

Surface Modification Studies of Polyimide Films Using Rutherford Backscattering and Forward Recoil Spectrometry

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We followed the surface imide ring hydrolysis of fully imidized polyimide films by aqueous base solutions using Rutherford backscattering spectrometry. The hydrolysis reaction was studied using several different polyimide films including spun-cast and thermally imidized PMDA-ODA, Kapton-H, and Upilex-S films. The boundary between the modified layer at the surface and the underlying film is a sharp front behind which the conversion of the polyimide into poly(amic acid) is complete and ahead of which there is almost no hydrolysis. The modified layer grows linearly with the time it is exposed to the basic solution. The growth velocity increased strongly with increases in the temperature of the basic solution. Under the reasonable hypothesis that the growth of the modified layer is controlled by the kinetics of the hydrolysis of the imide ring at the interface, we extract an activation energy for this process in Kapton-H films of 60 kJ/mol as compared to 68 kJ/mol for Upilex-S. Using forward recoil spectrometry, we studied the amount of interpenetration when a second layer of deuterium-labeled poly(amic acid) was spun-cast onto the surface-modified PMDA/ODA film. We determined that the interface between the spun-cast layer and the base layer is broader when the modification depth is greater. The fracture energy of such an interface, as measured with a T-peel test, rises rapidly as a function of modification depth and saturates at a value ~20 times the value for an interface formed from PMDA/ODA polyimide with an unmodified surface.

Introduction

Polyimides are a class of polymers widely used in aerospace and electronic applications where good thermooxidative stability is required. Two of the polyimides most commonly used in electronics are PMDA/ODA (derived from polymellitic dianhydride (PMDA) and bis-(4-aminophenyl) ether (ODA)) and BPDA/PDA (derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and *p*-phenylenediamine (PDA)). Making multilayer structures of these polymers is difficult. PMDA/ODA has a T_g of 380 °C and BPDA/PDA has a $T_g > 500$ °C.¹ As a result, individual films of these polyimides cannot be thermally welded together by heating them above their T_g . Furthermore, most polyimides are not soluble in common solvents. Polyimides are generally prepared in two stages. First, a soluble precursor polymer such as a poly(amic acid) or a poly(amic ester) is synthesized. Films are then deposited from solutions of poly(amic acid) (PAA) or poly(amic ester) (PAE) and chemically or thermally treated to cause the film to convert to the final polyimide form. Multiple layer structures are generally prepared by sequentially spin-casting a film, thermally treating it, spin-casting the next film onto the first, and thermally treating the bilayer. The strength of the bond between the two layers depends upon the amount of intermixing between them. The interface

between these sequentially spun-cast layers will be very sharp and weak if the first film is fully imidized before the second film is deposited.^{2,3}

Many surface-treatment methods have been developed to increase the interfacial strength between both metals and polymers and a substrate polyimide film. These include various ion beam and plasma treatment methods⁴ using as starting gases water,⁵ argon,⁶ oxygen,⁷ and oxygen-fluorocarbon mixtures.⁸ These processes work by altering the chemical structure of the surface to cause chemical bonding at the interface and in many cases by roughening the surface of the film to cause mechanical interlocking with the next layer. A different approach was developed by Lee et al. In this process a surface layer of polyimide is converted into poly(amic acid).^{9–11} This modified layer can be penetrated by the next deposited layer. The molecular interdiffusion produces strong bonding between the layers that is not susceptible to environmental degradation.

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This paper presents a detailed study of the kinetics of the surface modification process as determined by Rutherford backscattering spectrometry. The effectiveness of a variety of alkaline solutions was compared for several polyimide films. The films included spun-cast films of PMDA/ODA, and the commercially available films Kapton-H (PMDA-ODA), and Upilex-S (BPDA/PDA). The broadening of the interface between two sequentially spun-cast films was measured using forward recoil spectrometry.

Experimental Procedure

Materials. The potassium hydroxide (KOH), cesium hydroxide (CsOH), rubidium hydroxide (RbOH), hydrochloric acid (HCl), acetic acid (CH₃CO₂H), and 2-propanol were all purchased from Aldrich Chemical Company. Kapton-H film was obtained from E. I. Du Pont de Nemours and Co. Upilex-S was purchased from UBE Industries. The spun-cast PMDA/ODA films were prepared using Ciba-Geigy's Probimide 9767, a meta isomer of the poly(amic ethyl ester) (*m*-PAE) of PMDA-ODA. The spun-cast films were imidized by slowly heating to 400 °C in a nitrogen-purged oven.

