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### Improved Process for Producing Well-Adhered/Abrasion-Resistant Optical Coatings on an Optical Plastic Substrate

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# IMPROVED PROCESS FOR PRODUCING WELL-ADHERED/ABRASION-RESISTANT OPTICAL COATINGS ON AN OPTICAL PLASTIC SUBSTRATE

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## ABSTRACT

A well-adhered and abrasion-resistant coating on a typical optical substrate [polymethylmethacrylate (PMMA)] can be achieved by polymerizing organosilane in a low-temperature polymerization process. The substrate surface can be initially modified with hydrophilic functionalities in a radio-frequency plasma of argon/water vapor mixture in the pressure range 0.05–0.15 mbar to attach hydroxyl functionalities covalently to the substrate surface, which act as “anchorage sites” for polymerizing organosilane. This modified surface is then coated with polyvinyltrimethoxysilane at a power loading in the 20–60 W range and a flow rate of monomer in the 0.7–2.0 cm<sup>3</sup>·min<sup>-1</sup> range. The polymeric films deposited in this manner on PMMA substrates consistently passed adhesion and abrasive tests even after prolonged storage and thermal cycling in boiling water for at least 10 minutes as exposure to extreme differential thermal expansion conditions. The posttreatment of deposited films with plasmas of inert gases for stress relief had an insignificant effect on peel-off tests and, therefore, it was believed to be not as important as surface modification prior to coatings. The optical properties are essentially not affected by the organosilane coatings irrespective of film thickness, and the coated substrates are virtually transparent above 400 nm.

## INTRODUCTION

An optically transparent film of organosilane can be formed by a low-temperature polymerization process. Such films can be used for guiding light waves in integrated optical circuits [1], in moisture-resistant antireflection coatings of alkali metal halide crystals [2, 3], and, in particular, in improving the durability of plastics [4-10]. Plasma-polymerized organosilanes are usually harder than conventional polymers, and these films are used to provide protective layers as transparent plastics. There are, however, some severe problems in obtaining well-adhered and abrasion-resistant optical coatings on plastics: 1) it is difficult to obtain good adhesion between a hard film and a soft plastic, and 2) ablation of some plastics often occurs in the reactive organosilane/carrier gas mixture.

The coating of synthetic optical components made from polyacrylics, polystyrene, and polycarbonates gained popularity during 1978 to 1983 by utilizing glow discharge (plasma) polymerization of various organosilanes and corrosive compounds to achieve optical substrate coatings that are particularly resistant to environmental conditions [4-11]. The plasma polymerization processes have yielded uniform, somewhat abrasion-resistant and optically-clear coatings of physical thickness up to 2  $\mu\text{m}$ . However, all failed to show strong adherence to various substrates as measured using the Scotch tape peel-off test [12]. Moreover, the adhesive qualities degenerated further on prolonged storage. Since these coatings can be used as antireflection coatings on plastic lenses, it is important to solve these shortcomings.

In this work, various radio-frequency (RF) plasma chemistries have been examined in attempts to produce better quality thin film coatings. Production of abrasion-resistant coatings proved relatively straightforward by a number of processes, but the adherence of films, particularly on storage (and thermal cycling), proved inadequate. This problem has been overcome by developing a new three-part RF plasma-based process for surface activation:

1. Removal of low molecular weight "surface contaminants"
2. Crosslinking modifications of the plastic surface
3. Chemical modifications with groups as "anchorage sites" for the thin coating

This three-part process is a subset of the three-step coating procedure; namely, surface activation, polymerization, and posttreatment for well-adhered and abrasion-resistant films.

