

PLASMA-POLYMERIZED COATING FOR POLYCARBONATE: SINGLE-LAYER, ABRASION RESISTANT, AND ANTIREFLECTION

Theodore Wydeven
NASA Ames Research Center
Moffett Field, California 94035

ABSTRACT

Plasma-polymerized vinyltrimethoxy silane films were deposited on transparent polycarbonate substrates. The adherent, clear films protected the substrates from abrasion and also served as antireflection coatings. Post-treatment of the vinyltrimethoxy silane films in an oxygen glow discharge further improved their abrasion resistance. The coatings were characterized by elemental analysis of the bulk, ESCA analysis of the surface, transmission, thickness, abrasion resistance, haze, and adhesion. This patented process is currently used by the world's largest manufacturer of non-prescription sunglasses to protect the plastic glasses from scratching and thereby increase their useful lifetime.

INTRODUCTION

Traditionally, ground and polished tempered glass was the material of choice for manufacturing sunglass lenses. However, in recent years the many virtues of polarized and other plastic lenses have come into sharp focus. The advantages of plastic lenses include excellent optics, lightweight and therefore more comfortable than glass, easy to shape, reasonable to make, vastly better absorption of harmful ultraviolet radiation, and resistance to shattering. The major disadvantage of most plastic lenses is susceptibility to scratching. Uncoated plastic lenses develop a haze after a relatively short number of wearings which greatly reduces visibility.

There are many other commercial applications for transparent plastics. Two large industries, automobile and construction, have numerous needs for transparent plastics. Automobile lenses and dashboard covers and glazing applications in construction are just some of the needs of these industries for transparent plastics. As in the optics industry, resistance of the plastic to scratching and abrasion is desirable for most automobile and construction applications.

Space helmet visors are also made of plastic and it is this application that led NASA to develop a transparent scratch resistant coating for plastics. Polycarbonate, an impact resistant and transparent plastic is generally used for space helmets. However, polycarbonate also suffers from the disadvantage of most plastics for optics applications, i.e., it is highly susceptible to scratching. NASA therefore embarked on a program to develop a scratch resistant coating for polycarbonate space helmet visors. The coating process chosen for this development effort was plasma polymerization. This process was chosen for several reasons;

- a) deposition occurs near ambient temperature, making the process useful for coating temperature sensitive plastics.
- b) plasma polymerized coatings are conformal and uniform in thickness.
- c) practically any organic vapor can be used as starting material for depositing coatings by plasma polymerization; this feature allows one to deposit coatings covering a broad range of composition and properties.
- d) it can easily be scaled for coating large samples.
- e) multiple treatments and processes can be carried out in the same plasma reactor.

The starting material chosen for preparing a scratch resistant coating was based primarily on its chemical composition and structure. The composition was chosen so that the deposited film would mimic in some respects the composition of glass (a material rich in silicon and oxygen) which is known to be much more scratch resistant than plastic. The structure was chosen so that reasonable deposition rates

would be achieved thus minimizing the time required to deposit a coating of sufficient thickness to protect the underlying plastic from being scratched. Enhanced deposition rates can generally be achieved by plasma polymerization if the starting material contains a vinyl group or carbon-carbon double bond. With these requirements in mind the starting material chosen was vinyltrimethoxy silane $[(\text{H}_3\text{CO})_3\text{-Si-CHCH}_2]$. Since coatings are prepared from gases or vapors by plasma polymerization, the vapor pressure of the starting material was also considered in the selection process. Vinyltrimethoxy silane is a liquid with sufficient vapor pressure at room temperature to be a useful compound for plasma polymerization.

This paper describes the preparation and properties of a transparent scratch resistant and antireflection coating for polycarbonate. A two-step process was used for preparing the coating. The first step involved deposition of a plasma polymerized coating of vinyltrimethoxy silane on the polycarbonate surface and the second step involved hardening of the coating with an oxygen plasma. The second step of the process has been granted US Patent 4,137,365.

EXPERIMENTAL

Deposition Chamber and Materials

The deposition chamber shown in Figure 1 was used to deposit and harden the transparent scratch resistant coating. Copper sheet electrodes were wrapped around the outside of the reactor and were attached to a 13.56 MHz radiofrequency power supply through a manually controlled impedance matching network. The transparent plastic substrates used for the coating experiments were cut from 0.64 cm thick polycarbonate sheet stock manufactured by Rohm & Haas and sold under the tradename Zelux-C. The square substrates had an exposed surface area of 6.45 cm² during deposition and were held in a plastic frame supported on a glass plate located inside the reactor as shown in the figure. The frame ensured uniformity in thickness of the deposited coatings from the center to the edge of the samples. The substrates were cleaned before being coated by degreasing them in vapors of trichlorotrifluoroethane. The plasma polymerized coatings were prepared from vinyltrimethoxy silane vapor that was delivered to the deposition chamber from a degassed thermostatted reservoir of the liquid. The coatings were further hardened in the glow of an oxygen plasma. The oxygen for these experiments was obtained from a cylinder of oxygen having a reported purity of 99.5%.