The Kapton-H differs from the film spun-cast from PAE and thermally imidized. It is cast from a PAA solution onto a moving web, chemically treated to cause imidization and then thermally treated to remove solvent and conversion chemicals. Due to the methods used in its manufacture, Kapton-H has a rougher surface and is significantly more ordered than a PMDA-ODA film spun-cast from solution and thermally imidized.¹²

Surface Modification Study Using Rutherford Backscattering. When polyimide is soaked in a solution of moderate basicity, it converts the polyimide into a polyamate salt as shown in Figure 1. Subsequent treatment with acid will displace the alkali-metal ion and convert the polyamate salt into poly(amic acid). If too strong a base is used, the main-chain amide linkage will be cleaved as well, resulting in molecular weight reduction. Some industrial processes use this hydrolysis reaction to etch vias in Kapton-H.¹³

We followed the procedure for surface modification outlined in the paper by Lee et al.,⁹ with the exception that we used a variety of basic solutions. We prepared 1 M solutions of KOH, CsOH, RbOH, and (CH₃)₄NOH. Small pieces of polyimide film, ~1 in. square, were dipped into the base solution for measured intervals of time. After removal from the base, they were rinsed twice in deionized water for 3 min, and then rinsed in 2-propanol. The films were then blown dry with nitrogen and placed in a desiccator. At this point the surface layer will be modified to form a polyamate salt. The metallic ions (K⁺, Rb⁺, and Cs⁺) are detectable using Rutherford backscattering spectrometry.

The RBS technique measures the metallic ions bound up in the polyamate salt. For the case of the (CH₃)₄NOH, there are no heavy ions to be detected. Therefore, we had to perform an ion-exchange reaction in order to analyze the samples. Treated samples are soaked in 1 M KNO₃ for 24 h, and K⁺ ions are exchanged for (CH₃)₄N⁺. The KNO₃ solution was changed once during this time period.

Acidification Reaction. In Lee's method^{9,10} the conversion of the polyamate salt into the poly(amic acid) is accomplished using either 0.2 M HCl or 1 M acetic acid. The base-treated and rinsed sample is dipped into acid solution

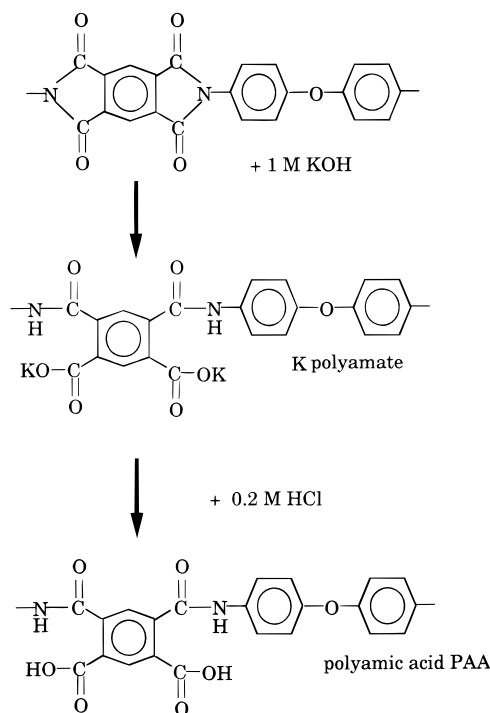


Figure 1. Surface-modification reaction. The base hydrolyses the imide ring to form a polyamate salt. The polyamate is converted to the poly(amic acid) through treatment with a weak acid such as a 0.2 M HCl solution or 1 M acetic acid.

for 5 min and then rinsed twice in DI water and once in 2-propanol. We used RBS to verify that the metallic ions were completely displaced by both the HCl and the acetic acid.

RBS and FRES Analysis. Ion beam analysis techniques were used to follow the hydrolysis reaction and to study the interdiffusion of a polymer film spun-cast onto the treated film. Rutherford backscattering spectrometry (RBS) was used to study the surface modification reaction by measuring the depth profile of potassium which is bound in the polyamate salt. (Cs or Rb are detected when RbOH or CsOH are the bases used.)

Forward recoil spectrometry (FRES)¹⁴ was used to determine the amount of interdiffusion which resulted when a deuterium-labeled PMDA-ODA polyimide precursor was spun onto the surface-modified PMDA-ODA polyimide layer. The tracer polymer was deuterium labeled on the oxydianiline group in order to provide contrast for FRES. The experimental diffusion profiles were analyzed using the solution to Fick's second law of diffusion for a sample consisting of a thin tracer layer on a semi-infinite substrate. From this fit an interpenetration distance $w = \sqrt{4Dt}$ was derived. It is important to realize that the interpenetration occurs only in the presence of the spin-casting solvent and that no separate value of the diffusion coefficient D can be inferred.¹⁵

Adhesion Sample Preparation and Testing. We prepared adhesion samples in order to correlate the thickness of the poly(amic acid) skin with measures of interfacial strength. Films were spun-cast from Ciba Geigy's Probimide 9767 onto glass plates. Probimide 9767 is a solution of the meta isomer of poly(amic ethyl ester) precursor (PAE) of the polymer PMDA/ODA in NMP. Due to the meta isomerism of the precursor molecule, the resulting films will be less ordered than a similar film cast from a poly(amic acid) or the para isomer of PAE.¹⁶ The films were slowly heated to 400 °C and held for 1 h in order to convert them into the polyimide of

