Scratch resistant polyimide coatings for aluminosilicate glass surfaces

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SCRATCH RESISTANT POLYIMIDE COATINGS FOR ALUMINOSILICATE GLASS SURFACES

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Several polyimide resins were tested as possible scratch resistant coatings for aluminosilicate glass centrifuge tubes. Tubes with siloxane pretreatments provided the best adhesion between the polyimide and glass surface. Resins synthesized with an alkoxysilane group incorporated into the polyimide chain also showed improved adhesion, but the results were not as significant as when the pretreatment was used. Elastic recovery and effective Young's modulus of the polyimide coatings were calculated from nano-scratching. The results indicate that polyimides with a lower modulus, and higher elastic recovery, protected the glass surface best, exhibiting compression of the coating layer. An example was poly-4-4'-oxydiphenylene pyromellitimide (PMDA-ODA), whereas the coatings with a high effective Young's modulus and low elastic recovery ruptured. An example of a failed coating was poly-4,4'-carbonyldiphenylene 3,3',4,4'-biphenylenetetracarboximide (BPDA-DABP) which had low amount of elastic recovery, high effective Young's modulus and a large amount of flaking during macroscratch testing.

INTRODUCTION

In this study we tested several polyimide systems as protective coatings on ion-exchange strengthened aluminosilicate glass. The coatings were applied to protect the glass from damage during normal use and

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handling. Damage to the glass such as chipping and abrasion has led to premature breakage.

Characteristics of polyimides, such as resistance to chemicals and excellent mechanical properties at high temperatures [1], make these structures desirable as scratch resistant coatings for glass. However, polyimides exhibit poor adhesion to glass because the adhesion is supported only by weak secondary forces, rather than much stronger primary forces (covalent bonds). Additionally, polyimides readily absorb water, up to 2−5% by weight [2], although most sources use a standard value of 3% [3]. Moisture will easily penetrate through the coating to the polyimide/glass interface and displace secondary bonding through hydrolysis, ultimately desorbing the coating [2]. The practice of using adhesion promoters with polyimides has been studied fairly extensively. In some cases the polyamic acid molecules are capped with siloxane end groups which will readily adhere to form Si-O-Si bonds to the glass surface. Another method is to precoat the glass substrate with an organo-siloxane compound, forming an attractive surface for polyamic acid bonding. In both cases the coupling agent bonds to a dianhydride site in place of an aromatic diamine. This effectively caps the molecule, ending growth.

Several polyimides were synthesized for testing as possible protective, scratch-resistant coatings for the aluminosilicate glass. Both adhesion promotion methods were used to improve film properties and integrity. Their protective abilities were determined from the results of environmental exposure, bulk scratch analysis, and nano-scratch analysis.

EXPERIMENTAL

Materials

Dianhydrides—3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), and 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA)—were purchased from Aldrich. The aromatic diamines 4,4′-diaminodiphenyl ether (ODA) and 4,4′-diaminobenzophenone (DABP) were also purchased from Aldrich Chemical Co., and p-phenylenediamine (PDA) from Fluka. The siloxane diamine 3-aminopropyltrimethoxysilane (APS) was purchased from Aldrich, as was the solvent dimethylacetemide (DMAc). APX-K1®, an organo-silane coupling agent, was purchased from Brewer Science. All chemicals were used as received. Corning COREX®II centrifuge tubes, composed of Corning Code No. 0331 aluminosilicate glass and strengthened *via* ion-exchange by Saxon

Glass Technologies, were donated by Saxon Glass. The glass composition, before ion-exchange, was SiO_2 (65%), Al_2O_3 (21%), Na_2O (8.7%), Li_2O (3.8%), MgO (0.8%) and K_2O (0.1%).

Synthesis of Polyamic Acid

Table 1 lists the polyamic acid systems formed. The polyamic acid was synthesized using 1.02 moles dianhydride to 1.00 moles aromatic diamine, with a total output of 15 grams polymer. The siloxane modified system had a different ratio, of 1.00 moles dianhydride, 0.95 moles aromatic diamine, and 0.05 moles aminopropyltrimethoxy silane (APS).

