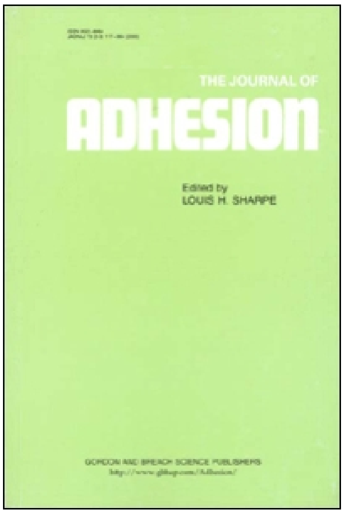

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# Effect of Surface Energetics of Substrates on Adhesion Characteristics of Poly (p-xylylenes)

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# Effect of Surface Energetics of Substrates on Adhesion Characteristics of Poly (*p*-xylylenes)

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In investigating the effect of the surface energetics of substrate materials on the adhesion characteristics of poly(p-xylylene) and poly(chloro-p-xylylene) by the "Scotch Tape" method, it was found that if the substrates had not been preconditioned (treated with argon or a methane plasma), the adhesion was poor. The characteristics of water resistant adhesion that were observed when coated substrates were boiled in 0.9% sodium chloride solution were found to vary from excellent (when the polymer did not peel from the substrate after three cycles of 8 hours of boiling and 16 hours at room temperature) to poor (when the polymer peeled off almost immediately). It was noticed that water resistant adhesion depends on the hydrophobicity of the substrate material (the greater the hydrophobicity, the greater the adhesion) and is not related to the dry adhesive strength of poly(p-xylylene). The oxygen glow discharge treatment of the substrates decreased both the dry and wet adhesive strength of the polymer. The effect of the argon glow discharge treatment depended on the surface energetics of the substrate, and the methane glow discharge treatment increased both the dry and wet adhesive strength of the polymer. These preconditioning processes are discussed in terms of the sputtering of the material from the wall of the reactor in contact with the plasma and the deposition of the plasma polymer of the sputtered material on the substrate surface.

## INTRODUCTION

The adhesion of a polymer is very crucial to successful coating applications. The desirable bulk properties of the polymer, such as its chemical resistance, electric volume resistivity, permeability to gases and liquids, and thermal properties, are often major considerations when one chooses a polymer to be used as a coating material. However, the choice of material is more restricted and determined by the need for good adhesion characteristics at the interface. Good interfacial bonding is not easy to obtain, especially between a polymer and a metal that have drastically different structural, electronic, and thermal properties.

According to the modern concept of adhesion, the bonding of two solid surfaces is due largely to adsorption or more specifically to the action of secondary valence forces, such as hydrogen bonding and Van der Waal's force. Consequently, water molecules, which are one of the strongest hydrogen bonding agents, can easily break the bonds when the coated material is immersed in water or an aqueous salt solution, creating a serious problem of water-sensitive adhesion. A similar phenomenon also occurs in the so-called dry state, because abundant amounts of water molecules are present in the atmosphere, which can permeate through most polymers rather readily, although the process is much slower than it is in wet conditions.

Poly(*p*-xylylenes)[1] (commonly known as Parylenes® by Union Carbide) are uniquely adaptable to an investigation of some of the important factors involved in adhesion of polymers to various substrates. Because these polymers can be deposited in a vacuum by spontaneously polymerizing the *p*-xylylene vapor on the substrate surface, the formation of voids at the interface can be virtually eliminated, and a good physical contact between the polymers and the substrates can be obtained regardless of the nature of the substrates. It is therefore possible to determine the true effect of the substrate surface energetics on the adhesion of the polymers.

Furthermore, because poly(*p*-xylylenes) are hydrophobic, solvent resistant polymers and are not influenced by water even at its boiling point, they provide one with an opportunity to investigate the effect of substrate surface energetics on the water resistant adhesion of polymers, specifically in the role of water at the poly(*p*-xylylene)/substrate interface.