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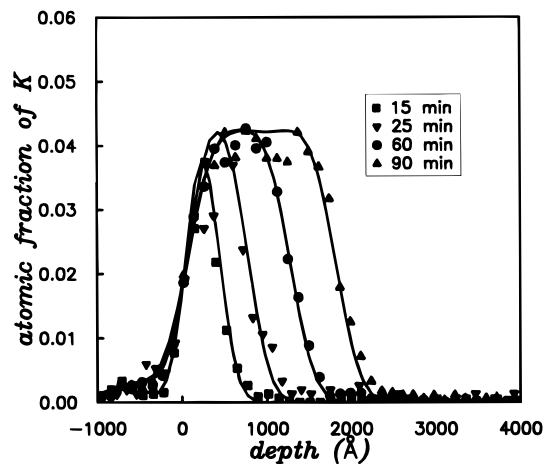


Figure 2. Potassium depth profiles from RBS overlaid to show the change in the potassium peak after the spun-cast and thermally imidized PMDA/ODA films are treated with 1 M KOH for various time intervals. There is a sharp interface between the K-rich region and the unmodified region which has almost no potassium. The height of the peak, when ratioed against carbon and oxygen peaks, indicates that there are two potassium nuclei per repeat unit of the polymer, corresponding to essentially full conversion of the surface region.

PMDA/ODA. After imidization, the film thickness was approximately 25 μm . The samples were dipped for varying time intervals into 1 M KOH solutions and rinsed twice in deionized (DI) water. The surface layer was converted into poly(amic acid) by dipping the sample into 0.2 M HCl acid for 5 min, rinsing twice in DI water, once in 2-propanol, and drying in a vacuum desiccator. A 1000 Å layer of gold was evaporated onto the region within $\frac{1}{2}$ in. of the edge of the film in order to act as a starter crack. A second layer of Probimide 9767 was then spun-cast onto the treated film. The sample was again heated to 400 °C for 1 h. The edges of the sample were scored with a razor, and then the samples were soaked in DI water for several hours. The films were then removed from the glass and dried in a vacuum oven at 80 °C. Strips 7 mm in width were cut. T-peel testing was performed using an Instron 1125 tensile testing machine at a cross-head speed of 0.5 in/min.

Results and Discussion

Growth of the Surface-Modified Layer on Spun-Cast PMDA/ODA Films. Figure 2 shows several potassium depth profiles, plotted as atom fraction versus depth, that have been obtained from corresponding RBS spectra. Each profile corresponds to a piece of the spun-cast and thermally imidized PMDA/ODA polyimide dipped into 1 M KOH for a different treatment time. It is clear from these data that there is a positive correlation between the length of treatment time and the depth of the modified layer. A K-rich layer of roughly constant composition forms and grows steadily with treatment time. The K composition of this surface layer indicates that there are two potassium nuclei per repeat unit of the polymer, corresponding to essentially full conversion of the surface region to the expected K polyamate salt. The interface between the underlying unmodified polyimide and the K-rich surface layer remains relatively sharp at all treatment times. These direct potassium depth profiles verify the assumption made by Lee et al.

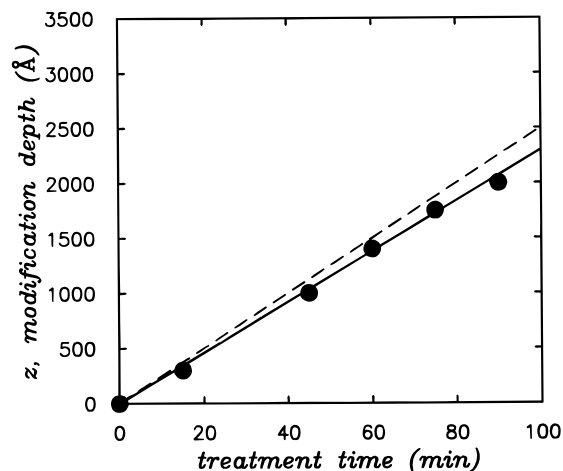


Figure 3. Thickness of the K-rich layer plotted as a function of time for the 1 M KOH treatment at room temperature on spun-cast PMDA/ODA films. The dashed line represents the data of Lee et al. on PMDA/ODA films cast from PAA. Their measurements of modification depth were made using external reflection infrared spectroscopy (ERIR).

that the surface modification treatment proceeds by formation of a surface-layer completely converted into polyamate salt, separated by a sharp interface from the underlying polyimide.

The thickness of the K polyamate layer after a KOH treatment at room temperature is plotted as a function of time in Figure 3. The depth of the hydrolyzed surface layer grows roughly linearly with time, consistent with the idea that the kinetics of growth is controlled by the chemical kinetics at the interface between the modified layer and the underlying polyimide. Also shown as a dashed line are the results of Lee et al.¹⁰ for substrates that were imidized from PAA and measured using external reflection infrared spectroscopy.