The syntheses were done in a three-neck, round-bottomed flask fitted with a rubber stopper, stirring rod with blade, and a nitrogen gas inlet. The flask was rinsed with acetone and deionized water and dried at 120°C for at least 24 hours. The vessel was purged with dry nitrogen before any addition of materials. The dianhydride powder was weighed and added to the flask, followed by 100 mL of DMAc. After a few minutes of stirring at a low rate, the aromatic diamine was slowly added. The flask was then sealed and purged with nitrogen. For the hybrid system, APS was added 30 minutes after the addition of the diamine, followed by another purge. Stirring was continued for 10−15 hours. The resulting viscous polyamic acids were stored at 35°C.

Coating of Glass

All centrifuge tubes were rinsed with deionized water and wiped clean with a fiber-free wipe. They were then hand dipped into hydrogen peroxide, rinsed with 2-propanol and set on a drying rack to eliminate all contact with their outer surfaces. All preparatory cleaning and actual coating was carried out in a class 10,000 clean room.

TABLE 1 Designation of Polyamic Acid Systems

Dianhydride	Aromatic Diamine	Siloxane (amine)
BTDA	ODA	
BTDA	PDA	
BPDA	DABP	
BPDA	ODA	
BPDA	ODA	APS
BPDA	PDA	
PMDA	ODA	

Hybrid coatings were applied to the cleaned glass tubes. Polyimide-only coatings were applied to tubes pretreated with APX-K1® (APX). After being dip coated, the APX films were cured for one hour at 200°C in an oven. Dip coating was used for all coating application to ensure uniform and reproducible coating thickness. Samples were coated using a DipMaster 201 from Chemat Technologies. The viscosities of the as-synthesized poly(amic acid) resins were too high for dipcoating. Therefore, 700 ml of DMAc was added to each as-synthesized system to reduce the viscosity. The initial concentrations were 0.150 g/ml. After dilution the concentrations were 0.019 g/ml. Eight glass tubes were fastened onto the dipping mechanism and dipped into the solution at a rate of 8 inches (20 cm)/min, held for 30 seconds, and removed at 10 inches (25 cm)/min. Immediately after dipping, the samples were dried at 80°C for 40 minutes in the dipcoater chamber. After applying the polyamic acid, an additional curing cycle was used to convert the polyamic acid to polyimide. The curing cycle for the polyimides was 90 minutes at 150°C, 60 minutes at 200°C, and 90 minutes at 250°C [4, 5]. Temperatures above 250°C were not used in order to avoid relaxation of the strengthened glass structure.

Analysis

Coating integrity was tested using several methods to emulate laboratory conditions. Separate sets of each coating were exposed to high humidity, solvent, concentrated acid, or thermal cycling. One set of tubes was placed in a humidity chamber at 85°C and 85% relative humidity for 13 days. A second set was heated to 300°C and held for 24 hours, followed by 24 hours at −15°C. The thermal cycle was repeated two times. A third set was immersed in concentrated H_2SO_4 and a fourth set in DMAc for 2.5 hours. All tubes exposed to these additional conditions were subsequently analyzed using the scratch tester and the results compared with earlier tests.

Scratch resistance tests were performed using a custom designed 45° scratch tester shown in Figure 1a. Two tubes of the same history—processing and coating system—were clamped into the instrument as displayed in Figure 1b. One was held on the moveable motor arm, while the second was clamped onto a hinged arm. The hinged arm was loaded with the desired amount of weight (100−700 g), and lowered so that the two tubes contacted each other at a 45° angle in the horizontal plane. The variable speed motor was used to slide the bottom tube back and forth nearly its entire length at a speed of about 2.5 cm/sec. The integrity of the coatings
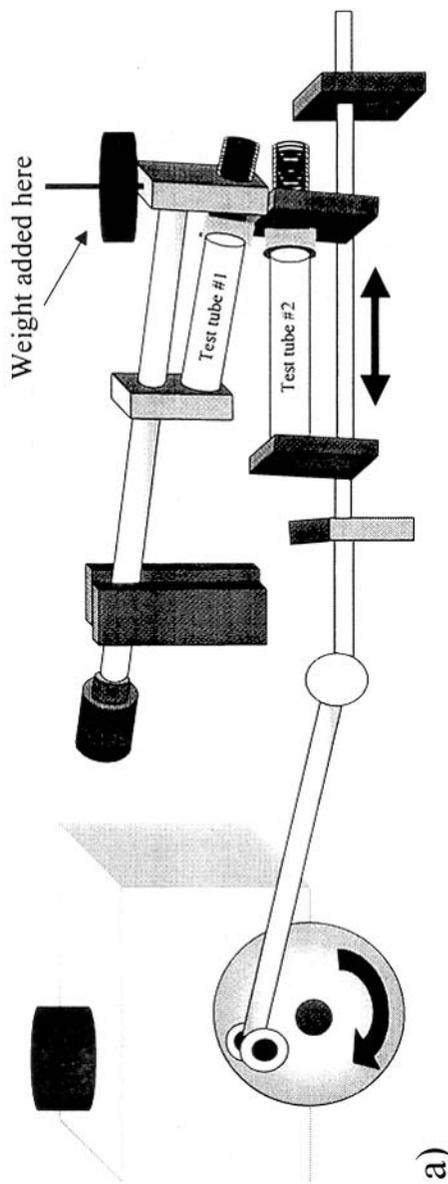
FIGURE 1 A) Schematic of the self-designed 45° scratch tester, B) with a schematic of the two tubes being tested (next page).