During the present study, glass substrates and polymer substrates with varying surface free energy (as indicated by water contact angle) were used to investigate the effect of substrate surface energetics on the adhesion characteristics of the poly(*p*-xylylenes). Special emphasis was placed on the sensitivity of the adhesion to water.

## EXPERIMENTAL

The substrates used in the investigation were polyethylene, polypropylene, poly(methyl methacrylate), poly(ethylene terephthalate), Nylon-6, poly(tetrafluoroethylene), glow discharge† polymerized methane (GDPM), and precleaned microscopic glass slides (Fisher Scientific Company). All the polymeric substrates were smooth up to a magnification of 500 × and with the

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† The terms "glow discharge" and "plasma" are interchangeably used.

exception of GDPM and poly(methyl methacrylate) all were used in the form of 25–125 μm thick films. Poly(methyl methacrylate) sheets (2 mm thick) were purchased from a local source, and the GDPM was synthesized as ultrathin coatings (~50 nm thick) on the glass slides by plasma polymerizing methane in a bell jar reactor operating at an ac frequency of 10 kHz. A monomer flow rate of 0.5 cc/min and a discharge power of 75 watts were employed. The polymer formed under these conditions was found to adhere extremely well to metal, plastic, and glass substrates and had excellent water vapor barrier characteristics

$$\left[P = 5.7 \times 10^{-14} \frac{\text{cc(STP)}\cdot\text{cm}}{\text{sec}\cdot\text{cm}^2\cdot\text{cm(Hg)}}\right].^2$$

In order to investigate the effect of surface morphology on the adhesion characteristics of poly($p$-xylylenes), a 100 μm thick "Goretex" [perforated poly(tetrafluoroethylene)] and a "Millipore" filter (1 μm pore size from Millipore Corporation, Cat. No. FALP09025) were also used as substrates.

A uniform, 1.5 μm thick coating of poly($p$-xylylene) (PPX) [or poly(chloro-$p$-xylylene)] was deposited on each of the substrates by the "Gorham method"[1] at room temperature. A 3.0 gm dimer charge, 160°C vaporization temperature, 650°C decomposition temperature, and a 5.46 Pa (41 mTorr) argon pressure were used. Poly(chloro-$p$-xylylene) (PCPX) films were deposited in the absence of argon and at a lower vaporization temperature of 140°C.

In order to investigate the effect of the glow discharge treatment of the substrate surfaces on the adhesion of the PPX and PCPX coatings, the substrates were selectively treated with argon, oxygen, and methane glow discharges just before the polymer coating was deposited in the reactor. The discharge power for this treatment was supplied by a Tegal RF generator operated at 13.5 MHz with a net power input of 85 watts (175 watts forward and 90 watts reflected). A gas pressure of approximately 5.5 Pa (41 mTorr) was used, and the treatment was applied for 10 minutes. Some of the oxygen glow discharge treatments were conducted separately in a bell jar reactor, and the samples were exposed to the air before the PPX was deposited.

## RESULTS AND DISCUSSION

### 1. Effect of substrate surface energetics on adhesion characteristics

The effects of substrate surface energetics on the adhesion characteristics of PPX are summarized in Table I-A, and the adhesion characteristics of PCPX polymer are summarized in Table I-B. The simple "Scotch Tape" test

TABLE I-A

Adhesion of poly(*p*-xylylene) to various substrates

| Substrates | Contact angle of $H_2O$ $\theta_{H_2O}$ | Adhesion test results Test A | Test B | Test C |
|---|---|---|---|---|
| *Porous* | | | | |
| "Goretex" | 140° | 5A | 5B | 5C |
| "Millipore" (1 μm) | 114° | 5A | 5B | 5C |
| *Nonporous (smooth)* | | | | |
| Poly(tetrafluoroethylene) | 108° | 0A | 5B | 2C–3C |
| Polypropylene | 100° | 2A | 5B | 2C |
| Polyethylene | 93° | 0A | 5B | — |
| Glow discharge polymerized methane | 76° | 5A | 4B | 5C |
| Poly(methyl methacrylate) | 73° | 1A | 3B | |
| Poly(ethylene terephthalate) | 70° | 0A | 2B–3B | 2C |
| Nylon-6 | 49° | 0A | 1B–2B | 2C–3C |
| Glass | 16° | 0A | 0B | 0C |