Films treated with 1 M CsOH and 1 M RbOH were etched by the solution. The thickness of the Cs- or Rb-rich layer did not grow with time but maintained a thickness of approximately 600 Å. We believe that the CsOH and RbOH solutions, at this concentration, hydrolyze both the imide ring and the amic acid, thus leading to etching away of the surface layer.

Treatment of the spuncast PMDA/ODA films with a lower solution concentration of 0.7 M CsOH produces very rapid growth of the polyamate layer as compared to KOH. The thickness of the Cs-rich polyamate layer for the CsOH treatments at room temperature is shown in Figure 4. While the depth of the modified layer grows linearly with time as for KOH, the rates are much faster, with a modified layer of 3000 Å produced within 10 min.

KOH Treatment on Kapton-H. For Kapton-H we discovered that in a 1 M KOH solution the hydrolysis of the imide rings occurs slightly slower on the "air" side of the film than on the "drum" side as shown in Figure 5. ("Air" and "drum" sides refer to the film positions during the initial film formation process where a solution was cast onto a moving web.) The overall rates of growth of the modified layer were $\sim 70\%$ faster than those observed for spun-cast films of PMDA/ODA thermally imidized from a *m*-PAE precursor.

Effect of Temperature Variations of the Basic Solution. At room temperature, the growth of the polyamate layer on both spun-cast PMDA/ODA films

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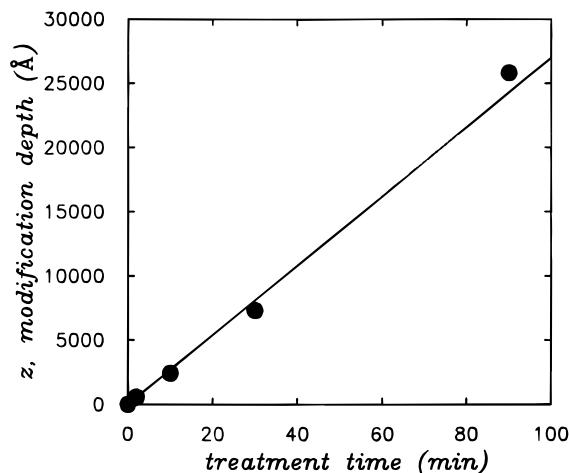


Figure 4. Thickness of the Cs-rich layer plotted as a function of time for PMDA/ODA films treated in 0.7 M CsOH at room temperature. The films were spun-cast from *m*-PAE precursors of PMDA/ODA and thermally imidized.

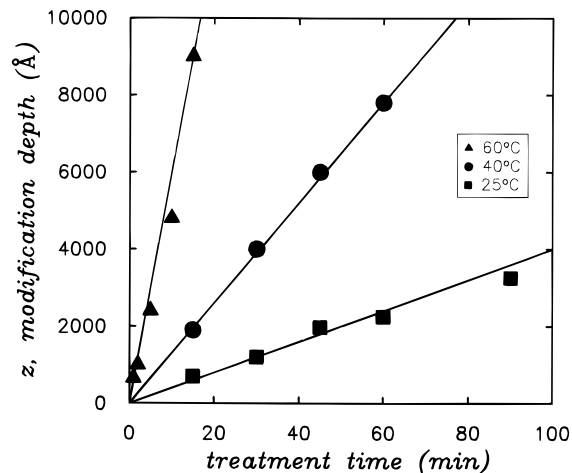


Figure 6. Modification depth of the air side of Kapton-H shown for a 1 M KOH treatment.

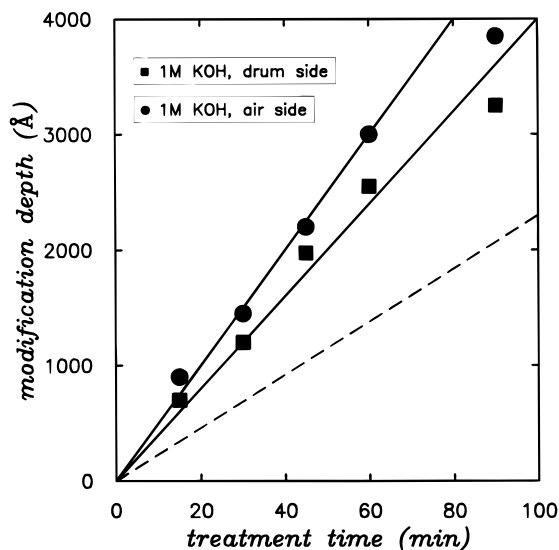


Figure 5. Modification rate of Kapton-H films differs slightly for the air and the drum side of the films. Comparable data for the spun-cast PMDA/ODA films are represented by the dashed line.

and Kapton-H films is rather slow. In fact a 25 min treatment is required to achieve sufficient conversion depths (~ 1000 Å) to reach maximum adhesion between the treated films and a layer of PMDA/ODA subsequently spun-on. For this reason, we have studied the effect of base bath temperature on the hydrolysis process. Plots of modification depth (Figure 6) versus time were linear for all temperatures, and a strong temperature dependence of the slope was observed. The time required to convert a surface layer of 1000 Å on the air side of Kapton-H with a 1 M KOH solution was ~ 25 min at 25 °C, ~ 10 min at 40 °C, and ~ 2 min at 60 °C. At temperatures greater than 60 °C etching of the films occurs. The logarithm of reaction rate was plotted as a function of reciprocal temperature in Figure 7. The activation energy for the propagation of the reaction front was found to be 60 kJ/mol.