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Test tube #1

Test tube #2
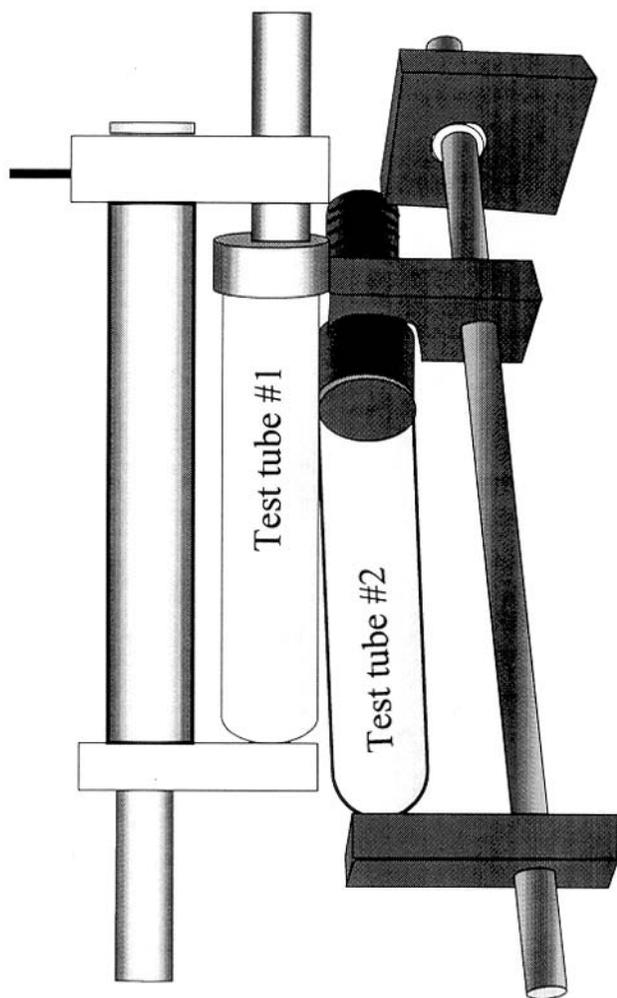
b)

FIGURE 1 (*continued*).

and glass substrates were monitored using an optical microscope. Alternative scratch testers, described in many published sources, use a diamond stylus or a typical hardness indentor [6, 7]. This study used another coated tube in the same manner that traditional glass bottle manufacturers test cold-end lubricious coatings to mimic actual usage conditions. In normal use, laboratory glassware could come into physical contact with anything ranging from the lab bench top to metal utensils to the floor. However, in the case of centrifuge tubes, one likely source of contact is another tube. Therefore, this study simply chose the object with the highest probability of being present when surface damage is caused. Failure was determined as whether a coating could stand up to itself; if not, it would be removed from further consideration.