TABLE I-B

Adhesion of poly(chloro-*p*-xylylene) to various substrates

| Substrates | Contact angle of water $\theta_{H_2O}$ | Adhesion test results Test A | Test B |
|---|---|---|---|
| *Porous* | | | |
| "Goretex" | 140° | 5A | 5B |
| "Millipore" (1 μm) | 114° | 5A | 5B |
| *Nonporous (smooth)* | | | |
| Poly(tetrafluoroethylene) | 108° | 0A | 5B |
| Polypropylene | 100° | 3A–4A | 5B |
| Glow discharge polymerized methane | 76° | 5A | 4B |
| Poly(methyl methacrylate) | 73° | 0A | 2B |
| Poly(ethylene terephthalate) | 70° | 0A | 2B |
| Nylon-6 | 49° | 0A | 2B |
| Glass | 16° | 0A–1A | 0B–1B |

(ANSI/ASTM D-3354-76)† used to evaluate the dry adhesive strength of the polymer is termed "Test A". The water and organic solvent resistant adhesions were evaluated by using a simple boiling test in which the coated substrates were boiled in a 0.9% sodium chloride solution, "Test B", and in n-hexane, "Test C". The test results shown in the two tables are expressed by a system of numerical grades, which are defined in Table II.

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† American Society for Testing and Materials, Philadelphia, PA.

TABLE II

| | |
|---|---|
| *Test A* (ANSI/ASTM D 3354-76 in air) | |
| 5A | No peeling |
| 4A | Trace peeling or removal along incisions |
| 3A | Jagged removal along incisions |
| 2A | Jagged removal along most incisions |
| 1A | Removal from most of the area of x-cut |
| 0A | Removal beyond the area of x-cut |
| *Test B* (Boiling test in 0.9% saline solution) | |
| 5B | No lifting of the film after 3 cycles of 8 hours of boiling and 16 hours of room temperature soaking |
| 4B | Lifting of the film after 3 cycles of 8 hours of boiling and 16 hours of room temperature soaking |
| 3B | Lifting of the film after 1 cycle of 8 hours of boiling and 16 hours of room temperature soaking |
| 2B | Lifting of the film after 60 minutes of boiling |
| 1B | Lifting of the film after 15 minutes of boiling |
| 0B | Lifting of the entire film almost immediately |
| *Test C* (Boiling test in n-Hexane solvent) | |
| Criteria of the test result—same as Test B. | |

The following aspects should be emphasized:

a) Excellent adhesion in both the dry and wet states was obtained when either PPX or PCPX was deposited on a porous surface.

b) Based on the pull test results, the adhesion of PPX or PCPX to smooth conventional polymeric substrates and glass was poor.

c) Both PPX and PCPX adhered relatively better to hydrocarbon polymer surfaces.

d) The adhesion of PPX and PCPX to a methane glow discharge polymer was excellent.

e) There was no correlation between dry adhesive strength and water resistant adhesion to smooth surfaced substrates.

f) Water resistant adhesion definitely correlated with the hydrophobocity of the substrate surface.

The excellent adhesion characteristics obtained with porous substrates are due to mechanical interlocking of the PPX polymer into the substrate surface on a macroscopic level creating more molecular contact at the interface. The physical evidence of this situation can be seen in the electron micrographs of the uncoated and coated surfaces of the porous substrates used in the study (Figures 1–4).