(CH₃)₄NOH Treatments on Kapton-H. Due to concerns about ionic contamination, we sought to replace the KOH used in the base treatment with tetramethylammonium hydroxide ((CH₃)₄NOH). The effectiveness of the (CH₃)₄NOH in modifying the surface

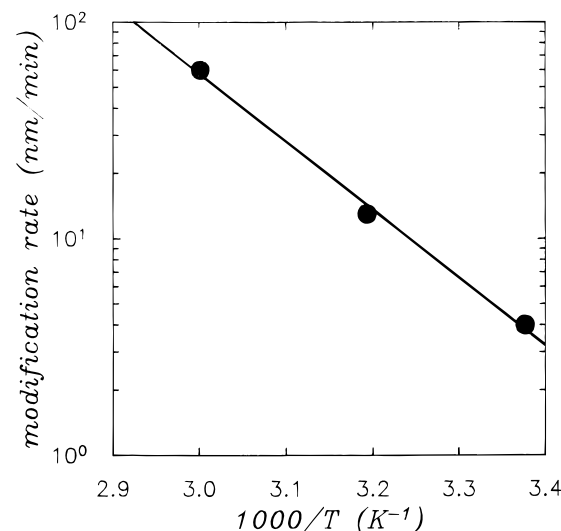


Figure 7. Modification rate of the air side of Kapton-H plotted as a function of reciprocal temperature for a 1 M KOH treatment. The activation energy for the propagation of the reaction front is determined from this plot and is 60 kJ/mol.

region is not directly observable with RBS since the salt formed contains no heavy elements. However, we were able to label the modified region with potassium via an ion-exchange reaction with KNO₃. Films untreated with (CH₃)₄NOH did not show a potassium peak after the ion exchange reaction. Figure 8 shows that for treatment of Kapton-H with 1 M (CH₃)₄NOH, the front between the polyimide and the modified polyamate layer moves at a slightly slower rate than for the 1 M KOH treatment. The measured activation energy for this hydrolysis process is 67 kJ/mol.

KOH Treatment on Upilex-S. Upilex-S is much more resistant to attack by base than is the Kapton-H film. Figure 9 shows that Upilex-S does not show significant surface modification at 40 °C after 90 min. At 60 °C the time required for hydrolysis of the imide ring to a depth of 1000 Å is ~ 60 min, while at 80 °C this modification can be achieved in ~ 12 min. While the movement of the front between the hydrolyzed and the unreacted regions is slow, the ratio of K to C and O is very close to that expected for formation of the K polyamate salt; no evidence of large-scale chain scission resulting in excess K is observed. Lee et al.¹⁰ shows a similar trend for the temperature dependence of the

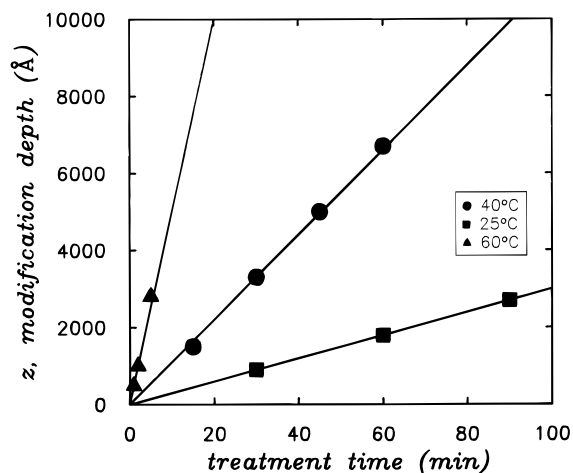


Figure 8. Modification depth of Kapton-H shown for a 1 M (CH₃)₄NOH treatment at 25, 40, and 60 °C. The activation energy of the hydrolysis process is 67 kJ/mol.

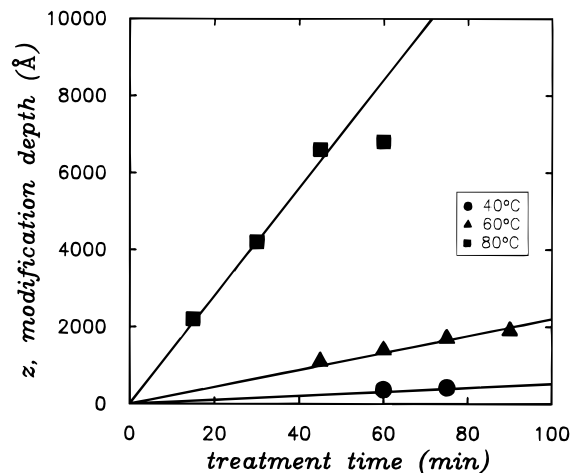


Figure 10. Modification depth of Upilex-S shown as a function of treatment time in a 1 M (CH₃)₄NOH solution at 40, 60, and 80 °C. The activation energy of the hydrolysis process is 74 kJ/mol.