## MATERIALS AND METHODS

### Preparation of Coated Plastic Substrates

Untreated polymethyl methacrylate (PMMA) pieces cut to size (25 mm  $\times$  25 mm  $\times$  2.5 mm) were heavily contaminated with dust and particles, making them unsuitable for plasma deposition of well-adhered and abrasion-resistant films. The samples were cleaned by subjecting each to a nitrogen gas jet followed by spraying with organic liquid (DuPont Freon-113, 1,1,2-trichlorotrifluoroethane) before introduction into the plasma reactor. High-pressure spraying with Freon caused some problems due to surface cooling, resulting in undesirable water vapor condensation

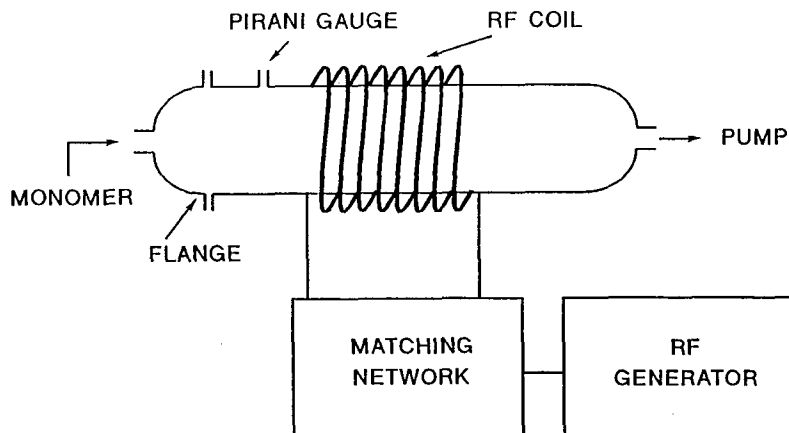


FIG. 1. Schematic of RF plasma coating system.

which can leave surface heterogeneities. However, this was prevented by spraying Freon in a dry nitrogen atmosphere.

### Monomers and Gases

All chemicals (vinyltrimethylsilane, vinyltrimethoxysilane, hexamethyldisilazane, xylene, vinylmethylethoxysilane, vinylpyrrolidone, dimethyldiethoxysilane and hexafluorobenzene) employed for coating the plastic substrates were first purified by vacuum distillation and subsequently degassed on a grease-free vacuum line by alternate freeze-thaw cycles.

Standard cylinder gases (BOC Ltd.) were used without further purification.

### Plasma Configuration

The reactor configuration (Fig. 1) used for the coatings of plastic substrates was connected to a vacuum line of grease-free construction pumped by a  $100 \text{ L} \cdot \text{min}^{-1}$  two-stage rotary pump. Pressure was monitored by a Pirani gauge, and the gas or the monomer vapor was introduced into the system via a leak valve at the required pressure (0.15 mbar). A liquid nitrogen trap was incorporated into the system to prevent backstreaming of rotary pump oil and to assist low pressure by collecting the vapor in a trap.

Plasmas were excited by a 13.56-MHz RF generator (EN1 Model ACG3) capable of delivering a power output to 350 W in a continuous mode. The generator was matched to the external inductive load via an impedance network. This network served to match the external load to the output impedance of the generator, thus ensuring maximum power transfer to the external circuit and protecting the generator.

The energy input per unit mass of monomer is a significant parameter in determining the properties of polymeric films on PMMA substrates. Thus, in general, a highly crosslinked (dense and brittle) polymeric layer is obtained when the following equation is satisfied:

$$W/FM = 10^9 \text{ to } 10^{11} \text{ J/kg}$$

where  $W$  = power input (watts)

$F$  = flow rate (moles per second) at standard temperature and pressure

$M$  = molecular weight of monomer (kg)

A relatively less dense coating is obtained when the  $W/FM$  value is in the  $10^7$  to  $10^8$  J/kg range.