It should be emphasized that we are dealing with the adhesion of a non-polar hydrophobic polymer. It is interesting to note that the dry adhesive strength of PPX, when applied to smooth surfaces, was very low, but the degree of water resistivity was not what one would expect from the dry adhesive strength. It indicates that water has a very small role in destroying the bond at the hydrophobic/hydrophobic interface. This argument is further

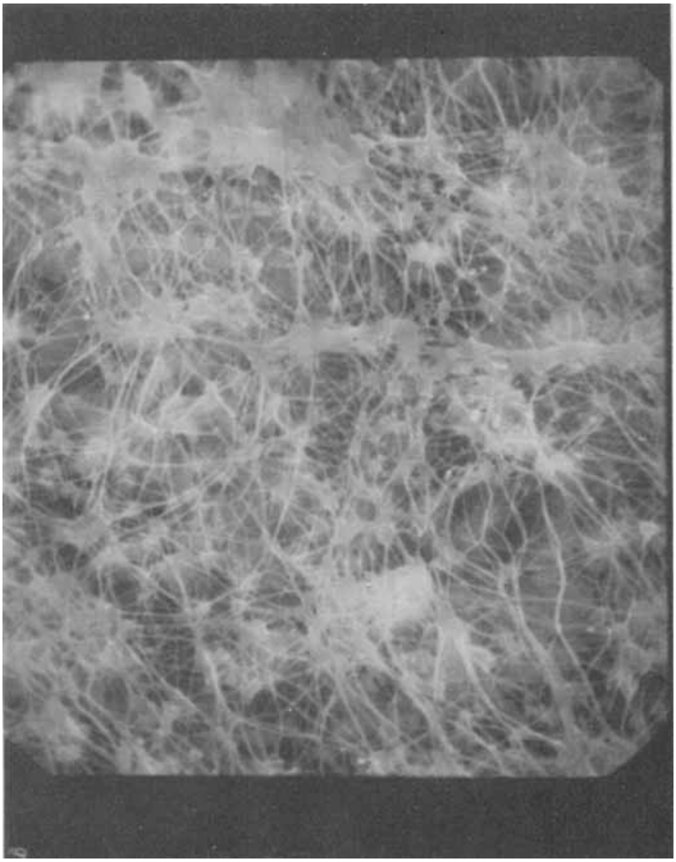

FIGURE 1 Scanning electron micrograph of an uncoated "Millipore" filter (1 μm) (5000 ×).

confirmed by the results obtained when the substrate surfaces were treated with oxygen plasma to render the surfaces more hydrophilic as seen in Table IV. This characteristic is discussed in more detail in the next section.

By making the substrate surface hydrophilic, dry adhesive strength and water resistant adhesion decreased drastically. In these cases, we are dealing with adhesion at a hydrophobic/hydrophilic interface. It is a general practice to treat polymer surfaces by using either an oxygen glow discharge or a corona discharge method to increase wettability and subsequently adhesion.[3,4] Such a process is intended to improve adhesion at a hydrophilic/hydrophilic interface for most polar adhesive polymers. When such a process is used to improve the adhesion of PPX, which is a hydrophobic polymer, the results are detrimental, indicating that the surface energetics are far more important than

