

Plasma Assisted Coatings for the Plastics Industry

By: O.S. Kolluri, S.L. Kaplan, D.A. Frazier

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ABSTRACT

Plasma processes are being used in a myriad applications in all industries employing plastics. Medical disposables, prosthetic devices, high voltage coils, electronic housings, painted fascias, adhesively bonded plastic assemblies, and metallized plastics all use plasma processes to enhance the effectiveness and permanency of the secondary process.

As plasma processing becomes commonplace in the plastics industry, more attention is being given to complex applications. This paper discusses plasma assisted coatings as they relate to modifying materials for composites, barrier applications, and for treating materials whose surface can be modified only with great difficulty using conventional techniques. The structure of coatings obtained through the use of different monomers is related to process conditions and end-use performance. Suggestions for future research and the potential benefits offered by plasma assisted deposition are described.

BACKGROUND

A designer typically has to make several compromises in the selection of materials. The preferred material may not be useable due to a lack of essential surface properties for the application. In the case of products made of plastics, the balancing of bulk to surface property requirements has always been the Achilles heel of optimum design. For example, the use of polypropylene, a low cost resin, may be the preferred material for a specific packaging application. Preferred because of its processability, weight, strength and cost, but unusable by itself because of its gas permeation properties.

The methods available to the processor for modifying surface properties have been limited to flame or corona treatment or wet chemical techniques. Flame and corona treatments, though useful in oxidizing the surfaces of plastics, have limited utility in many applications and the transitory nature of these modifications prevent their widespread use in many situations. Unlike plasma discharges which are typically conducted in a vacuum, corona processes rely on the ionization of air resulting from a high voltage point discharge across a small gap. As a consequence, not only are internal surfaces of complex shapes difficult to treat but sensitive materials can be damaged very easily. Wet chemical treatments, which offer an alternative method, suffer from problems of toxicity and environmental effects.

For many of these applications, cold gas plasma surface treatment has become the preferred industrial processing technique. Applications range from surface modifications of plastics in the electronics industry to treatment of plastic automotive components and biomedical devices. This technology has facilitated the development of many products and increased use of plastics in these applications.

Plasma processing is not one process but a "field of opportunities" which can be classified into three categories that often overlap. These are: (1) plasma activation, (2) plasma-induced grafting, and (3) plasma polymerization. Plasma activation is the alteration of surface characteristics by the substitution of chemical groups or moieties for groups normally present on the polymer chain being modified. The assumed mechanism is free radical creation and coupling of these free radicals with active species from the plasma environment. Depending on the process gas selected, a large variety of chemical groups can

be incorporated into the surface. These groups may be hydroxy, carbonyl, carboxylic, amino, or peroxy groups. Most importantly, the insertion or substitution of these groups in the polymer chain is under the control of the operator. Therefore, the surface energies and the surface chemical reactivity of plastics can be completely altered without affecting their bulk properties.

Plasma-induced grafting offers another method by which plastic surfaces can be modified. If a noble gas is employed to generate a plasma, a multitude of free radicals are created along the polymer backbone. If after the plasma is extinguished but prior to the introduction of air, an unsaturated monomer such as allyl alcohol is introduced into the reaction chamber, it will add to the free radical yielding a grafted polymer. The range of functional and reactive sites that can be incorporated onto a surface is significantly increased with this technique. This process differs from activation in that instead of functional modification of the surface polymer chains, material is added on to the polymer backbone.

The third category of plasma processes - plasma deposition - utilizes gases or vapors that fractionate and undergo polymerization under the influence of RF energy. For instance methane (CH_4) under the influence of plasma will deposit as a polyhydrocarbon that has a density approaching 1.6 gm/cc. Any material that can be introduced into the process chamber is a potential candidate as a feed material for plasma polymerization. The properties of materials polymerized in this manner are unique from polymers obtained from these same materials via conventional polymerization methods. These properties include a high degree of crosslinking and the ability to form pinhole-free films that adhere tenaciously to various substrates.