Elastic modulus and percent recoverable deformation were calculated from nanoscratching data. The samples used in this test were standard glass microscope slides coated five times with polyamic acid, allowing for ten minutes of drying at 80°C between each coat. The coatings were subsequently imidized using the curing schedule given previously. The coatings had thickness of about 50-nm determined by optical interferometry and atomic force microscopy. Therefore, in order to analyze the material properties of these films, it was necessary to go to the nanoscale level. A Nano Indentor II from Nano Instruments was used with a Berkovich indenter. The indentor had the geometry of a three-sided pyramid. The leading edge for scratching was an edge as opposed to the flat triangular face. Both imaging portions were done at a load of 20 μN in order to avoid damage to the surface, much like contact AFM. Imaging was done before and after scratching to determine scratch depths for the different coatings. During scratching the normal load was increased at a rate of 7.5 μN/sec to a maximum of 600 μN while the sample was translated in the horizontal direction at 10 μm/sec. The scratch length was 800 μm. Additionally, unloading curves were produced so that effective modulus of elasticity (E_{eff}) values could be calculated. A typical scratch test experiment consisted of 1) approaching the surface, 2) indenting the sample at a load of 20 μN, 3) transversing a line at a load of 20 μN, 4) transversing the line in the opposite direction while ramping the load to 600 μN, 5) unloading the tip to 20 μN, 6) transversing the line again at a load of 20 μN, and 7) final unloading of the tip. The images were made during steps 3 and 6. Data for calculating the elastic modulus was collected during step 5 and the scratch was created during step 4. No further imaging of the topographical features was done on the samples after the nanoscratch testing.

RESULTS AND DISCUSSION

Scratch Test

The first set of scratch tests was conducted using the custom designed 45° scratch tester with applied loads of 100 to 700 g at 100 g intervals. Each pass was made on a fresh surface of both tubes. Uncoated, ion-exchange-strengthened glass and those with APX pretreatment only scratched at a load of 100 g. Several tested coatings showed no scratches at the glass surface up to loads of 700 g. Other coated tubes were scratched at lower loads; those that were scratched at loads less than 700 g were designated as failures.

As a consequence of the scratch tests, three major deformation behaviors were observed: flaking, plowing and ironing. The former two resulted in failure of the coating, while the latter did not. Flaking caused irregular-shaped chips of polyimide to pile up near the scratch path. The path itself had rough, poorly defined edges. Those coatings that plowed resulted in scratch paths with very sharp, well-defined edges and large pile-up regions at either end. The ironing behavior was defined by areas of surface compression within the scratch path, but no removal of coating material.

Coatings applied to glass without any siloxane adhesion promoter resulted in flaking and a large amount of scratching at loads as low as 200 g. The addition of a siloxane segment to the polymer structure (or as a tie-coating) greatly increased the adhesion and, therefore, the scratch behavior. However, there were some systems with the pretreatment that still exhibited flaking behavior, albeit to a lesser degree. Systems BTDA-ODA and BPDA-DABP with APX, and the hybrid BPDA-ODA-APS, showed flaking behavior. They also had scratches at the glass surface, but only at higher weights such as 600 or 700 g. System BPDA-PDA with APX was the only coating that was removed in a plowing fashion. This coating exhibited scratches to the glass surface at low weights. All coatings that displayed flaking or plowing behavior resulted in scratching at the glass surface. The remaining three systems, BPDA-ODA, PMDA-ODA and BTDA-PDA, all with APX tie-coats, exhibited the desired ironing behavior and protected the glass surface from scratching in nearly all cases up to 700 g.

Integrity Tests

The successful coatings, relative to their ability to protect the glass surface, were exposed to high humidity, thermal cycling or sulfuric acid immersion and then scratch tested. The coatings were BPDA-

ODA, PMDA-ODA and BTDA-PDA, all with APX tie-coats. The humidity test reduced the adhesion of the coatings, as indicated by lower loads needed to remove the polyimide from the glass. System BPDA-ODA scratched at a load of only 100 grams after exposure. The other two coatings scratched at only slightly lower loads than previously. The thermal cycling test was more destructive than humidity exposure. Again, BPDA-ODA failed at low loads. Additionally, BTDA-PDA scratched at only 200 grams. However, while system PMDA-ODA scratched at 300 grams with two passes, it provided protection up to 500 grams of load on single passes. Because of these results, only PMDA-ODA was used for acid and solvent soaking. No additional scratches were observed after the solvent soak, while there was further scratching at higher weights following the sulfuric acid immersion. Had the polyimide been cured above 300°C, the subsequent cross-linking would have greatly decreased the solubility in acid.