Thus for vinyltrimethoxysilane monomer at  $F = 1.0 \text{ cm}^3 \cdot \text{min}^{-1}$  and  $W/FM = 3 \times 10^8 \text{ J/kg}$ , the input power would be approximately 30 W to obtain a fairly dense film of approximate thickness  $0.5 \mu\text{m}$  in 40 minutes, with good adhesion and abrasion-resistant characteristics. Polymeric films obtained at high-power loading are colored and adhere weakly to the PMMA substrate while the abrasion resistance remains effectively unchanged. A variety of monomers and polymer deposition methods has been utilized to achieve well-adhered and abrasion-resistant films within the "Scotch tape specification."

### Synthesis of Polymeric Films in Plasmas

The polymeric films on plastic substrates were obtained via a glow-discharge polymerization excited in a monomer vapor at preset conditions. The typical procedure for coating the substrate consisted of three steps, namely, surface activation, polymerization, and posttreatment. Between each subsequent step, the sample was centrally located and the reactor evacuated to  $10^{-4}$  mbar.

*Surface Activation.* The surface was activated using an RF plasma generated in an inert gas under preset conditions. This process was considered important for the surface modification of PMMA substrate by crosslinking and removing low weight molecules, and increased the wettability of the surface, thus facilitating the adhesion of plasma-deposited films.

*Polymerization.* This was effected while the activated substrate was in the plasma reactor under vacuum. The process in a selected monomer was initiated by an EN1 generator operating in a continuous mode for 40 minutes at preset conditions. In this way, films of a known thickness ( $\sim 0.5 \mu\text{m}$ ) were obtained.

*Posttreatment.* The polymer-coated plastic substrate in the evacuated reactor was then subjected to argon plasma at higher power-loadings for a few minutes. This caused further crosslinking of the interface [13, 14].

### Abrasion Resistance

The abrasion resistance of coated and uncoated substrate was tested with a rubber eraser in essentially the manner prescribed by US Military Specification MIL-E-12397B where a stylus is drawn repeatedly under pressure across a sample to produce a series of scratches. Visual inspection of the abraded surface for damage, as suggested in the specification, was considered sufficient.

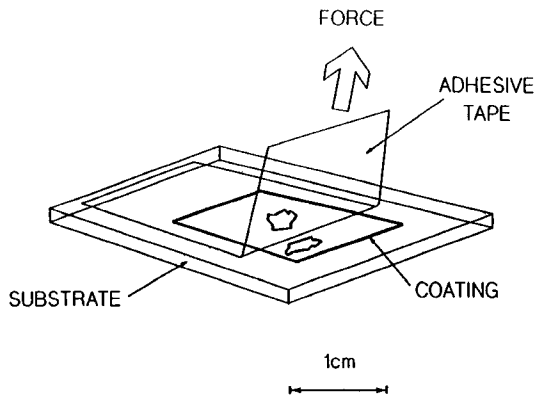


FIG. 2. Schematic of Scotch tape test.

### Adhesion of the Coatings

The adhesion of the abrasion-resistant coatings to PMMA substrates was tested with fresh Scotch tape (Type 51, 3M Industrial Products Limited). The tape was stuck to the coated film and then peeled off, perpendicular to the substrate, to see if the film adhered to the substrate or was torn off together with the tape. This is schematically shown in Fig. 2. The test is essentially qualitative, indicating only either success or failure.

### Optical Properties of Polymeric Films

Optical micrographs of plasma-deposited films on PMMA substrates for abrasion resistance and adhesion tests were obtained by using a Nikon Labophot-2 with the aid of Nomarski differential interference contrast.

A Pye Unicam PU8800 ultraviolet/visible spectrophotometer was used for optical characterization of coated films.

## RESULTS AND DISCUSSION

It is convenient here to present only representative examples of a variety of monomers explored for coatings on PMMA substrates. Table 1 indicates a number of monomers were used for plasma polymerization on PMMA substrates. The coatings in Table 1 were applied without surface activation and posttreatment by plasmas. Vinyltrimethoxysilane and vinyltrimethylethoxysilane were found to form the most desirable films, while the other monomers were observed not to form films at all. Vinyltrimethoxysilane combined high abrasion resistance and adhesion with optical clarity, and this particular monomer was therefore selected for the plasma coatings of PMMA substrates.