Gases in plasma may undergo polymerization, usually via a free radical initiation process. When a gas is ionized by radio frequency energy, the resulting plasma contains free electrons as well as other meta stable particles. When the process gas mixture used consists wholly or in part of hydrocarbon gases, the hydrocarbon is fractured into free radical fragments. These free radical fragments become the sites at which the polymerization process is initiated. As the molecular weight of the plasma polymerized product increases, it is deposited onto the substrate placed within the plasma chamber. Since the fragmentation of the feed gas in the plasma generates free radical species for initiating the polymerization process, gases such as methane (CH_4), which have zero functionality, can be used to form plasma polymers.⁽¹⁾ In addition to methane, plasma polymers have been formed from other hydrocarbon gases such as ethylene or propylene, and organosilicon compounds such as hexamethyldisiloxane (HMDSO) or vinyltrimethylsilane (VTMS).^(1,2,3) Due to the complex nature of the fragmentation process, the resulting polymer structure is unlike any that can be deduced from conventional polymerization mechanisms. The degree to which the monomer is fragmented is dependent on the amount of energy supplied per unit weight of monomer that is allowed to flow through the reactor. When sufficient energy is supplied to break all the bonds of the monomer molecule, the recombination or polymerization process becomes atomic in nature. In addition, the structure of the plasma polymers can be varied by changing reaction conditions including the use of co-monomers or the introduction of oxygen, nitrogen, or ammonia into the reaction chamber during the polymerization process.⁽⁴⁾

EQUIPMENT CONSIDERATIONS

Numerous types of reactors are used for the deposition of plasma polymers. Glass/quartz reactors or aluminum chambers with metal parallel-plate electrodes seem to predominate in the literature, although several investigators have used inductively or capacitively coupled systems with external electrodes. The radio frequency (RF) excitation used by various equipment manufacturers can be as low as 2 KHz

to 4 KHz, or can be the more typical 13.56 MHz (high frequency). Microwave plasma systems have also been used for the deposition of plasma polymers. Previous studies have shown that the densities of films deposited by low frequency systems are significantly lower than films deposited either by the high frequency or microwave plasma systems. The choice of equipment used for plasma polymerization and deposition is thus dictated by both the rate of deposition desired, the film properties that can be obtained by the various systems and practical considerations such as the size of the parts to be treated and processing rates that are feasible in any given system.

The films evaluated in this study were deposited in a Plasma Science PS 0500. This reactor uses capacitively-coupled internal electrodes for generating a primary plasma. A 550 watt RF source operating at 13.56 MHz is used for ionizing the process gases.

Monomers such as methane, hexamethyl-disiloxane, propylene, and vinyltrimethoxysilane were used to deposit films on either silicon wafers or 2 mil Mylar™ films. Gaseous monomers were introduced into the reactor through one of three mass flow controllers that are a part of the system. In the case of liquid monomers, a flask containing these monomers was connected directly to the reactor chamber via a stainless steel tubing with a shut off valve installed in the line. Since the end of the tube in the flask was above the liquid level, we were assured that only monomer vapor would be drawn into the reactor by the vacuum system. Permeation properties were measured with an instrument manufactured by Modern Controls. ESCA was used to determine the chemical nature of the films.

RESULTS AND DISCUSSION

Table I below shows some typical deposition rates that have been reported for various monomers in continuous and pulsed RF discharges.⁽⁴⁾

TABLE I
Deposition Rates of Various Compounds

Compound	Deposition Rate	
	D(x 10 ⁸ gm/cm ² *min)	D/Do
Hexamethyldisiloxane	233 = Do	1.00
Acrylic acid	28	0.12
Styrene	173	0.74
Tetramethylclisiloxane	191	0.82
Divinyltetramethy1disiloxane	641	2.75
Ethylene	42	0.18
Benzene	110	0.47