Nano-Scratching

Elastic recovery and the effective Young's modulus of five polyimide coatings were calculated from nano-scratching test data. This information was used to correlate mechanical behavior of the polyimide to scratch behavior of the polyimide as a coating.

As the test proceeded, firstly, an 800 μm long line on the sample surface was profiled using a Berkovich tip with a force of 20 μN ($\sim$2 mg), secondly, scratched at progressive loads up to 600 μN ($\sim$61 mg) and, thirdly, re-profiled at a force of 20 μN. This was repeated three times per sample. An example of the height profiles over the vector corrected lateral distance returned from a scan of the PMDA-ODA polyimide system is shown in Figure 2. The plot orientation shows the pre-scan (line-1) on the top, the scratch (line-2) on the bottom, and the post-scan (line-3) falling somewhere in the middle. Figure 2 is representative of the other samples.

The difference in height between the scratch depth and the post-scratch profile gives an idea of the amount of elastic recovery that occurred after the normal load was removed. Two plots showing the percentage of unrecovered *versus* recovered deformation for differently behaving coatings are given in Figures 3 and 4. Recovered deformation refers to the elastic recovery after nano-scratching. Unrecovered deformation refers to the lack of elastic recovery, and could be the result of flaking, plowing or permanent compression. There is a correlation between the coating's ability to protect the glass surface and the amount of elastic recovery. Those with higher elastic recovery protected the glass surface from scratching.
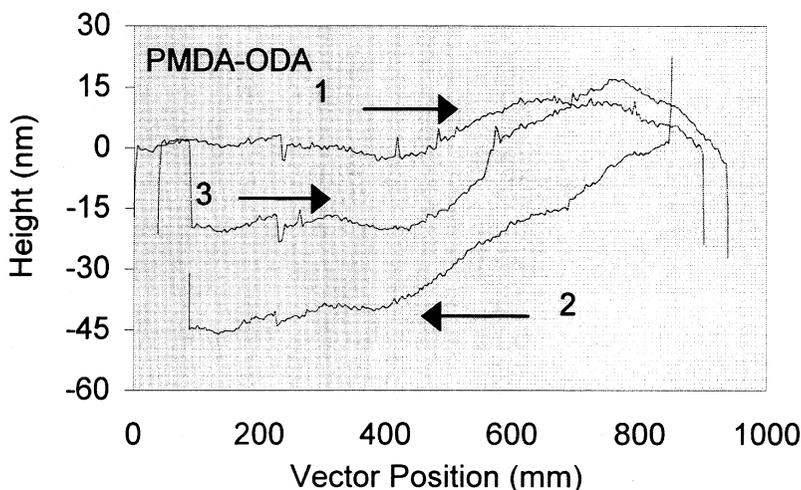
FIGURE 2 Nanoscratching profiles for pre-scan, scratch, and post-scan for system PMDA-ODA.

Figures 3 and 4 demonstrate the difference in nano-scratch behavior between two similar polymer structures, BPDA-ODA and BPDA-DABP. The two polyimides are identical in structure with the exception of the hinge group within the diamine. BPDA-DABP, with a carbonyl group, exhibited much less elastic recovery than BPDA-ODA, which possesses an ether oxygen link. Additionally, BPDA-DABP showed flaking behavior representative of chain scission. BPDA-ODA showed ironing behavior representing that the ether oxygen bonds stored energy during scratching and elastically recovered.

Effective Young's modulus (E_{eff}) values were calculated from the unloading portion of the nano-scratch test. At the end of each scratch, the tip was held stationary while the load was reduced from 600 μN to 20 μN. By graphing load *versus* depth in this region, the effective Young's modulus was determined. The effective elastic modulus is related to the elastic modulus (E) and the slope by the Sneddon equation, Equation (1).