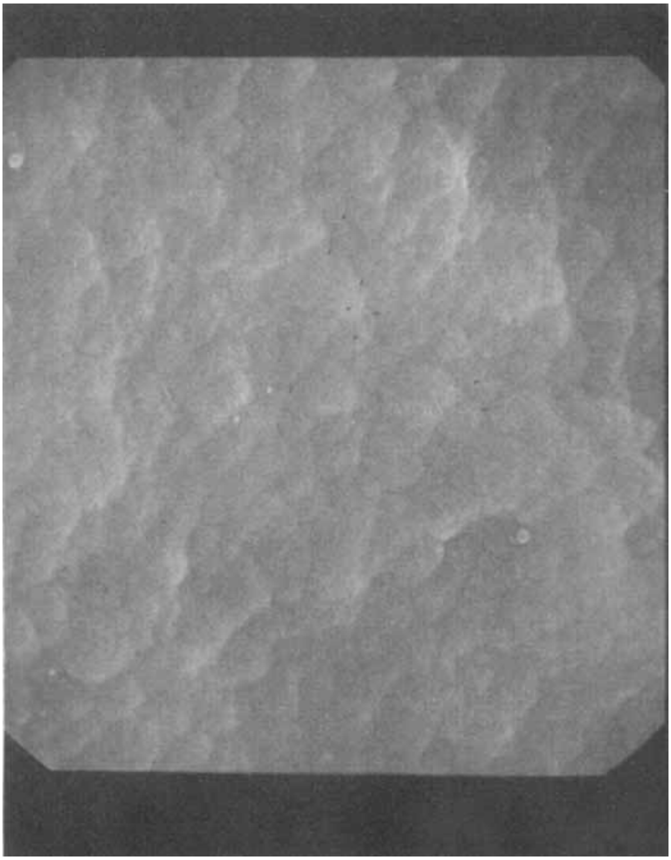

FIGURE 2 Scanning electron micrograph of the "Millipore" filter after coating with 1.5 μm thick film of poly($p$-xylylene) (5000 × ).

any other factor in the surface treatment of substrates for the improvement of adhesion. As far as the adhesion of PPX is concerned, there is a definite indication that the principle of "like adheres to like" applies. Any treatment of surfaces, such as in the case of the oxygen glow discharge treatment, which causes a deviation from the similarity of surfaces, causes detrimental effects in both dry and wet adhesive strengths. The remarkable improvement in adhesion characteristics of PPX and PCPX observed on coating a glass substrate with a GDPM polymer can be attributed partly to the formation of a more hydrophobic substrate surface and partly to the covalent bond formation at the interface by the interaction of the residual free radicals of glow discharge polymer with the growing species of the xylylene polymer.

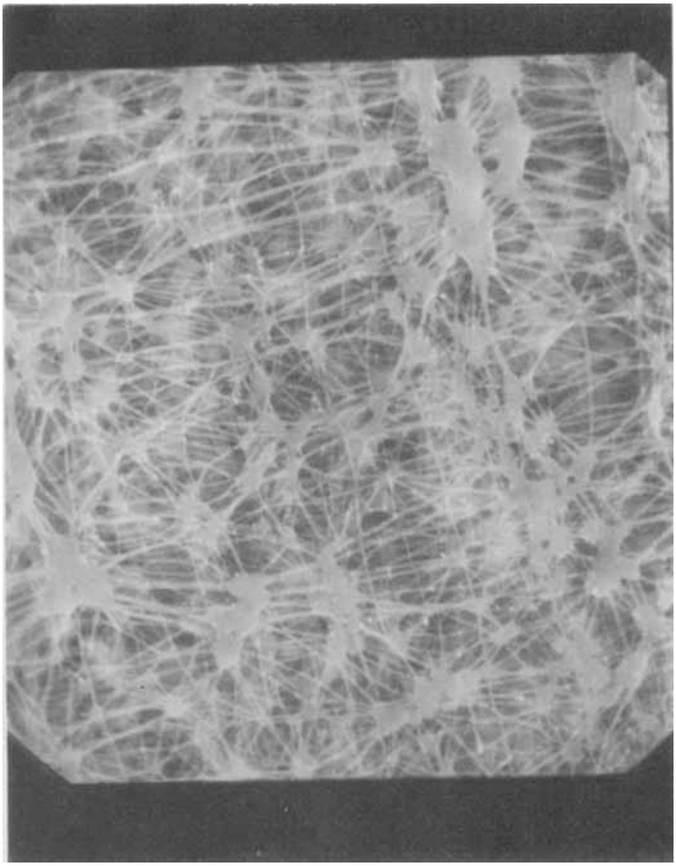

FIGURE 3 Scanning electron micrograph of an uncoated "Goretex" polymer (5000 × ).

Based on the principle discussed above, a glow discharge polymer used as a primer on a nonpolymeric surface may change the extremely high surface energy of a metal or other nonpolymeric material to the surface energy of the glow discharge polymer. Thus, the primer makes the surface of the material more compatible with PPX.

Of course, this approach would not improve the overall adhesion of PPX if the primer itself did not adhere well to the substrate material. Therefore, the adhesion of the glow discharge polymer to nonpolymeric substrates also becomes important. However, the experimental results clearly show that the water resistant adhesion of the hydrophobic PPX depends on the hydrophobicity of the substrate to which it is applied.

