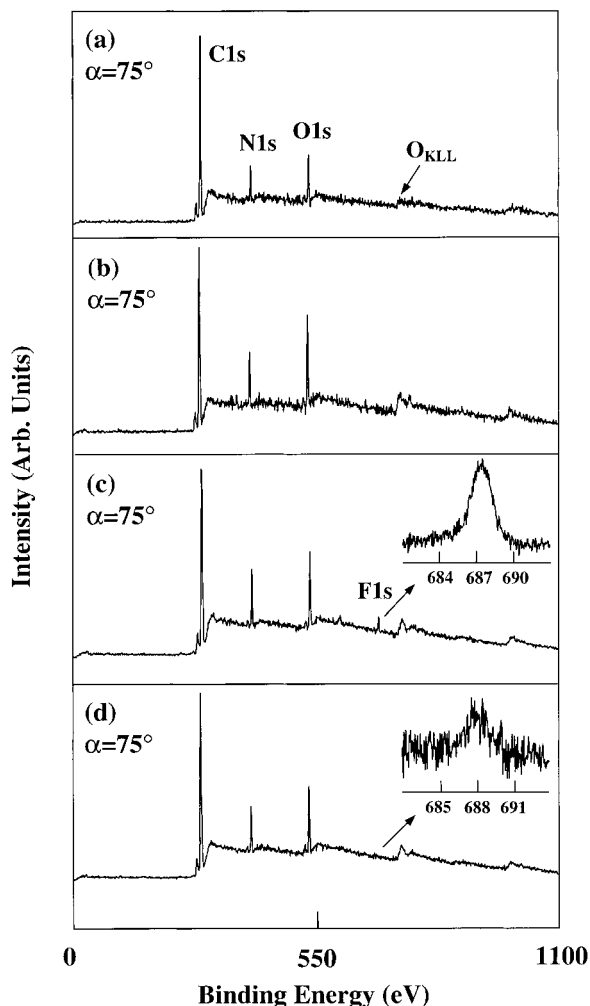


Figure 3 XPS wide scan spectra at a take-off angle of 75° of (a) a pristine nylon-6,6 surface, (b) a 30-s Ar plasma-treated surface, (c) the 30-s plasma-pretreated surface after UV-induced graft polymerization with APFB, and (d) the 30-s plasma-pretreated surface after thermally induced graft polymerization with APFB.

induced graft copolymerization with APFB, the F1s core-level signal becomes prominent and the intensity of the oxygen signal diminishes, indicating that the APFB has been graft copolymerized onto the nylon surface. Only a weak F1s signal is observed when the plasma pretreated nylon film is subjected to thermal graft copolymerized with APFB, as indicated in Figure 3(d). Nevertheless, the F1s core-level spectrum in the insert of Figure 3(d) clearly demonstrates the existence of the grafted APFB polymer on the nylon surface. The fluorine concentration on the modified substrate from the thermally induced graft copolymerization is substantially lower than that on the mod-

ified substrate from UV-induced graft copolymerization. This result suggests that UV irradiation is more effective than thermal activation in the initiation of graft copolymerization on the nylon surface.

Figure 4 shows the F/N ratio as a function of the Ar plasma pretreatment time of the nylon-6,6 substrate after 30 min of UV or 30 min of thermally induced graft copolymerization with APFB. This ratio is directly related to the graft concentration on the surface. It is apparent that the F/N ratio increases with the plasma pretreatment time. However, prolonged plasma treatment does not result in a continuous increase in graft concentration. The optimum graft concentration is achieved on film with the plasma pretreatment time of about 15 s. This result is entirely consistent with the optimum peroxide concentration observed at the same extent of plasma treatment, as shown in Figure 2. It also provides further support for the peroxide initiated mechanism proposed for the present surface graft-polymerization process. The maximum F/N ratio obtained from the UV-induced surface graft copolymerization is about 0.25, which is much higher than the maximum graft concentration obtainable from the thermally induced graft copolymerization. Considering that one APFB molecule contains five fluorine atoms, the optimum ratio of grafted APFB molecules per repeat polyamide unit is 0.05, or 1 APFB molecule per 20 polyamide repeat units within the probing depth of the XPS technique (~ 7.5 nm in organic matrix).^{17,25} Thus, the actual APFB polymer concentration at the outer-