The PMMA substrates in Table 2 were pretreated with various excited gases for surface activation before plasma depositing polymeric silane films. The polymer-coated plastic substrate was not subjected to a plasma for posttreatment. The

TABLE 1. Coatings on PMMA Substrate (flow rate =  $1.0 \text{ cm}^3 \cdot \text{min}^{-1}$ , pressure = 0.15 mbar, duration = 40 minutes)

	Power, W	Thickness, $\mu\text{m}$	Remarks
Vinyltrimethylsilane	20–60		Powder formed. No adhesion. Poor stability
Vinyldimethylethoxysilane	20–60	0.5	Sporadic adhesion. Good durability. High deposition rate.
Dimethyldiethoxysilane	20–60		No polymerization. No deposition.
Hexamethyldisilazane	20–60		Very low deposition rate. Tenacious adhesion. Poor durability.
Vinyltrimethoxysilane	20–60	0.5	Sporadic adhesion. Good durability.

substrate surface modified with hydroxyl functionalities in a plasma of argon/water vapor mixture revealed very good adhesion and abrasion resistance properties.

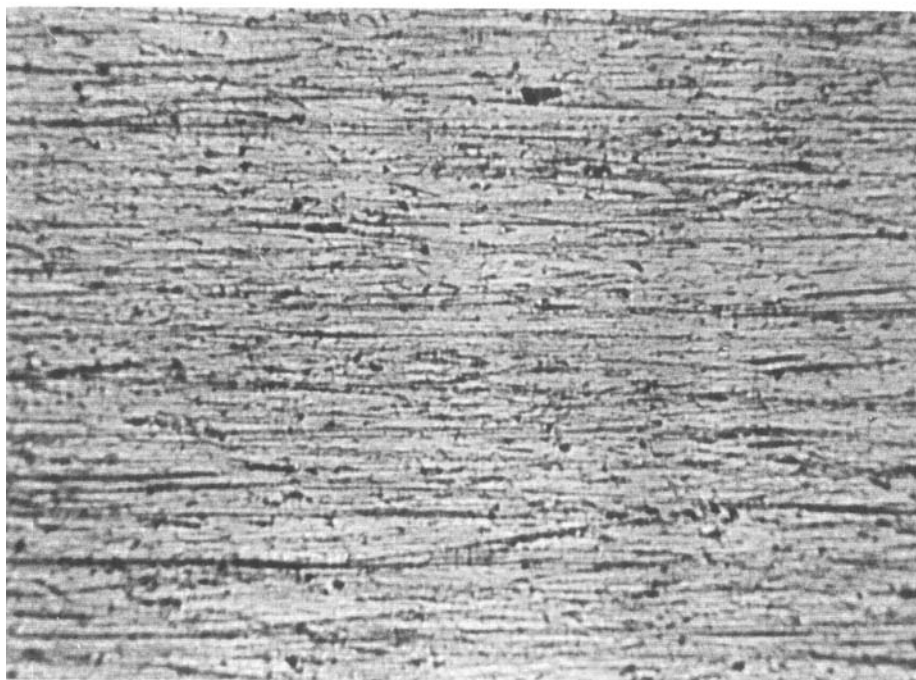
Tables 1 and 2 clearly indicate that the history and surface activation of plastic substrates are very important parameters for good adhesion and abrasion resistance of plasma-deposited films. Different levels of water and low molecular weight initiator molecules, initially present at the surface of the PMMA substrate, are believed to be mainly responsible for poor adhesion and the indicated irreproducible results. When the PMMA substrate was coated with polyvinyltrimethoxysilane to a depth of approximately  $0.5 \mu\text{m}$ , the surface abrasion resistance properties investigated by the scratch method in Fig. 3 were satisfactory immediately after coating, but the peel-off test for adhesion failed after a few days. However, this problem was circumvented to the best of our knowledge by removing the low weight molecules on the surface, modifying the surface by crosslinking to a depth of approximately