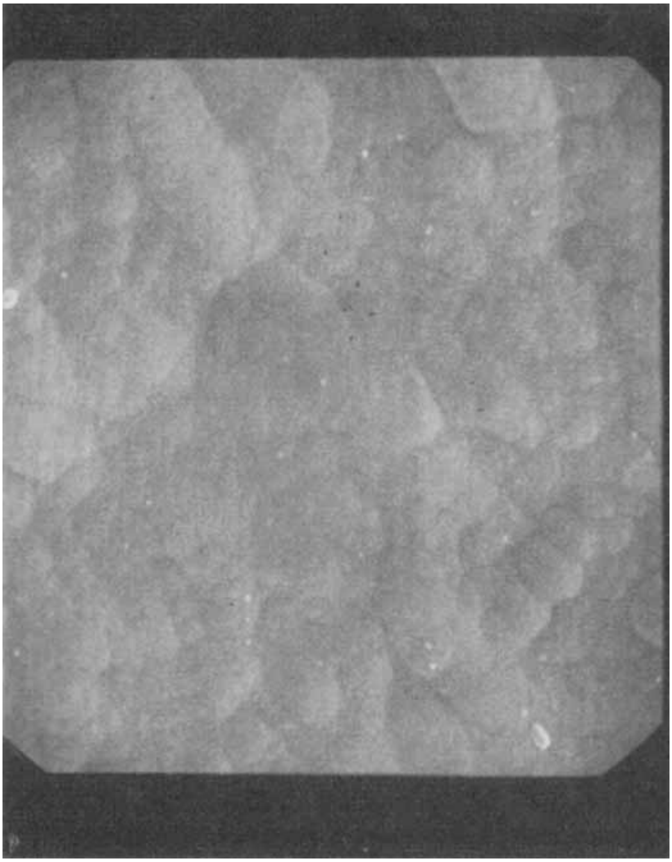

FIGURE 4 Scanning electron micrograph of the "Goretex" polymer after coating with 1.5 $\mu$m thick film of poly($p$-xylylene) (5000 ×).

## 2. Pretreatment of surfaces by glow discharge

It is generally considered, perhaps intuitively, that exposing a substrate surface to a plasma created by the glow discharge of a gas, such as argon or oxygen, cleans the surface by plasma etching the organic impurities from the surface. Plasma etching actually does take place when surfaces are analyzed by ESCA and Auger spectroscopy for a depth profile. In practice, the surfaces are not necessarily cleaned by the glow discharge treatment and a much more complicated phenomenon may occur depending on the actual condition of the experiment.

An important aspect one must keep in mind is that plasma is generally contained by solid surfaces and that the treated substrate surface constitutes only a small fraction of all the surfaces that come in contact with the plasma. The plasma that affects the substrate surface also interacts with the other surfaces that are exposed to it, such as the wall of the reactor. Consequently, the net effect to the treated substrate surface is likely to be influenced by the surroundings of the substrate material.

According to the Competitive Ablation and Polymer formation (CAP) mechanism of plasma polymerization,[5] substances ablated from a surface exposed to a plasma can be deposited on the same surface and other surfaces as well. In the absence of organic materials in the system, this process may be visualized as the sputtering of material from one surface and the depositing of the sputtered materials elsewhere. This process is utilized in the sputter coating of metals and inorganic materials. Because argon is chemically inert, this sputtering process occurs primarily as a momentum exchange of impinging ions and atoms at the substrate surface and in its vicinity. When oxygen is used as the plasma gas, the reactivity of the oxygen plasma seems to be the predominant factor, and sputtering by the momentum exchange process is less important. Consequently, oxygen plasma cannot be effectively used in the sputter coating process.

