

## **Effects of Corona Treatment on Composite Formation. Adhesion Between Incompatible Polymers\***

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### **Synopsis**

Polypropylene-nylon 6 10 composites were prepared by the in situ polymerization of the nylon monomers on polypropylene films. The adhesion between the nylon and the polypropylene was markedly improved by a brief corona discharge treatment of the films in nitrogen prior to coating. This improvement was demonstrated by an increase in the peel strength of the nylon coating and a decrease in brittleness of photo-oxidized composites when corona treatment was used. Adhesive bonding between the nylon and substrate was sufficiently strong to cause cohesive failure in the corona-treated polypropylene. Only interfacial failure was observed at untreated surfaces. These effects were demonstrated by electron microscopy of the surfaces produced in peel tests. The effects of corona treatment on adhesive bonding characteristics of surfaces are discussed in terms of the chemical and physical changes observed in treated surfaces.

### **INTRODUCTION**

Composite formation involves the permanent adhesive bonding together of two or more materials to give a product which can possess a combination of desirable properties of each component. Examples of polymeric composites include bicomponent fibers and laminated films. Composite formation between organic polymers is generally restricted to polymers which are inherently compatible, that is, polymers which are capable of adhering together strongly, or to polymers which can be rendered compatible by a suitable pretreatment. Compatible polymers can include two polymer samples differing only in tacticity, molecular weight, or molecular weight distribution or alternatively a pair of polymers belonging to the same generic group.

The need to bond normally incompatible polymers has led to the interposition of adhesive layers between the components, or to the use of surface activation techniques which include plasma discharge treatment of one or more of the preformed components.<sup>1</sup> Such plasma treatment may be conducted at below 100 torr (glow discharge), or near atmospheric pressure with low (corona discharge) or high (arc plasma) current density.<sup>2</sup> During or after plasma treatment, composites may be prepared directly

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by pressing together the activated polymer films<sup>3</sup> or by the deposition of a second polymer on the activated surface.<sup>4-7</sup>

In spite of the widespread industrial use of the plasma activation techniques, relatively little has been published on the physical and chemical changes that take place during these treatments.<sup>4,8</sup> Even less is known about the relationship between these changes and the degree of adhesive enhancement which the surfaces undergo as a consequence of these treatments. We have investigated the effect of nitrogen corona treatment on polypropylene films as related to the physical properties of bicomponent films prepared by the in situ polymerization of nylon 6 10 monomers on the treated films.

## EXPERIMENTAL

### Apparatus

The corona treatment apparatus is shown in Figure 1. All cross-hatched parts were of metal. The inner and outer drums were 3-mm-wall Pyrex tubing of 8.5 cm and 11.0 cm O.D., respectively. The corona discharge was maintained between the three outer metal electrodes and the inner grounded metal cylinder. Samples were taped around the outside of the inner Pyrex drum, which rotated at  $\sim 30$  rpm during treatment. High tension (25 KV at 0.5 MHz) was supplied to the three outer electrodes by three separate generators (Fisher Scientific Instruments).