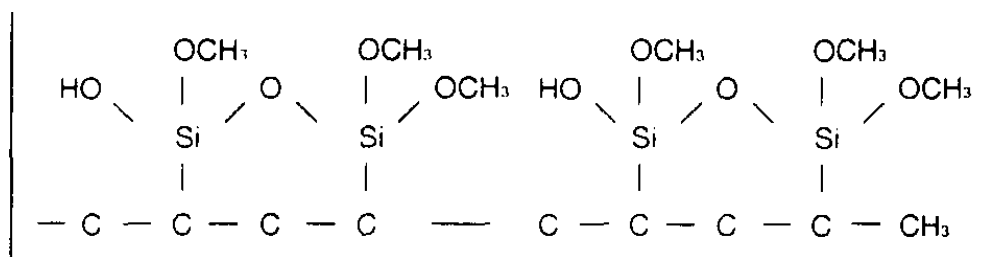
The thickness of the films deposited in the experiments reported in this paper were not sufficient to provide an accurate measure of deposition rates in the PS 0500. We polymerized hexamethyldisiloxane, propylene, methane, and vinyltrimethoxysilane monomers for the purpose of depositing barrier films. Mylar™ film with a thickness of 2 mils was chosen as the substrate for measuring oxygen transmission rates. Both methane and propylene gave us barrier-films that reduced oxygen transmission rates of the Mylar™ films by approximately 56%. The oxygen transmission was reduced from 2.15 cc/ 100 in /day for a 2 mil Film to 0.95 cc/ 100 in/day. Samples with films deposited from vinyltrimethoxysilane and hexamethyldisiloxane, however, did not show any improvement in barrier properties when compared with untreated films. Barrier properties are best obtained when dense pinhole free films such as glass are deposited on to substrates. ESCA analysis of the films that were deposited can help explain the observed phenomenon. Table 2, pg. 6 shows elemental analysis of films deposited from continuous polymerization of vinyltrimethoxysilane for various exposure times. In all cases the reactor power was set at 200 watts.

From these results we postulated the following:

- 1) The C-C/OCH₃ ratio has increased from 0.67 for the monomer to 1.63 in the film indicating loss of the OCH₃ groups resulting in formation of an Si-O-Si linkage.
- 2) The composition data suggests an enrichment of Si and O relative to carbon. This is primarily due to the loss of methyl groups from the fragmentation of the ether bond in the methoxy radical.
- 3) Cleavage within the methoxy fragment is further evidenced by the decrease in the -OCH /Si ratio from a value of 3.0 for the monomer to an average value of 1.4 for the deposited films.
- 4) The average -OCH₃ /Si ratio of 1.5 and the average O/Si ratio of 2.5 suggests that there are 1.5 -OCH₃ groups per Si atom and 2.5 oxygen atoms per Si atom.

The following structure for the deposited film is suggested in contrast to the glassy SiO_x coating that we originally attempted to deposit with this monomer:

Deposited Film Structure



If the key ratios for the theoretical model are compared with those obtained for our films, the structure that has been postulated appears. This comparison is shown in table 3, pg. 6. It should be noted that H atoms are not included in the calculation of atomic percentages.

The bulky and open structure that resulted from our process can explain the poor barrier performance against a small molecule such as oxygen. Post treatment of the films deposited in this manner with an oxygen plasma did not improve the permeability characteristics. Wydeven reported a similar type of

film when polymerizing vinyltrimethoxysilane monomer in a pulsed RF discharge.⁽⁶⁾ From the ESCA data that was reported, the following comparison can be made between the atomic composition for the proposed model and the film deposited by Wydeven (table 4). The data suggests that similar structures are obtained with both continuous and pulsed RF discharges with vinyltrimethoxysilane monomer.

TABLE 4 Wydeven Data- vs Proposed Model

	Wydeven Data	Proposed Model
C ₁	16.0%	15.0%
C ₂	8.0%	10.0%
O	17.0%	16.0%
Si	6.4%	6.4%
H	53.0%	53.0%

Previous work by Rose et al⁽⁷⁾, has shown that plasma polymerization of organic monomers can lead to both atomic rearrangement, as in the case of acrylonitrile, or no rearrangement as in the case of styrene. The films that we evaluated by ESCA were deposited onto silicon substrates. ESCA spectrum of plasma polymerized styrene shows a perfect likeness to that of polystyrene (figure 1 and figure 2. pg. 7).

The pi-pi* intensity is identical in plasma polymerized styrene and conventional polystyrene indicating that the phenyl ring was deposited intact onto the wafer substrate. In contrast, acrylonitrile is atomically rearranged during plasma deposition. Using ESCA data (fig. 3 and fig. 4, pp. 7,8), the plasma polymer was characterized as having an 80:20 C:N ratio, with a carbon structure suggesting a 1: 1 ratio of C-C: C-C = N and C =N. The compositions of these films deposited onto silicon wafers and carbon fiber are shown in table 5, pg. 6.