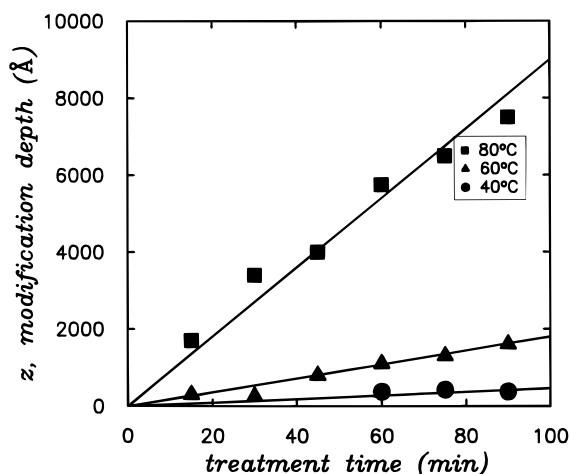


Figure 9. Modification depth of Upilex-S shown as a function of treatment time in a 1 M KOH solution at 40, 60, and 80 °C. The activation energy of the hydrolysis process is 68 kJ/mol.

adhesion for spun-cast films of BPDA/PDA. The activation energy for this process is 68 kJ/mol.

The relative slowness of the hydrolysis of Upilex-S relative to Kapton-H can be explained by several factors. The BPDA/PDA polymer will be more ordered than the PMDA/ODA polymers. The greater packing density will make it more difficult for the solution to penetrate and hydrolyze the imide groups. Our data are consistent with data gathered by Croall and St. Clair²⁰ on the changes in polyimide tensile strength and modulus after exposure to various bases. They found that the resistance to hydrolysis depended strongly on the dianhydride component of the polymer, with the PMDA-based polymers being the least resistant of the polyimides studied. The PMDA dianhydride has greater electron affinity than the BPDA dianhydride.²¹ In the PMDA/ODA polyimide, both imide groups will be on the same phenyl ring, and the PMDA-based imide will be a more electron-deficient structure than the BPDA-based imide. As a result the carboxyl groups will be more activated and more susceptible to nucleophilic attack.

(CH₃)₄NOH Treatments on Upilex-S. Figure 10 shows that tetramethylammonium hydroxide can effectively convert Upilex-S polyimide to polyamic acid. The rates are similar to those achieved using KOH. The measured activation energy was 74 kJ/mol.

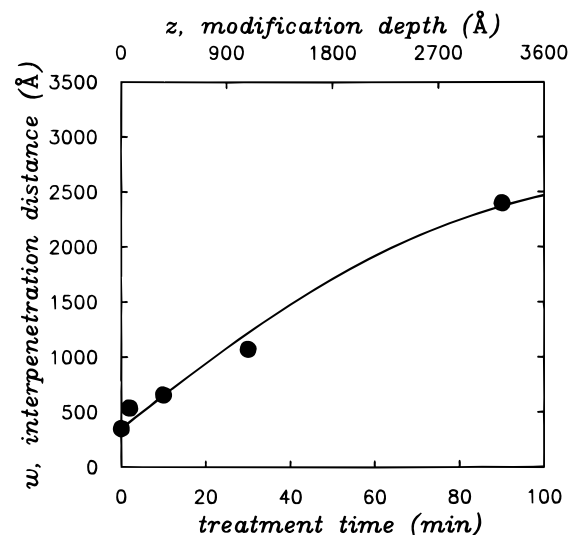


Figure 11. Interpenetration distance *w* of a spun-on on deuterium-labeled poly(amic acid) into a polyimide base layer plotted as a function of the modification time of the polyimide base layer in 1 M KOH. The base polyimide layers were spun-cast from *m*-PAE precursors of PMDA/ODA, thermally imidized, and treated with 1 M KOH and 0.2 M HCl at room temperature before the dPAA layer was deposited. The depth of modification is represented on the top axis to illustrate differences between the modification depth and the interdiffusion distance.