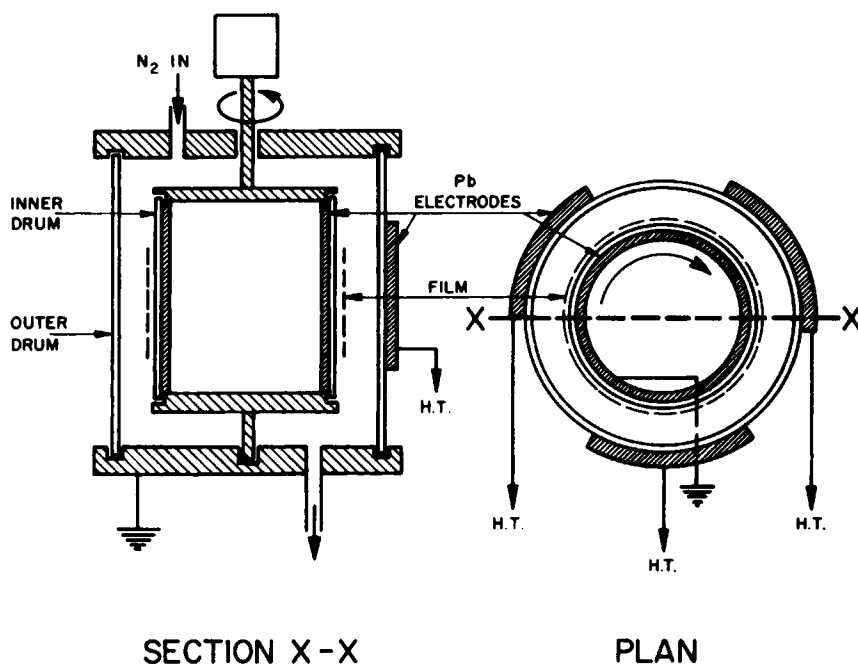


Fig. 1. Corona treatment apparatus.

Prior to corona treatment, nitrogen (Linde, 99.996%) was passed over the sample in the apparatus for 15 min at 60 ml/min, and this flow was maintained during the treatment and for 30 min after treatment. For comparative purposes, some corona treatments were performed in argon. Weight loss of films after N<sub>2</sub> corona treatment was determined on a microbalance after static charge dissipation with a small radioactive source.

### Materials and Coating Procedure

The substrate was a 22-micron-thick film of predominantly isotactic polypropylene (Eastman), which was Soxhlet extracted with acetone for 48 hr prior to use, to reduce the level of surface contaminants.

The polypropylene films were either spray or dip coated with solutions of sebacyl chloride and hexamethylenediamine to produce nylon 6 10. The sebacyl chloride (0.059*M*) was dissolved in carbon tetrachloride or tetrachloroethylene and the hexamethylene diamine (0.1*M*), in 0.20*M* aqueous sodium hydroxide. Dip coating was effected by first immersing the film sample for 10 sec in the solution of sebacyl chloride, allowing the dipped film to drain, and then immersing for 10 sec in the solution of hexamethylenediamine. Polymerization was spontaneous upon dipping the treated film into the diamine solution. The resultant film with its coating of nylon 6 10 was then washed in methanol for 20 sec. Spray coating was effected by first spraying the films with the solution of sebacyl chloride and then with the solution of hexamethylenediamine. The sprayed films were then immediately washed in methanol for 10 sec. Here also polymerization was spontaneous upon the application of the second monomer. Spraying was carried out with a corrosion-resistant, external-mix syphon feed spray gun set to give a finely atomized fan pattern. After spray or dip coating, the film samples were dried for 3 min at 130°C to give nylon coatings which were not tacky. Application of the monomer solutions in the reverse order of the sequence described above always resulted in irregularly coated films.

### Photo-oxidation

The unstabilized polypropylene films were irradiated in air with an Atlas Carbon-Arc Fade-Ometer for 25 hr at an ambient air temperature of 35°C.

### Contact Angle

The contact angles of water or sebacyl chloride sessile droplets (0.005 ml) on various films were determined at 24°C, using a microscope fitted with a goniometer eyepiece, essentially as described by Bright and Malpass.<sup>9</sup> Measurements were made on each side of fresh droplets, and averages were calculated from values obtained from at least five separate droplets. Only advancing angles are reported. Observed angles usually agreed within ±1° for a given surface.

The properties of the nylon-coated polypropylene films were evaluated in the following tests:

### IR Analysis

The presence of surface coatings and the completeness of polymerization were checked by attenuated total reflection (ATR) infrared (IR) spectroscopy on a KRS-5 (TlBr-TlI) reflection element. The experimental procedure used to obtain ATR spectra has been described previously.<sup>8</sup> The ATR technique allows the direct recording of the IR spectrum of thin surface layers on samples. Coating thicknesses were estimated by comparing the  $1638\text{ cm}^{-1}$  amide absorption band detected by transmission IR with the absorbance given by amide standards.