$$E_{\text{eff}} = \frac{E}{1 - v^2} = \frac{S}{1.128\sqrt{A}}, \tag{1}$$

Here, S is the instantaneous slope of the unloading curve, v is Poisson's ratio and A is the area of contact between the indentor and the
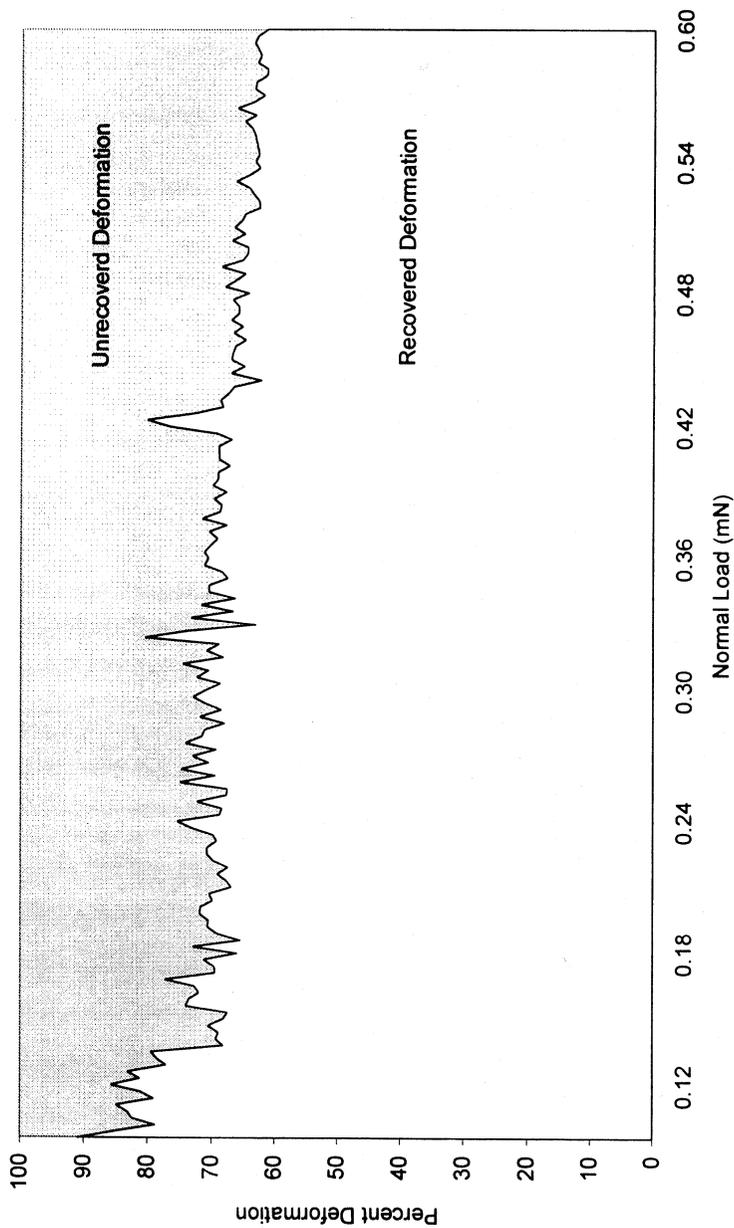
FIGURE 3 Nanoscratching data showing the percentage of unrecovered and recovered deformation in polyimide system BPDA-ODA.
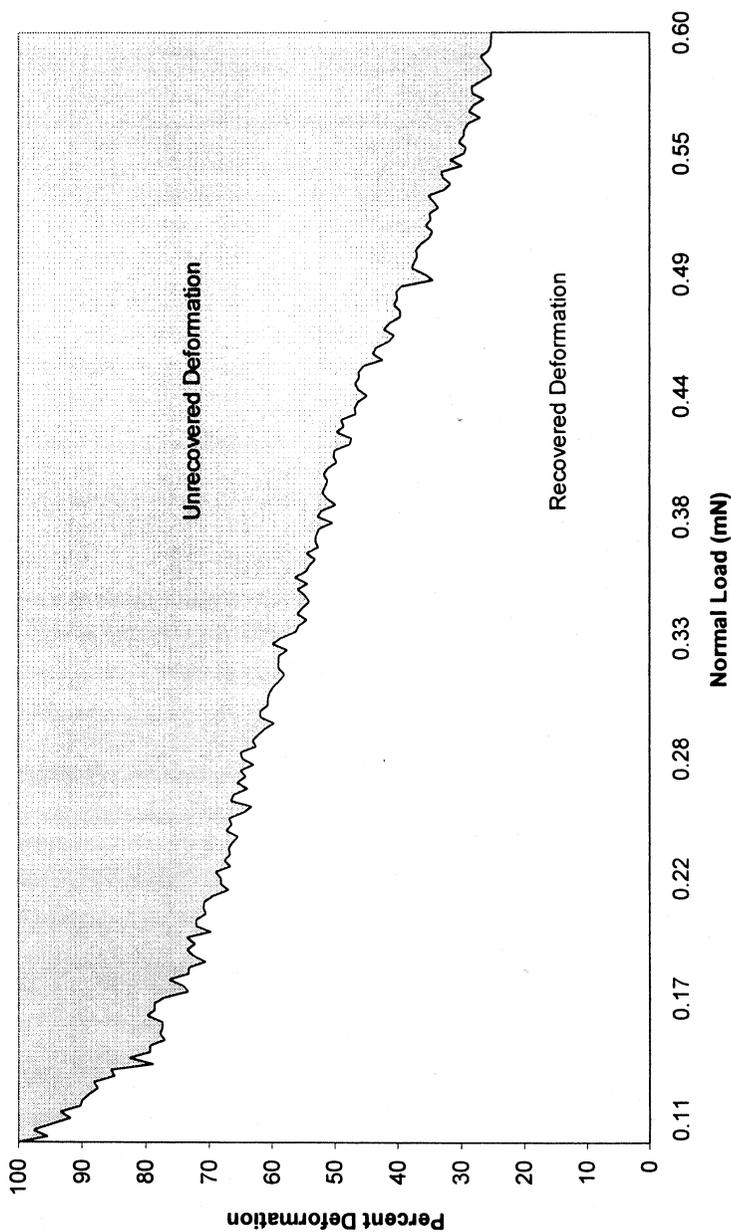
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FIGURE 4 Nanoscratching data showing the percentage of unrecovered and recovered deformation in polyimide system BPDA-DABP.