TABLE 2. Coatings of Polyvinyltrimethoxysilane on PMMA Substrate (flow rate =  $1.0 \text{ cm}^3 \cdot \text{min}^{-1}$ , pressure = 0.15 mbar, polymerization power = 30 W for 40 minutes, duration = 0.5–5 minutes)

Surface activation gas	Power, W	Remarks
Helium	10–40	Sporadic improvement in adhesion. Good durability.
Argon	10–40	Sporadic improvement in adhesion. Good durability.
H <sub>2</sub> O	10–40	Poor adhesion. Good durability.
Air	10–40	Poor adhesion. Good durability.
Argon/water vapor	10–100	Very good adhesion. Good durability.



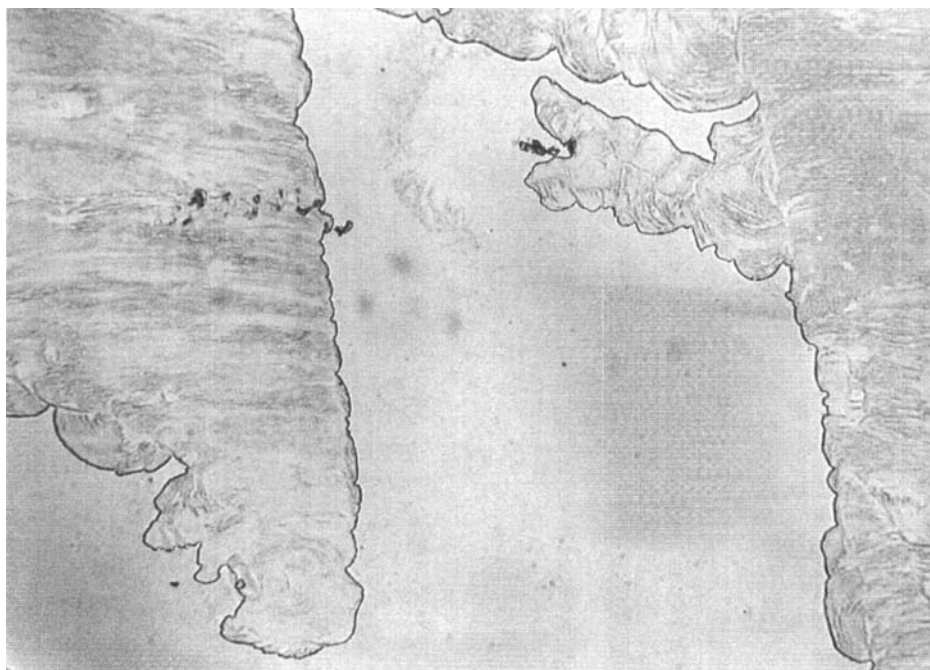