### Tensile Testing

Stress-strain curves were recorded on an Instron tensile tester (Type TT-C) by a method similar to the micromethod ASTM #D882-67. The films were 2.0 mm wide, the initial grip separation was 1.3 cm, and the crosshead speed was 5.2 cm/min with load cell C (500 g full-scale deflection).

### Coating-Substrate Bonding

The relative strength of the nylon-polypropylene bonding resulting from various experimental conditions was evaluated in the following peel test. Polypropylene films were spray coated on one side only with the nylon monomers and dried. The uncoated sides of the polypropylene films were fastened to rigid metal backing plates by double-surface adhesive tape. One arm of a perforated metal  $90^\circ$  angle bracket (1.5-cm-long arms, and  $1.5 \times 1.5$  cm contact area) was cemented to the exposed, coated surface of each film with a 50% aqueous solution of polyacrylic acid (PAA). After drying at  $25^\circ\text{C}$  (15 hr), this PAA layer completely enveloped one arm of the bracket. For a peel test, the metal backing plates were clamped in a vertical plane so that the protruding arm of the angle bracket was above the cemented arm (i.e., in the configuration  $\Gamma$ ). Loads were applied directly downward to this protruding arm at 1.3 cm from the vertically mounted composite surface. Loads were increased steadily until the polypropylene-nylon bond failed, and the average of three or more values was recorded. In all cases, dyeing or microscopy showed that the system cleaved at the nylon-polypropylene interface, or that the polypropylene substrate failed. For a given composite, peel loads usually agreed to within  $\pm 50$  g.

### Microscopy

Optical and electron microscopic techniques were used in the investigation of films and their coatings. Optical microscopy provided information on the gross details of the films before and after coating.

Direct surface replicas and detachment replicas of the films were viewed in transmissive mode with the aid of a Philips 100 electron microscope (TEM) at magnifications in the range of 1,000 to 50,000 times. Direct replicas were made by vacuum evaporating approximately 10 to 25 Å of platinum at an angle of 45° followed by about 250 Å of amorphous carbon normal to the surface of the film. This replica was subsequently stripped off the polymer with a temporary backing layer of PAA. This method also removed material which was loosely bound to the film surface. Consequently, certain direct replicas showed a surface topography over which zones of relatively electron transparent, detached material were present. Detachment replicas were made by first stripping off the surface layer with PAA and then coating the detached surface with platinum and carbon. This latter method emphasized surface detail at the separation interface which, on some samples, occurred below the original polypropylene surface.

Large areas of film as well as PAA-stripped separation interfaces were also examined directly in a Cambridge-Kent scanning electron microscope (SEM) after 200 Å of evaporated gold had been applied. This technique permitted the rapid survey of large areas of the films and established that the higher resolution TEM data were representative of the samples investigated.

## RESULTS

Dip or spray coating of polypropylene with nylon 6 10 monomers resulted in hard, translucent surface coatings of the nylon. Transmission IR analysis showed weak bands representative of amides ( $\sim 3300$  and  $1638$   $\text{cm}^{-1}$ ), and these were resolved in greater detail by an ATR examination of the coated surfaces. Examples of transmission and ATR curves for nylon 6 10-coated ( $\sim 0.25$   $\mu$  in thickness) polypropylene are shown in Figure 2. The absence of an absorption at  $\sim 1800$   $\text{cm}^{-1}$  in the ATR spectrum indicates complete consumption of the acid chloride by the amine. Since corona modification is mainly restricted to the surface facing the air gap,<sup>8</sup> the activation of both sides of a sample required two separate discharge treatments in the corona apparatus (Fig. 1). Only