material [8]. The contact area is calculated from the depth of penetration and the tip geometry. Equation (2) shows the formula to calculate the area for a Berkovich indentor.

$$A = 24.56h_c^2 \qquad (2)$$

Here, h_c is described as the critical depth [9], and is different from the maximum depth ($h_{\max}$). The results for the E_{eff} calculations are shown in Table 2. A value for each replicate is given.

Statistically, there is no significant difference between the E_{eff} values for BPDA-DABP and BPDA-ODA. Similarly, there is no difference between BPDA-ODA-APS, BPDA-PDA and PMDA-ODA. However, the two groups are significantly different from each other. The low E_{eff} from PMDA-ODA could explain the desirable behavior during macroscratching tests. To recount, PMDA-ODA showed ironing behavior indicating that it was able to carry more stress through deformation without rupture. Therefore, PMDA-ODA deformed without failure at loads that caused other coatings to flake and chip.

In another case, the siloxane-capped hybrid polymer, BPDA-ODA-APS, also possessed a low modulus but performed poorly during scratch testing. This system had a lower modulus than the BPDA-ODA polyimide due to the plasticizing effect of the APS. The Tg of APS is about 120°C while the Tg of BPDA-ODA was measured in this study to be about 282°C. Addition of APS decreased the Tg to about 240°C, also decreasing the effective modulus. The poor macroscratching behavior was a result of an entirely different variable. It was concluded that the difference between the results of the two methods of adhesion promotion was not due to interfacial stress but, instead, was related to the number of sites available for covalent bonding. The use of a tie-coat creates an entire surface of organic sites for direct bonding to a polyamic acid macromolecule, and will cause chain scission to reduce the

TABLE 2 Effective Young's Modulus Values for Polyimide Coatings

		BPDA-DABP	BPDA-ODA	BPDA-ODA-APS	BPDA-PDA	PMDA-ODA
E_{eff} (MPa)	Rep 1	677.5	636.3	284	479.6	263.7
	Rep 2	589.6	532.7	254.6	355.4	262.6
	Rep 3	504.9	477.3	260.1	326.6	243.1
Mean (MPa)		590.7	548.8	266.2	387.2	256.5
Std. Dev. (MPa)		86.3	80.7	15.6	81.3	11.6

average molecular weight and increase the average molecular number [10]. Therefore, while macromolecules have been reduced in size, more molecules are adhered due to primary bonding. By capping the end of polyamic acid molecules with a finite number of APS groups the amount of covalent bonding has been predetermined. At the 5% siloxane diamine used in this study, it is also possible that the ether oxygen atoms in the ODA structure hydrogen bonded to the aluminosilicate glass surface. This type of bonding was shown to result in early failure.