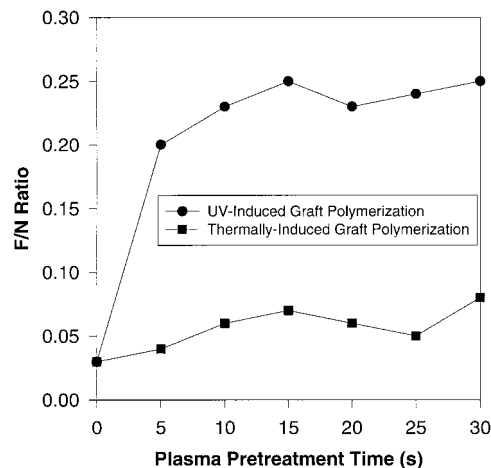


Figure 4 Dependence of the surface F/N ratio on the Ar plasma treatment time. (Graft copolymerization time = 30 min).

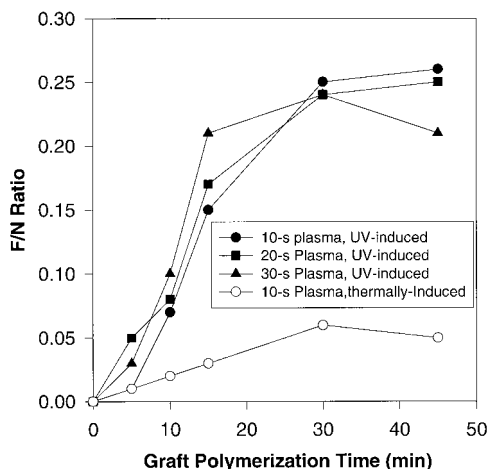


Figure 5 Dependence of the surface F/N ratio on the graft polymerization time.

most surface of the nylon film must be substantially higher than that determined from the XPS technique. Finally, the observation of an initial $[F]/[N]$ ratio of approximately 0.03, even if the samples were not subjected to plasma pretreatment, suggests that a finite amount of APFB can be incorporated onto the nylon surface in the presence of prolonged (30 min) UV or thermal exposure.

Figure 5 shows the changes in F/N ratios as a function of the graft copolymerization time when the nylon-6,6 surfaces are subjected to UV and thermally induced graft polymerization with APFB. The nylon surfaces were subjected to different plasma treatment time. It is obvious that the F/N ratios increase with UV graft copolymerization time, albeit not to the same extent, in all the cases. Between 0 to 30 min of UV graft polymerization time, the N/F ratio increases rapidly and approaches an asymptotic value after 30 min. The graft concentration from the UV-induced graft copolymerization is higher than that from the thermally induced graft copolymerization. However, there appears to be no appreciable difference in the dependence of graft concentration on the UV graft polymerization time among the samples with plasma pretreatment time of 10 s to 30 s. This result is consistent with the previous results shown in Figures 2 and 4. The deviation in surface $[F]/[N]$ ratio for the nylon substrate with 30-s of argon plasma pretreatment probably has resulted from the combined effect of long plasma treatment time and long UV exposure time.

Figure 6 shows the water contact angles of the APFB graft copolymerized nylon-6,6 film as a

function of graft copolymerization time. The contact angles of APFB graft copolymerized surfaces are almost independent of the UV graft polymerization time after 30 min of UV irradiation, probably because the thicknesses of the grafted APFB polymer on the nylon surfaces are beyond the surface sensitivity of the contact angle measurement. Contact angle measurement is known to have surface sensitivity typically in the order of 1 nm or less.²⁶ Although the graft concentration of the fluoropolymer on the nylon film is not high when taking the full probing depth of the XPS technique into account, the graft polymerized layer must be restricted mainly to the outermost surface of the film. This surface microstructure can then account for the fact that the nylon surfaces after the UV-induced graft copolymerized with APFB are hydrophobic in nature, having contact angles typically in the order of 90° , which are characteristic of those of the fluoropolymers. In the case of the nylon surfaces from thermally induced graft copolymerization, the contact angles approach asymptotic values of about 60° after 30 min of graft polymerization, indicating that the graft concentration is too low, or the kinetic chain length of the surface graft is too short, to form a fully hydrophobic surface.