As we stated earlier in the introduction, the structure of the polymer film that is deposited is determined by the degree to which the monomer is fragmented by the ionization process. When polymerizing methane onto MylarTM film substrates in our laboratory, we appear to have deposited a film that is similar to glassy carbon. Upon comparison of the ESCA spectrum obtained on this film (figure 6, pg. 8) with the spectra for glassy carbon shown by McFeeley et al,⁽⁸⁾ a number of similarities are observed if one ignores the contribution of oxygen in figure 6. The residual oxygen that we see could result from oxidation of the surface of the carbon film. Since films deposited or modified by plasma can retain residual free radical activity, oxidation of these films on exposure to air is highly probable.

When discussing plasma polymerization, Yasuda⁽¹⁾ defines two regimes in which deposition can occur: a monomer deficient regime and an energy deficient regime. The operating characteristic that distinguishes these two regimes is the relationship between the composite power parameter (W/FM) and

the sum of the bond energies in the monomer per unit weight. W is the power supplied to the reactor in watts, M is the molecular weight and F is the monomer flow rate in standard cc/min. When a sufficient amount of energy is supplied such that (W/FM) exceeds the sum of the bond energies per unit weight of the monomer, all bonds in the monomer are broken during the ionization process. The polymerization occurs by a true atomic process. In the case of methane deposition, the value for (W/FM) was 134×10^6 Joules/Kg. Since this value is greater than the energy required to break all the bonds in the monomer - 104×10^6 Joules/Kg - we suspect that the polymerization of methane occurred by an atomic process. Values of (W/FM) could not be calculated for deposition from the other monomers studies since accurate flow data was not available.

Future work will focus on developing better correlations between the composite power parameter, the deposition rate, and the structure of the film deposited in a capacitively-coupled commercial system that develops a primary plasma. ESCA and FTIR analytical techniques will be used to follow bond rearrangement and binding of carbon and hydrogen. This work will also be extended to using the composite power parameter to define process conditions for selectively breaking specific bonds along the chains of the polymer substrate. Process conditions necessary to replace these bonds with chemical groups of choice (molecular re-engineering) will be investigated.

Table 2
Elemental Composition of
Vinyltrimethoxysilane Monomer and Films
Deposited at Various Exposure Times

Sample	Atom%				Key Ratios		
	C 1	C 2	O 3	Si	C2/ Si	O/(C2+S I)	O/Si
Monomer	2 2	3 3	3 3	11	3.0 0	0.75	3.00
1 minute exposure	3 5	1 8	3 4	13	1.3 9	1.10	2.62
3 minute exposure	3 8	1 7	3 3	12	1.4 2	1.14	2.75
5 minute exposure	2 4	2 2	4 0	15	1.4 7	1.080	2.67
10 minute exposure	3 0	1 9	3 7	14	1.3 6	1.12	2.64
20 minute exposure	2 7	1 8	4 0	16	1.1 3	1.18	2.50
Average	3 1	1 9	3 7	13	1.4 1	1.12	2.63
Standard Deviation	5 7	1 9	3 3	1.6	0.0 47	0.038	0.09

Table 3
Atomic Percentages and Key Ratios
Deposited Film vs. Model

	ESCA Data for Film	Proposed Model
C1	31%	32%
C2	19%	21%
O	37%	36%
Si	13%	14%
-OCH3/Si ratio	1.4	1.5
O/Si ratio	2.6	2.5
where C = C-C; C-H C2 = -OCH3 O = Si-O; -O-CH3 and Si = Si-O; Si-(OCH3)3		

Table 5
Composition of Plasma Polymerized Coatings
as Determined by ESCA(7)

	C	O	N	Si
Control silicon wafer	19	36	0.5	44
Control carbon fiber	86	12	1.8	----
Polystyrene-theoretical	10 0	----	----	----
Styrene polymerized onto silicon wafer	94	5	1.4	----
Styrene polymerized onto carbon fiber	94	5	1.4	----
Polyacrylonitrile- theoretical	75	----	25	----
Acrylonitrile polymerized onto silicon wafer	78	1.5	21	----
Acrylonitrile Polymerized onto carbon paper	81	3.0	17	----