A



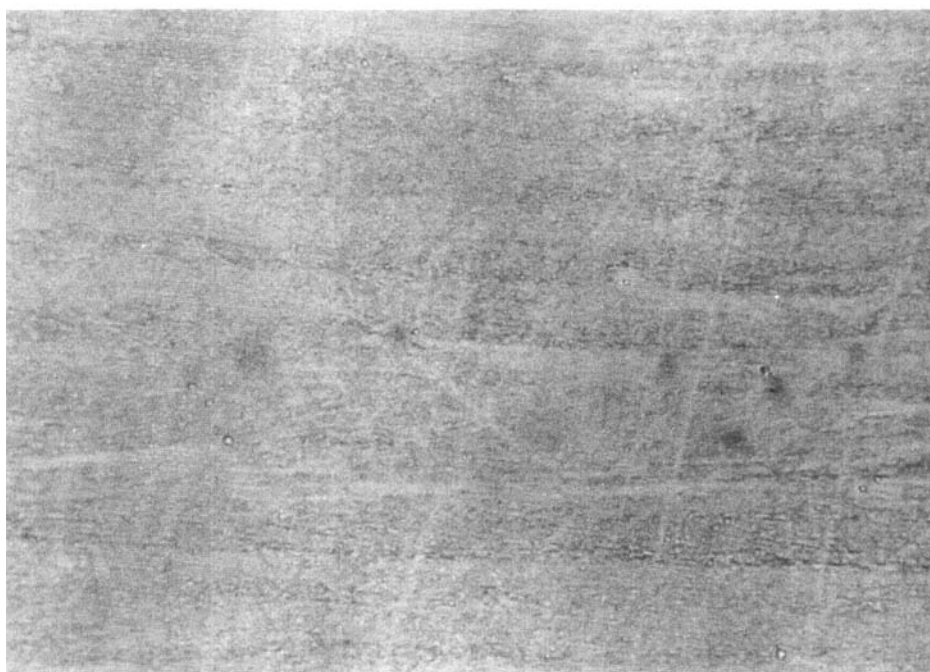
B

FIG. 3. Optical micrographs of a plasma-coated film of polyvinyltrimethoxysilane (A) and uncoated PMMA substrate (B) after performing abrasion resistance tests.





A



B

FIG. 4. Optical micrographs of plasma-coated films of polyvinyltrimethoxysilane onto PMMA substrates with poor adhesion (A) and good adhesion (B) after performing peel-off tests.

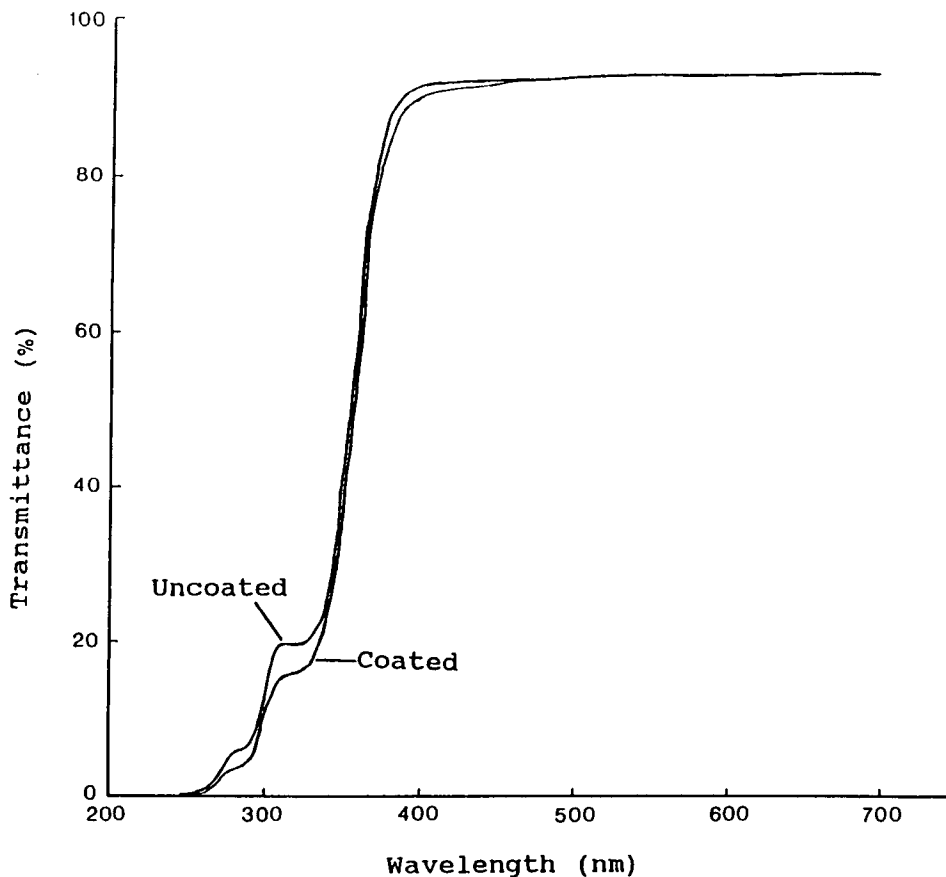


FIG. 5. Spectral transmittance of a plasma-coated film of polyvinyltrimethoxysilane and uncoated PMMA substrate.