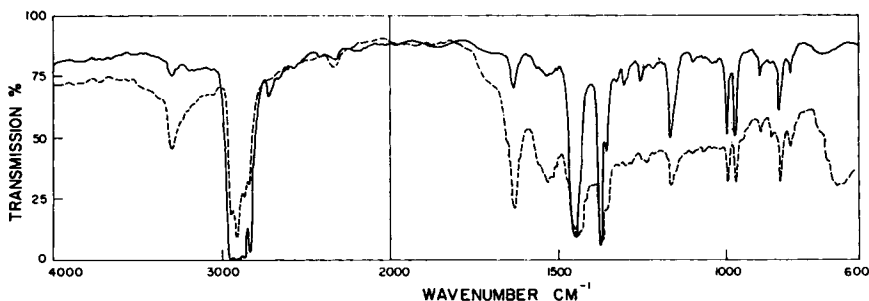
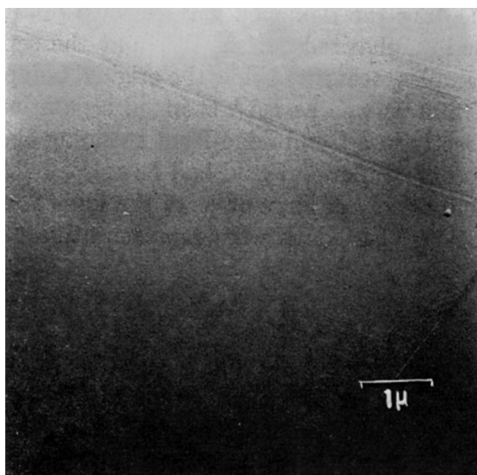


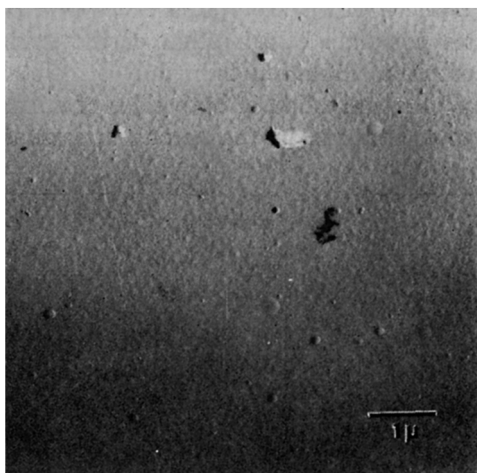
Fig. 2. IR spectra of nylon 6 10-coated polypropylene. (—) transmission spectrum; (---) ATR spectrum on a KRS-5 reflection element at 45°.

small weight losses were detected after prolonged  $N_2$  corona treatment. For example, a 0.01% weight loss was detected after 15 min corona treatment of one side of a 22- $\mu$  polypropylene film. Weight changes were undetectable with shorter treatment periods.

Transmission electron micrographs of direct replicas of a polypropylene substrate both before and after corona treatment are shown in Figure 3, together with micrographs of these same surfaces after undergoing identical spray coatings with nylon 6 10 monomers followed by the usual heat treatment. These micrographs showed that the corona-treated surfaces were covered with small, circular mounds even after brief corona treat-



(a)

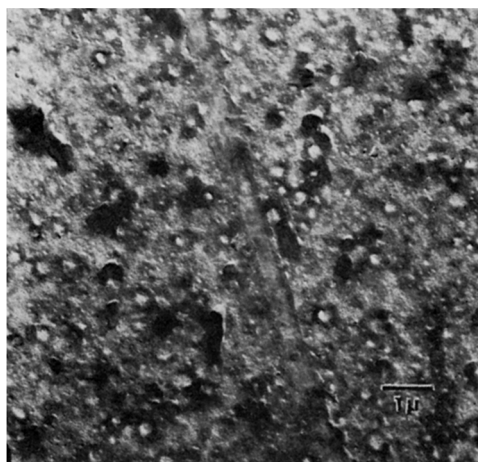


(b)