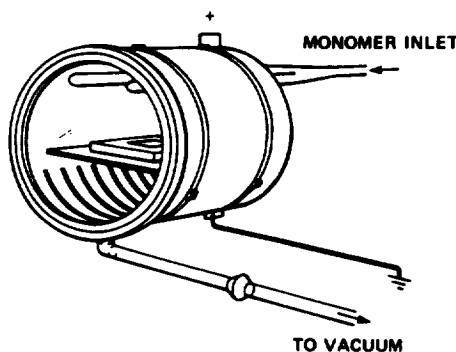


Figure 1. Chamber for depositing and hardening coatings using a low temperature plasma.

Deposition and Film Hardening Procedure

The reactor, with substrate in position, was initially evacuated to a background pressure of 0.7 N/m² (0.005 torr) or less before initiating flow of vinyltrimethoxy silane vapor. The flow rate of the monomer was adjusted to 3.2x10⁻⁹m³ (STP)/sec (0.19 cm³(STP)/min), which yielded a pressure of 2.8 N/m² (0.021 torr), before striking a discharge. A pulsed plasma mode, instead of a continuous wave (CW) mode, was used for film deposition. The pulsed mode reduces substrate heating during deposition. The peak-to-peak voltage during the on-time of the pulse was 400 V and the peak-to-peak current to ground was 0.6 A. The pulse time was 1.5 msec on and 1.5 msec off. At the end of a pre-determined deposition time,

monomer flow to the deposition chamber was shutoff and residual monomer was pumped from the chamber. The hardening of the deposited coating was then begun without removing the coated substrate from the reactor. The following conditions were used for hardening the siloxane coating with an oxygen plasma:

Mode of plasma operation:	CW
Peak-to-peak voltage:	390 V
Peak-to-peak current:	0.58 A
Oxygen flow rate:	$2.9 \times 10^{-8} \text{ m}^3(\text{STP})/\text{sec}$ ($1.7 \text{ cm}^3(\text{STP})/\text{min}$)
Initial oxygen pressure (discharge off):	13 N/m^2 (0.098 torr)
Post-treatment duration:	600 sec

Following the hardening step, substrates were removed from the reactor for evaluation of the coatings.

Analytical Procedures for Evaluating the Coatings

The test equipment and procedures followed for determining the elemental analysis, x-ray photoelectron spectra (ESCA), transmission, abrasion resistance, haze, adhesion, and thickness of the siloxane coatings on polycarbonate can be found elsewhere (1,2).

RESULTS AND DISCUSSION

Samples for elemental analysis of plasma polymerized vinyltrimethoxy silane films were obtained by scraping the coating from a glass plate which was coated with the polymer. The average weight percent of carbon, hydrogen and silicon dioxide in plasma polymerized vinyltrimethoxy silane films (without oxygen post-treatment) derived from elemental analysis by a combustion method of three samples was:

Element	Weight Percent
C	35.84
H	6.64
SiO ₂	48.56
Si	22.69

Since this analysis was done by a combustion method, the amount of oxygen in the samples could not be measured. The amount of silicon in the samples was calculated from the amount of silicon dioxide. The stoichiometric composition of vinyltrimethoxy silane is 40.52, 8.16, and 18.95 weight percent carbon, hydrogen, and silicon, respectively. In comparing the elemental analysis of the bulk plasma polymer with the starting monomer composition it is apparent that plasma polymerized vinyltrimethoxy silane films are deficient in carbon and hydrogen and rich in silicon relative to the starting monomer. A deficiency in carbon and hydrogen could have arisen if a carbon/hydrogen entity, such as a methyl group, was stripped from the starting monomer during plasma deposition, leaving a film with an enhanced amount of silicon but deficient in carbon and hydrogen.

X-ray photoelectron spectral analysis was chosen to determine the elemental composition of the surfaces of untreated and oxygen plasma post-treated vinyltrimethoxy silane plasma polymerized films. The results derived from these analyses were:

Element	Untreated film, atom %	O ₂ plasma treated, atom %
C	21.7	13.7
O	12.1	24.2
Si	13.3	9.21

Since ESCA cannot be used to analyze for hydrogen, it was assumed that the hydrogen concentration on the surface was the same (52.87 atom %) as in the bulk plasma polymer before calculating surface composition from the ESCA data. The atom % of the elements carbon, oxygen, and silicon in stoichiometric vinyltrimethoxy silane monomer are 23.81, 14.28, and 4.76, respectively. It is clearly

evident from the ESCA results that oxygen post-treatment of the plasma polymerized vinyltrimethoxy silane coating enriched the surface in oxygen at the expense of carbon, possibly by volatilizing the carbon as carbon monoxide or carbon dioxide. The oxygen plasma treated surface is also greatly enriched in oxygen and silicon and deficient in carbon relative to the starting monomer.

The intent in treating plasma polymerized vinyltrimethoxy silane coatings with an oxygen plasma was to change their composition into more of a glass-like material, rich in silicon and oxygen, while maintaining transparency and improving resistance to scratching and abrasion. It is clear from analysis of the treated surface that the composition has been transformed by the oxygen plasma into a more oxygen rich material having less surface carbon.