CONCLUSIONS

Several polyimide systems were tested as possible scratch-resistant coatings for aluminosilicate glass substrates. Results from bulk scratch testing, nanoscratch testing, exposure to high humidity, solvents, acids, and thermal cycles were used to determine the performance of the coatings. Coatings applied to the glass surface without any adhesion promoter (organically modified siloxane) had very poor performance. Once a tie-coat of APX was applied to the glass surface, coating performance increased substantially. A coating system was also made by incorporating APS directly into the coating by capping the polyimide chains with the siloxane group. This coating did show improved performance, but it was still not as good as systems with the tie-coating. The poorer behavior of the siloxane-capped polyimides was attributed to the lower number of available bonding sites. The initial performance of the systems was determined by noting the scratch behavior and load from the bulk scratch tests. Systems that showed ironing behavior at higher loads passed the initial selection process.

Coatings tested prior to environmental exposure had bulk scratch values ranging up to 700 g without damaging the surface. After exposure to different environments, the performance of the coatings deteriorated. In some cases the deterioration was substantial, and in others it was minimal. While three separate systems were found to provide adequate protection, one polyimide, PMDA-ODA, continued to resist scratching after humidity, thermal cycling, and chemical resistance tests.

Elastic recovery and elastic modulus calculated from nanoscratching data were correlated to the bulk scratch behavior. It was found that coatings with a low elastic modulus and high percent elastic recovery also showed ironing behavior. Coatings showing ironing behavior permitted no damage to the glass surface at high loads using the bulk scratching method. Relative to the seven coatings tested, PMDA-ODA presented the best protective abilities, which were attributed to its higher elastic recovery coupled with the lower modulus.

REFERENCES

[1] Wu, K. H., Chang, T. C., Wang, Y. T. and Chiu, Y. S., Organic-Inorganic Hybrid Materials: I. Characterization and Degradation of Poly(imide-silica) Hybrids. *J. Polym. Sci., Part A: Polym. Chem.* **37**(13), 2275 (1999).

[2] Hu, D. C. and Chen, H. C., Humidity Effect on Polyimide Film Adhesion. *J. Mat. Sci.* **27**, 5262 (1992).

[3] Guastavino, F., Effect of Humidity on the Time to Breakdown of Polymers Subject to Partial Discharges. *Polym. Eng. Sci.* **38**(1), 119 (1998).

[4] Dimitrakopoulos, C. D., Kowalczyk, S. P., and Lee, K. W., Growth of ODPA-APB Polyimide Films using Molecular Beam Deposition, and their Characterization. *Polymer* **36**(26), 4983 (1995).

[5] Twite, R. L., The Role of a Functionalized Polyimide as the Reinforcing Agent in a Polyimide/Polybenzoxazine Molecular Composite. M.S. Thesis, Case Western Reserve University, Cleveland, OH, 1995.

[6] Li, K., Shapiro, Y. and Li, J. C. M., Scratch Test of Soda-Lime Glass. *Acta Mater.* **46**(15), 5569 (1998).

[7] MacGill, R. A., Yao, X. Y., Castro, R. A., Dickinson, M. R. and Brown, I. G., Poor Man's Scratch Tester. *J. Vac. Sci. Technol., B* **11**(5), 2856 (1993).

[8] Sneddon, I. N., The Relation Between Load and Penetration in the Axisymmetric Boussinesq Problem for a Punch of Arbitrary Profile. *Int. J. Eng. Sci.* **3**, 47 (1965). As cited in Strange, D. J. Micromechanical Properties of Glass in the Ge-Sb-Se System. M.S. Thesis, Alfred University, Alfred, NY, 2000.

[9] Jardret, V., Zahouani, H., Loubet, J. L. and Mathia, T. G., Understanding and Quantification of Elastic and Plastic Deformation during a Scratch Test. *Wear* **218**, 8 (1998).

[10] Linde H. G. and Gleason, T. G. Thermal Stability of the Silica-Aminopropylsilane-Polyimide Interface. *J. Polym. Sci., Polym. Chem. Ed.* **22**(11), 3043−3062 (1984).