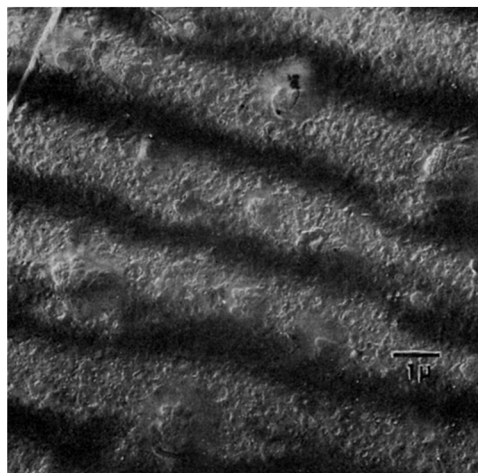
Fig. 3 (continued)

ment (2 to 3 sec). These protuberances generally increased in size and number with continuing exposure to the corona discharge.

The relative effect of the duration of the substrate corona pretreatment of the nylon-substrate adhesive bonding was investigated by determining the load required to peel off brackets firmly bonded to the nylon coating with PAA. The bonding appears to reach a limit after  $\sim 2$  sec discharge treatment, as shown in Figure 4. The penetration of the PAA adhesive through the relatively thin, but continuous nylon coating to the poly-



(c)



(d)

**Fig. 3.** Transmission electron micrographs of surfaces, direct replicas (carbon-platinum shadowed): (a) polypropylene before corona treatment; (b) polypropylene after 100 sec  $N_2$  corona treatment; (c) surface in (a) after spray coating with nylon 6 10 monomers; (d) surface in (b) after spray coating with nylon 6 10 monomers.

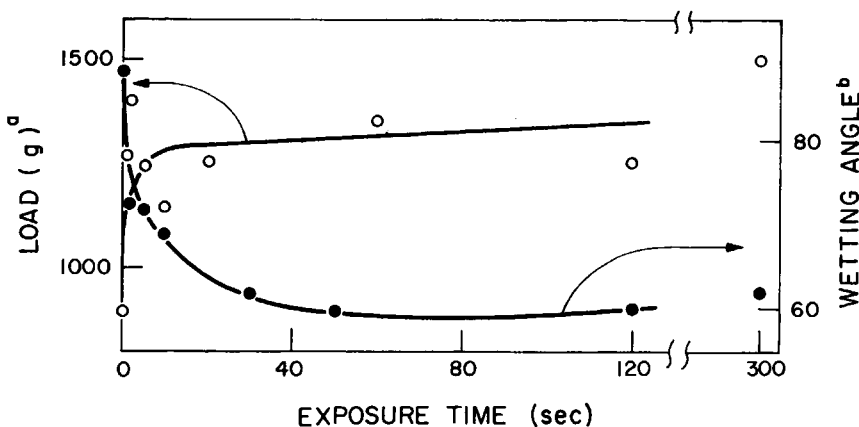


Fig. 4. Effect of corona duration on nylon peel strength and polypropylene wettability: (a) load required to peel angle brackets from the composite; (b) advancing contact angle for water, in degrees.

propylene substrate is unlikely in view of the high molecular weight and high viscosity of the PAA solution. Thus the PAA cannot directly contribute to the observed peel loads. Detachment replicas were prepared from nylon coatings which had been peeled from 100-sec corona-treated polypropylene. Transmission electron micrographs of these replicas are shown in Figure 5 (a and b). The surfaces shown in Figure 5 (a and b) originally faced into the polypropylene substrate and were shadowed after stripping off the nylon coating with the PAA. Direct replicas of the residual polypropylene films were not possible due to local stretching of the thin films when the nylon layer was stripped. Scanning electron microscopy was used to examine polypropylene films which had been nylon coated without corona pretreatment and then exposed to the above peel test. Figure 5c shows a boundary between the intact portion of a composite film (left-hand side) and the bare polypropylene surface exposed by the peel test (right-hand side of the micrograph).