When organic impurities are present in a reactor, the situation becomes much more complicated because of the very likely occurrence of glow discharge polymerization of the ablated substances. Nonetheless, the major difference between an oxygen plasma and argon plasma still exists. Namely, the argon plasma ablates surface materials by the momentum exchange sputtering process, and glow discharge polymerization of the ablated materials occurs. On the other hand, oxygen plasma chemically etches the surface material, but it prohibits or retards the glow discharge polymerization of the ablated materials. It has been established that oxygen-containing compounds have a significantly lower rate of polymer deposition in a glow discharge.[6] Consequently, oxygen plasma will etch a surface and very likely introduce oxygen containing functions on the surface of polymeric substrates, but the deposition of a glow discharge polymerized compound from gases resulting from ablation would be minimal.

Empirically, advantageous effects, in so far as adhesion is concerned, have been produced by the glow discharge treatment of substrate surfaces. Such an advantageous effect might be more adequately called "preconditioning" rather than "precleaning" or etching. This situation was studied by using the glow discharge treatment with oxygen, argon, and methane to prepare the surfaces of the polymers and examining the adhesion of PPX to the preconditioned surfaces.

Because the wall of the reactor used in the experiments was coated with PPX polymer, the deposition of a glow discharge polymer of hydrocarbons was the most important factor to be considered. The plasma of methane, which would deposit a polymer coating similar to the GDPM polymer synthesized in the bell jar reactor (see Part I), was used as a reference. In other words, it was anticipated that an argon glow discharge treatment would produce a similar effect as a methane glow discharge treatment, but an oxygen plasma would cause the opposite effect. The results of the glow discharge treatments of the substrates are summarized in Tables III, IV, and V.

All the substrates showed an improvement in the dry bonding strength (Test A) of the PPX polymer after the argon glow discharge treatment. The wet bonding strength (Test B) of the polymer was also improved, especially for the high surface energy substrates [poly(methyl methacrylate), poly(ethylene terephthalate, and Nylon-6], but the wet bonding strength for the low surface energy substrates [poly(tetrafluoroethylene) and polypropylene] was reduced. Apparently the action of the argon plasma conditioned the substrates and made them more compatible to PPX bonding by plasma polymerizing the sputtered material from the wall of the reactor, which was previously coated with a PPX polymer. The newly formed surface was presumably a hydrocarbon and, therefore, not as hydrophobic as poly(tetrafluoroethylene) or polypropylene but more hydrophobic than poly(ethylene terephthalate), poly(methyl methacrylate), Nylon-6, or glass. Therefore, there was an improvement in the wet bonding strength of the PPX polymer when it was applied to the latter set of polymers.

The effect of oxygen glow discharge treatment is opposite to that of argon glow discharge treatment, and a hydrophilic surface is generated in each case

TABLE III

Effect of *argon* glow discharge treatment of substrate surface on adhesion of poly($p$-xylylene)

| Substrates | Adhesion test results<br>Test A | <br>Test B |
|---|---|---|
| Untreated poly(tetrafluoroethylene)(PTFE) | 0A | 5B |
| Ar glow discharge treated PTFE | 5A | 4B–5B |
| Untreated polypropylene (PP) | 2A | 5B |
| Ar glow discharge treated PP | 2A | 3B–4B |
| Untreated glow discharge polymerized methane (GDPM) | 5A | 4B |
| Ar glow discharge treated GDPM | 5A | 3B |
| Untreated poly(methyl methacrylate) (PMMA) | 1A | 3B |
| Ar glow discharge treated PMMA | 4A | 4B–5B |
| Untreated poly(ethylene terephthalate) (PET) | 0A | 2B–3B |
| Ar glow discharge treated PET | 5A | 4B–5B |
| Untreated Nylon-6 | 0A | 1B–2B |
| Ar glow discharge treated Nylon-6 | 5A | 5B |
| Untreated glass | 0A | 0B |
| Ar glow discharge treated glass | 5A | 1B |