Figure 7 shows the moisture sorption behavior as a function of aging time at 25°C and 100% relative humidity for the pristine nylon-6,6 film, the thermally graft-copolymerized film (graft concentration $[F]/[N] = 0.07$), and the UV graft-copolymerized film (graft concentration $[F]/[N] = 0.25$). The graft-copolymerized films were pretreated with Ar plasma for 30 s and subjected to

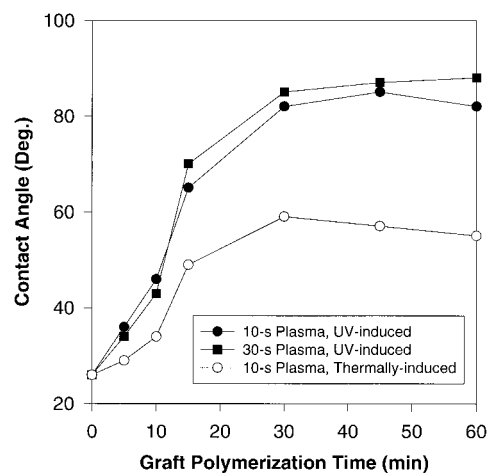


Figure 6 Dependence of the surface water contact angle on the graft polymerization time.

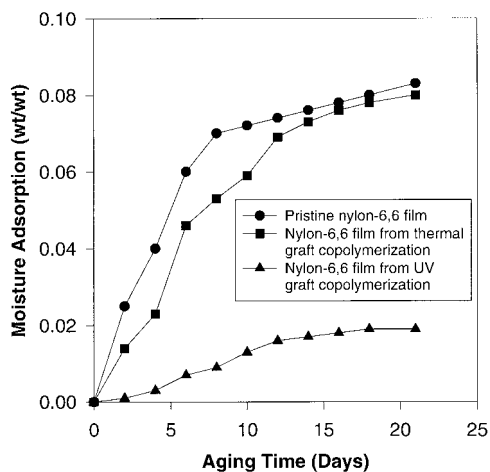


Figure 7 Extent of the moisture sorption as a function of aging time for the various nylon-6,6 films.

45 min of thermal graft copolymerization or 30 min of UV graft copolymerization. The maximum moisture sorption for the pristine nylon-6,6 film is about 8.5 wt % after 21 days of aging. During the first 10 days of aging, the moisture sorption increases rapidly and then gradually becomes saturated thereafter. After the UV-induced graft copolymerization with APFB, the extent of moisture sorption of the nylon-6,6 film decreases substantially from 8.5 to 2.0 wt % under the same test conditions and duration, suggesting that the hydrophobic graft layer has served as an effective surface barrier for moisture sorption into the nylon-6,6 film. The rate of moisture sorption is also much slower in the case of the UV graft-copolymerized film. For the thermally graft-copolymerized nylon films, the moisture sorption behavior is only marginally lower than that of the pristine film. The results suggest that the lower graft copolymerization efficiency of APFB by thermal induction has failed to provide an effective surface barrier to moisture sorption.

CONCLUSION

A hydrophobic polymer layer on the nylon-6,6 film as a surface barrier to moisture sorption was obtained by surface graft copolymerization of the argon plasma-pretreated nylon-6,6 films with a hydrophobic monomer, allyl pentafluorobenzene (APFB) at elevated temperature or under UV illumination. The plasma pretreatment introduced peroxides that were degraded into radicals to initiate the graft copolymerization of APFB on the

nylon surface. The graft copolymerization was affected by the plasma pretreatment time, as well as by the UV or thermal grafting time. The UV graft-copolymerized nylon-6,6 film exhibited a substantially lower extent of moisture sorption compared to that of the pristine films. However, the moisture sorption behavior for the thermally graft-copolymerized films was only marginally lower than that of pristine films. The contact angle measurements and XPS results suggested that the reduced moisture sorption for the UV graft-copolymerized nylon-6,6 film was attributable to the fact that a thin hydrophobic polymer layer with fairly complete coverage was formed on the nylon-6,6 film surface.