1  $\mu\text{m}$ , and attaching the hydrophilic functionalities in a plasma generated in an argon/water vapor mixture. Argon was bubbled through deionized water at room temperature, thus saturating the inert gas with water vapor. Then the argon/water vapor mixture at 0.1 mbar was excited by the RF field in order to attach the hydroxyl moieties covalently to the substrate surface so that they acted as "anchorage sites" for polyvinyltrimethoxysilane. This modified surface, initially centrally located in the plasma reactor, was then coated with polyvinyltrimethoxysilane in a plasma of vinyltrimethoxysilane. The pretreatment of PMMA substrates using a plasma generated in an argon/water vapor mixture in the 0.05 to 0.15 mbar pressure range has provided high levels of hydroxyl functionalities as "anchorage sites" whereas the plasma of water vapor alone revealed poor adhesion.

The polymeric films of organosilane can be satisfactorily formed at power loadings in the 20 to 60 W range with flow rates of monomer in the 0.7 to 2.0  $\text{cm}^3 \cdot \text{min}^{-1}$  range. The silane coatings deposited in this manner on argon/water plasma-treated PMMA substrates consistently passed the adhesion and abrasive resistance test so that not even small fragments (visible to the naked eye) of silane

film adhered to the Scotch tape on removal (Fig. 4). Furthermore, the coated samples were exposed to extreme differential thermal expansion conditions by boiling in water for at least 10 minutes. Again, very good adhesion characteristics were observed and there was no evidence for any "peel-off" effect after performing the test. The silane coatings deposited on argon/water plasma-treated substrates were subjected to plasma of different inert gases, preferably argon and helium, for further crosslinking of the interface [13, 14]. This posttreatment caused very little change in adhesion and abrasion resistance properties. It can therefore be concluded that surface activation of PMMA is a prerequisite for good adherence of films.

Figure 5 shows the spectral transmission of a plasma-coated film of polyvinyltrimethoxysilane and uncoated PMMA substrate. The optical properties are essentially not affected by the silane coatings irrespective of film thickness, and the coated substrates are virtually transparent above 400 nm.

The conventional approach in the scientific and patent literature for adhering films to substrate surfaces emphasizes the removal of water by a variety of methods: 1) heating the substrate in an oven under vacuum [15] and 2) treating with a glow discharge (plasma) of corrosive compounds such as boron trifluoride [8, 10]. Here, a novel approach has been developed to increase the level of covalently linked hydroxyl functionalities at the substrate surface by introducing external hydroxyl functional groups and by binding the existing noncovalently bound water molecules in the substrate structure. This particular method of surface modification appears to show significantly enhanced adherence of films on the substrate surface compared to previously known methods. It also has the significant advantage that it can be applied to a variety of organic polymers and inorganic surfaces whereas previous protocols tend to be limited in use to particular polymers.

## CONCLUSION

Various RF plasma chemistries have shown that well-adhered, abrasion-resistant, and optically-transparent thin films of silane can be obtained on organic polymers by pretreating the plastic substrates with a plasma of argon/water vapor mixture. The coatings deposited on argon/water plasma-treated PMMA substrates consistently passed the adhesion and abrasion resistance tests even after exposing them to extreme differential thermal expansion conditions by boiling in water for at least 10 minutes. The posttreatment with plasmas of rare gases had very little effect on adhesion and abrasive properties.

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