TABLE IV

Effect of *oxygen* glow discharge treatment of substrate surface on adhesion of poly(*p*-xylylene)

| Substrates | Contact angle of water $\theta_{H_2O}$ | Adhesion test results | | |
|---|---|---|---|---|
| | | Test A | Test B | Test C |
| Untreated polypropylene (PP) | 100° | 2A | 5B | 2C |
| $O_2$ glow discharge treated PP (20 min old) | 57° | 0A | 2B | — |
| $O_2$ glow discharge treated PP† (2 days old) | 68° | 0A | 2B | 2C |
| $O_2$ glow discharge treated PP† (over 1 month old) | 85° | 0A | 2B–3B | — |
| Untreated glow discharge polymerized methane (GDPM) | 76° | 5A | 4B | 5C |
| $O_2$ glow discharge treated GDPM (20 min old) | 33° | 0A | 0B | — |
| $O_2$ glow discharge treated GDPM (aged over 1 month)† | 35° | 0A | 1B | 2C–3C |
| Untreated poly(methyl methacrylate) (PMMA) | 73° | 1A | 3B | |
| $O_2$ glow discharge treated PMMA (20 min old in vacuum) | 50° | 0A | 2B–3B | — |
| Untreated glass | 16° | 0A | 0B | 0C |
| $O_2$ glow discharge treated glass | — | 0A | 0B | — |

† Oxygen glow discharge treatment done separately in a bell jar reactor.

TABLE V

Effect of *methane* glow discharge treatment of substrate surface on adhesion of poly(*p*-xylylene)

| Substrates | Adhesion test results | |
|---|---|---|
| | Test A | Test B |
| Untreated poly(tetrafluoroethylene) (PTFE) | 0A | 5B |
| Methane glow discharge treated PTFE | 5A | 5B |
| Untreated polypropylene (PP) | 2A | 5B |
| Methane glow discharge treated PP | 4A | 5B |
| Untreated polyethylene (PE) | 0A | 5B |
| Methane glow discharge treated PE | 5A | 5B |
| Untreated poly(methyl methacrylate) (PMMA) | 1A | 3B |
| Methane glow discharge treated PMMA | 4A | 3B–4B |
| Untreated poly(ethylene terephthalate) (PET) | 0A | 2B–3B |
| Methane glow discharge treated PET | 5A | 4B–5B |
| Untreated Nylon-6 | 0A | 1B–2B |
| Methane glow discharge treated Nylon-6 | 5A | 5B |
| Untreated glass | 0A | 0B |
| Methane glow discharge treated glass | 5A | 2B |

as evidenced by the low contact angle of water. Both the dry bonding strength (Test A) and wet bonding strength (Test B) of the polymers were reduced because of the formation of a hydrophilic/hydrophobic interface.

The most advantageous effect of surface conditioning was found with the methane glow discharge treatment. Improvements in both dry and wet bonding strengths were observed with all the substrates, indicating that a polymer similar to the glow discharge polymer of methane was formed. Methane plasma, unlike either oxygen or argon plasma, is polymer forming, consequently the sputtering effect is less pronounced. The glow discharge polymer of methane cited in Tables I-A and I-B was deposited on glass in a different reactor under conditions specifically tailored to produce good adhesion. Details of the latter process will be presented elsewhere.

## CONCLUDING REMARKS

Polymer coatings applied to the surface of metals, ceramics, and glasses often peel off when the coated objects are subjected to environments of high humidity or aqueous salt solutions at elevated temperatures. This phenomenon, according to our findings, is caused by the spreading of water at the polymer/substrate interface. Whether or not this phenomenon occurs is largely determined by the surface energetics of the substrates. Namely, if the substrate surface has a low surface energy, the peeling occasioned by the action of water does not take place regardless of bonding strength between the coating and the substrate. Because the peeling that results from the action of water is not caused by an external peeling force in most cases, there is no correlation between the bonding strength measured under dry conditions and the resistance to the peeling by the action of water, as previously reported by Inagaki and Yasuda.[7]

In order to obtain coatings that do not peel off as a consequence of the action of the water, it is necessary to modify the substrate surface to reduce its surface energy and/or create special bonds which are not affected by the presence or action of the water. Glow discharge treatment of substrate surface sometimes accomplishes both of these features by inadvertent glow discharge polymerization of sputtered organic material emanating from materials exposed to plasma, but not by cleaning of the surface.

## Acknowledgement

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