Interpenetration. To determine how the depth of the surface-modified layer affects the amount of penetration of a subsequently spun-cast layer into the modified layer, we measured the interpenetration distance using FRES. The samples of thermally imidized PMDA/ODA from *m*-PAE were treated with the KOH solution to form the polyamate salt and then rinsed and treated with the HCl solution to create a layer of polyamic acid. A polyamic acid of PMDA/ODA, which had been deuterium labeled on the ODA group, was spun-cast onto the surface-modified film. Forward recoil spectrometry (FRES) was used to measure the deuterium and hydrogen profiles. The interpenetration dis-

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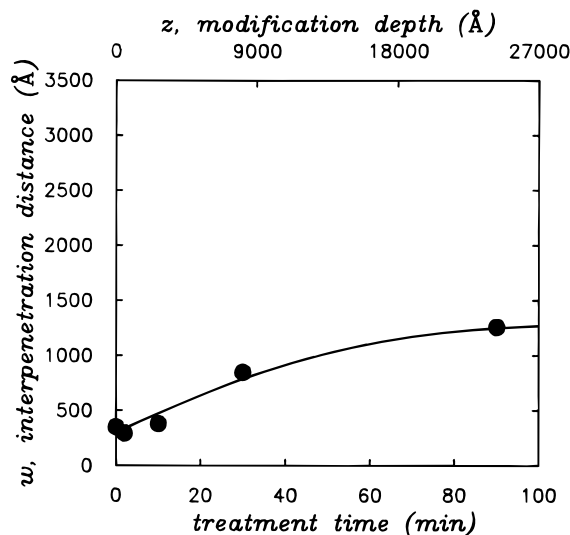


Figure 12. Interdiffusion distance w of a spun-on deuterium-labeled poly(amic acid) plotted as a function of the modification time of the polyimide base layer. The base polyimide layers were spun-cast from *m*-PAE precursors of PMDA/ODA, thermally imidized and treated with 0.7 M CsOH and 0.2 M HCl at room temperature before the dPAA layer was deposited. The depth of the modified layer is represented on the top axis to illustrate the large difference between the modification depth and the interdiffusion distance.

tance, w , of the deuterium-labeled precursor into the surface-modified substrate was derived from fits to the data and is plotted in Figure 11 as a function of the surface treatment time. As expected, we find w is larger when the modification time and thus the modification depth is greater. Except for the very short treatment times where the measured interpenetration distances are within the resolution of FRES, and thus misleadingly high, w is always less than the depth z of modification. The probable reason is that when the poly(amic acid) layer becomes thick, part of it is dissolved into the solution used to spin-cast the top layer and is spun off, yielding effectively a thinner poly(amic acid) layer to be penetrated by the deuterium-labeled precursor. It may be useful to partially imidize the new polyamic acid layer prior to deposition of the second layer to prevent dissolution of the surface layer without sacrificing the enhancement in adhesion. A layer of PAE spuncast onto a partially imidized base PMDA/ODA film will have excellent interpenetration.³

Figure 12 shows the dPAE interpenetration distance w measured on samples treated by 0.7 M CsOH. As long as w is larger than the depth resolution of FRES, it is always less than the depth z of modification. This inequality is presumably due to the dissolution of the thick poly(amic acid) layer discussed above. This discrepancy is more pronounced than in the case of the samples treated with KOH. Since a 1 M CsOH solution etches the film by hydrolyzing main-chain amide linkages as well as imide bonds, it is reasonable to expect that for a 0.7 M solution some chain scission will accompany the conversion of polyimide to poly(amic acid). The resulting reduction in molecular weight would make the shorter chains more susceptible to dissolution. The percentage of main-chain scission events apparently increases as the ionic radius of the cation increases. (Rb^+ and Cs^+ have larger ionic radii than K^+ .)

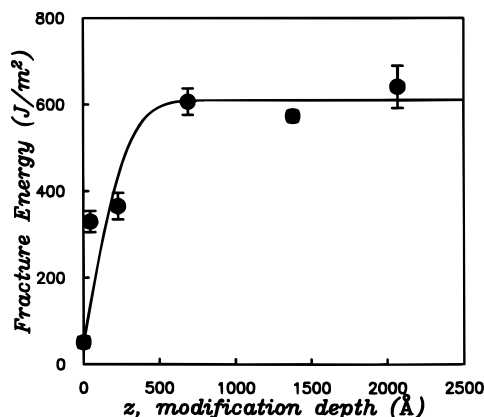


Figure 13. Interfacial fracture energy, as measured by a T-peel test, plotted as a function of the thickness of the modified layer. The base polyimide films were cast from *m*-PAE precursors of PMDA/ODA, thermally imidized, and modified with 1 M KOH and 0.2 M HCl at room temperature before deposition and thermal imidization of the second layer.

The amount of penetration of the dPAE tracer into a base polyimide layer is determined by several factors. These include the glass transition temperature of the base layer, the presence of a solvent, and the enthalpic repulsions between the two polymer types, as measured by the Flory interaction parameter, χ . In the situation where a poly(amic acid) is spun onto a PMDA/ODA or BPDA/PDA film, the glass transition temperature of the base layer is very high, $>350^\circ\text{C}$, and the interface will not broaden during subsequent heat treatments. The conversion of a surface layer of polyimide into poly(amic acid) assists penetration in several ways. First, a partially imidized layer will swell with NMP solvent faster and to a higher volume fraction than will the polyimide.¹⁸ The solvent enhances the mobility of the spun-on polymer into the base layer and dilutes the contacts between chemically different base and tracer molecules. Secondly, the conversion of a surface layer of polyimide into poly(amic acid) essentially reduces enthalpic repulsion between the two dissimilar polymers (the base polyimide and the spun-on tracer). The spun-on second layer (either a poly(amic ethyl ester) or a poly(amic acid)) is nearly identical with the poly(amic acid) structure of the modified region. χ is reduced to near zero in the PAA surface layer, and hence the spun-on second layer penetrates to the depth of modification.