The authors thank Dr. Han Huisheng, Department of Physics, National University of Singapore, for XPS measurements.

REFERENCES

- Nelson, W. E. *Nylon Plastics Technology*; Newnes-Butterworths: London, 1976.
- Serpe, G.; Chaupart, N.; Verdu, J. *Polymer* 1997, 38, 1911.
- Chaupart, N.; Serpe, G.; Verdu, J. *Polymer* 1998, 39, 1375.
- Knopp, B.; Suter, U. W. *Macromolecules* 1997, 30, 6114.
- Lim, L. T.; Britt, I. J.; Tung, M. A. *J Appl Polym Sci* 1999, 71, 197.
- Vergelati, C.; Imberty, A.; Perez, S. *Macromolecules* 1993, 26, 4420.
- Chapman, T. M.; Benrashid, R.; Marra, K. G.; Keener, J. P. *Macromolecules* 1995, 28, 331.
- Honeychuck, R. V.; Ho, T.; Wynne, K. J.; Nissan, R. A. *Chem Mater* 1993, 5, 1299.
- Golub, M. A.; Lopata, E. S.; Finney, L. S. *Langmuir* 1994, 10, 3629.
- Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. *Macromolecules* 1986, 19, 1804.
- Ikada, Y. *Biomaterials* 1994, 15, 725.
- Beekow, T.; Kroner, K. H.; Anspach, F. B. *J Colloid Interface Sci* 1997, 196, 278.
- Ulbricht, M. *Reactive Funct Polym* 1996, 31, 165.
- Uyama, Y.; Kato, K.; Ikada, Y. *Adv Polym Sci* 1998, 137, 1.
- Ranby, B. In *Current Trends in Polymer Photochemistry*; Allen, N. S.; Edge, M.; Bellobono, J. R.; Selli, E., Ed.; Ellis Horwood: New York, 1995.
- Hoffman, A. S. *Macromol Symp* 1996, 101, 443.
- Kang, E. T.; Neoh, K. G.; Tan, K. L.; Uyama, Y.; Morikawa, N.; Ikada, Y. *Macromolecules* 1992, 25, 1959.

18. Zhang, X.; Kang, E. T.; Neoh, K. G.; Tan, K. L.; Kim, D. Y.; Kim, C. Y. *J Appl Polym Sci* 1996, 60, 625.
19. Wang, T.; Kang, E. T.; Neoh, K. G.; Tan, K. L.; Cui, C. Q.; Lim, T. B. *J Adhesion Sci Technol* 1997, 11, 679.
20. Wu, S.; Kang, E. T.; Neoh, K. G.; Han, H. S.; Tan, K. L. *Macromolecules* 1999, 32, 186.
21. Da, Y. X.; Griesser, H. J.; Mau, A. W. H.; Schmidt, R.; Liesegang, J. *Polymer* 1991, 32, 1126.
22. Zhang, J.; Cui, C. Q.; Lim, T. B.; Kang, E. T.; Neoh, K. G. *J Adhesion Sci Technol* 1998, 12, 1205.
23. Iwata, H.; Kishida, A.; Suzuki, M.; Hata, Y.; Ikada, Y. *J Polym Sci Part A: Polym Chem* 1988, 26, 3309.
24. Foerch, R.; Kill, G.; Walzak, M. J. In *Plasma Surface Modification of Polymers: Relevance to Adhesion*; Strobel, M.; Lyous, C. S.; Mittal, K. L. Ed.; VSP, Zeist: The Netherlands, 1994, p99.
25. Chan, C.-M. *Polymer Surface Modification and Characterization*; Hanser/Gardner: New York, 199.
26. Holmes-Farley, S. R.; Whiteside, G. M. *Langmuir* 1987, 3, 3120.