An image viewed through a lense covered with an antireflection coating appears sharper than the image viewed through an uncoated lense. Hardened plasma polymerized vinyltrimethoxy silane was found to be an antireflection coating for polycarbonate. Figure 2 shows transmission spectra for an uncoated polycarbonate substrate and substrates coated with oxygen post-treated plasma polymerized vinyltrimethoxy silane films. It is apparent from these spectra that the coated samples of polycarbonate transmit more light in the visible region than the uncoated sample. For example, at 5500 Å, the midpoint of the visible region of the spectrum, the transmission of the coated samples is greater by about 5%. In the cases of the coated samples, two different coating thicknesses were deposited, 939 and 2818 Å. These physical thicknesses correspond to optical thicknesses of 1375 and 4125 Å, respectively. The optical thickness, nd , where n is the refractive index and d is the physical thickness of the coating, was calculated using 1.464 for the refractive index of the coating. The refractive index at 5893 Å (the Na_D line) was measured with an Abbe refractometer.

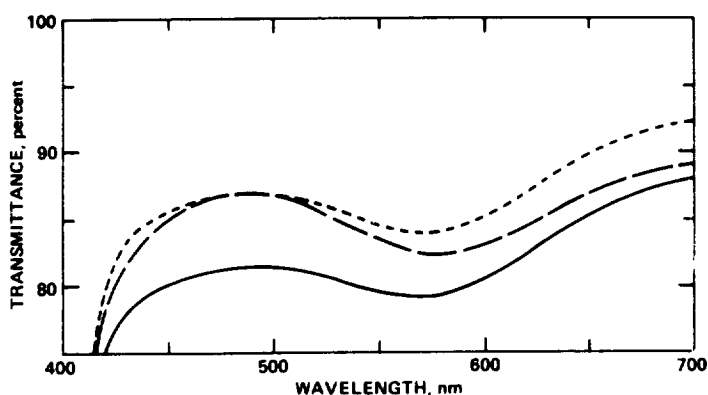


Figure 2. Transmission spectra of uncoated and coated (both sides) polycarbonate. — uncoated, - - - coated with 939 Å of plasma polymerized vinyltrimethoxy silane, and - · - coated with 2818 Å of vinyltrimethoxy silane.

The abrasion resistance of samples of uncoated and coated polycarbonate were determined by measuring haze before and after abrasion with an eraser. The force applied to the eraser when abrading the samples using the apparatus and procedure described previously was $1.4 \times 10^3 \text{ kg/m}^2$ (1). The following table shows haze values for the various samples studied:

Sample description	% Haze	Notes
Uncoated PC	5.2 ± 0.8	Ave. for 10 samples
*Coated PC	4.1 ± 0.5	Ave. for 3 samples
*Coated & O_2 treated PC	2.5 ± 0.2	Ave for 6 samples
Uncoated & unabraded PC	2.3 ± 0.1	Ave. for 10 samples
*Coated & unabraded PC	2.2 ± 0.1	Ave. for 3 samples

PC = polycarbonate

*Coating thickness = 2818 Å

From this data it is evident that the least amount of damage from abrasion occurred in those coated samples which were post-treated in an oxygen plasma. The haze for oxygen post-treated samples was only 0.2% greater than uncoated and unabraded polycarbonate. It is also evident from this data that coated and unabraded samples had the same haze as uncoated and unabraded polycarbonate within experimental error. This finding shows that neither the plasma polymerized silane coating nor oxygen post-treatment increased the haze of polycarbonate. Another important conclusion that can be derived from the haze data is that oxygen post-treatment improved the abrasion resistance as evidenced by a reduction in haze of 1.6% when compared with coated polycarbonate without oxygen treatment. It should also be noted that untreated plasma polymerized vinyltrimethoxy silane coatings also increased the abrasion resistance of polycarbonate as indicated by a reduction in haze of 1.1%. The improved abrasion resistance that the coatings developed here provide for a polycarbonate surface may be due to a greater hardness of the coating compared with uncoated polycarbonate, as well as less friction between the coating and the abrading material, in this case the eraser.

Adhesion of the plasma coating to polycarbonate was measured using the cellophane tape test as described in Military Specification MIL-C-675A. The coatings consistently passed this test without any special treatment of the polycarbonate surface other than the cleaning procedure described in the experimental section of this paper.

CONCLUSIONS

A two step low temperature plasma process has been developed for depositing a transparent and antireflection scratch resistant coating on polycarbonate. The first step of the process involves the deposition of a plasma polymerized coating of a siloxane on a clean polycarbonate surface. The second step is a hardening step and involves the treatment of the siloxane coating with an oxygen plasma. Both steps are carried out in the same reaction chamber.

REFERENCES

1. Wydeven, T.: Plasma Polymerized Coating for Polycarbonate: Single layer, Abrasion Resistant, and Antireflection. Applied Optics vol 16, no. 3, 1977, pp. 717-721. See also Applied Optics vol 16, no. 5, 1977, p. 1138.
2. Wydeven, T.; and Hollahan, J.: United States Patent 4,137,365: Oxygen Post-treatment of Plastic Surfaces Coated with Plasma Polymerized Silicon Containing Monomers, Jan. 3, 1979.