Adhesion. Measurements of the interfacial fracture energy G_c were made on bilayer samples of PMDA/ODA (prepared from PAE) using T-peel tests and correlated with the depth of the surface modification and the interpenetration distance w . The results are seen in Figure 13, where the fracture energy rises rapidly as a function of modification depth and then saturates. (Data generated by Lee et al. for PMDA/ODA layers cast from polyamic acid shows a more rapid increase in G_c with modification depth than our data. In their work, a modified layer of 250 Å resulted in a 40-fold increase in adhesion from the untreated interface. The source of this difference is not well understood, although it could be related to the difference in surface morphology between polyimides cast from poly(amic acid) and those cast from *m*-poly(amic ethyl ester) precursors.) The plateau in G_c could be the result of the dissolution of the surface-modified layer as mentioned above or could be the result of chain scission events. The main-chain

amide bonds will also undergo hydrolysis, although they are less reactive than the imide rings. The localized reduction in molecular weight will alter the stress transfer. A study of the mechanical properties of PMDA/ODA-based polyimides showed that both the stress at break and the elongation at break were sensitive to the molecular weight.¹⁹ The stress at break increases with increasing M_w and levels off above $M_w = 30\,000$. Below $M_w = 10\,000$, the elongation at break falls rapidly. A small number of chain scission events by the base could significantly decrease molecular weight and affect the mechanical properties of the PMDA/ODA interface.

There have been suggestions that the crystallization of polyimide plays a role in poor adhesion. Lee et al.⁹⁻¹¹ hypothesize that the adhesion improvement gained through the surface modification process is due to the formation of an amorphous poly(amic acid) surface layer. This surface layer allows penetration by the spuncast PAA layer because of its amorphous character. While the amorphous character may be an important mechanism for PMDA/ODA formed from PAA, which tends to be crystalline, this mechanism seems unlikely for PMDA/ODA formed from *m*-PAE which never achieves much crystallinity even after annealing at 400 °C.¹⁶ Weakness of the interfaces between PMDA/ODA formed from *m*-PAE precursors after curing at 400 °C thus cannot be attributed primarily to crystallization. The effect of surface modification then seems unlikely to be primarily due to the amorphous character of the PAA layer. On the contrary, we attribute this increase in interpenetration not to the amorphous character of the polyamic acid but rather to the ease of swelling of the polyamic acid by the solvent and to the reduction of any enthalpic barrier to intermixing with the chemically different spun-on precursor.

Conclusions

Rutherford backscattering spectrometry (RBS) is a valuable technique for studying the surface-modification reaction of polyimide films where an aqueous basic solution is used to hydrolyze the imide ring to form a polyamate salt, and an acid treatment is subsequently used to convert the polyamate salt into a poly(amic acid). Depth profiles from Rutherford backscattering spectrometry demonstrated that there is a sharp front between the hydrolyzed and unmodified region. When the films are treated with 1 M KOH, the modified region has a constant potassium composition corresponding to roughly complete conversion of the imide rings into potassium polyamate salt. The reaction front moves

with constant rate into the bulk of the film. The rate of the movement of the reaction front was increased substantially by increasing the base solution temperature. The modification process was studied on spuncast PMDA/ODA as well as on Kapton-H and Upilex-S. The movement of the reaction front into Kapton-H is much faster than into Upilex-S. We attribute this difference to differences in the rate of hydrolysis of the imide bonds. The activation energy for the movement of the reaction front was found to be 60 kJ/mol for Kapton-H and 68 kJ/mol for Upilex-S in a 1 M KOH solution bath. The reaction of a nonmetallic base (1 M tetramethyl ammonium hydroxide) with Kapton-H and Upilex-S was followed by exchanging the tetramethylammonium ions with potassium ions and measuring the potassium depth distribution with RBS. RBS also demonstrated that both the acetic acid and hydrochloric acid treatments were effective in fully converting the potassium polyamate into poly(amic acid).

Forward recoil spectrometry showed that the amount of interpenetration of a second layer into the base polyimide film is strongly correlated to the depth of modification. The penetration is allowed because of enhanced solvent solubility in this layer of poly(amic acid) and because enthalpic penalties for penetration of a poly(amic acid) into the base layer have been removed for the depth of modification. The increase in the interfacial fracture energy will depend upon the modification depth. The interfacial fracture energy reaches a plateau at a value ~ 20 times that of the untreated film. Presumably this limit is due to some molecular weight degradation within the modified surface layer.

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