Advancing contact angle measurements were made on polypropylene films after various periods of corona treatment. The first measurements were made within 60 sec of removing the samples from the cell and repeated periodically during 30 min. The observed values were not dependent on the time elapsed between treatment and measurement. Average values for water contact angles are shown in Figure 4. Contact angles obtained after argon corona treatment were virtually identical to those shown in Figure 4. Sebacyl chloride drops showed contact angles of 30° on untreated polypropylene and 23° on polypropylene which had received 100 sec of N<sub>2</sub> corona treatment. Tetrachloroethylene had zero (or very low) contact angle on untreated polypropylene.

The influence of corona treatment is also illustrated by the effect of an adherent nylon coating on the stress-strain behavior of extensively photo-



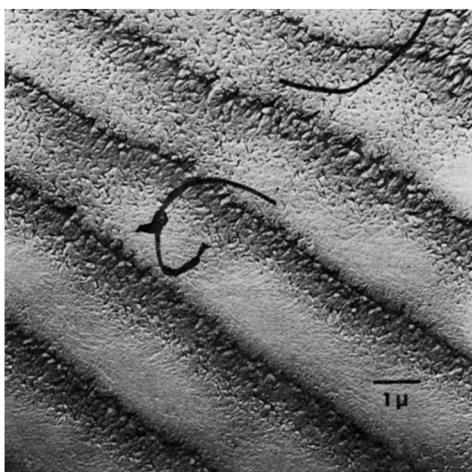
oxidized polypropylene films. After UV irradiation, parts of the oxidized film were nylon coated ( $\sim 0.5 \mu$  thickness) on both sides. An oxidized film which had been nylon coated without corona pretreatment gave only a 50% elongation before failure, as did both an uncoated but otherwise identically treated film sample and an uncoated but  $N_2$  corona-treated sample. However, samples of this oxidized film that were given a similar nylon coating preceded by  $N_2$  corona treatment gave approximately a two-fold increase in percentage elongation at break. (The unoxidized polypropylene film, both nylon-coated and uncoated, gave a 600% elongation at break.) The nylon coating did not affect either the yield load or the load at break of the samples.

### DISCUSSION

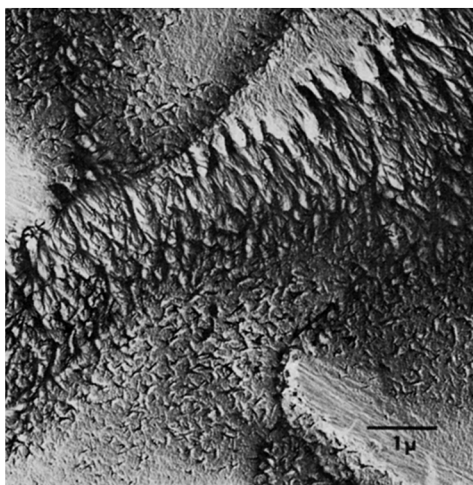
The results shown in Figure 4 illustrate the improvement in coating-substrate adhesion brought about by the corona pretreatment. The effect of corona treatment on surface texture is illustrated by Figure 3, micrographs c and d. These show that a relatively smooth, continuous nylon coating is formed on the corona-treated surface, whereas a droplet-like layer is obtained on the untreated substrate. In addition, optical microscopy showed that uniformity in coating and the absence of uncoated patches were found only in the corona-treated samples.

For well-bonded surfaces, failure during peel tests took place principally within the interior of one of the components and not at the bonded interfaces. An example of the cohesive failure in polypropylene is shown in Figure 3d, where a diffuse banded structure is visible, together with the surface texture of the direct replicas. Réplication has removed the nylon coating from the corona-treated polypropylene substrate together with a thin surface layer of polypropylene, which shows periodic fluctuations in thickness. The thicker bands give rise to the dark shadows visible in the micrographs. The appearance of a typical cohesive failure plane is shown in Figure 5a. This figure shows a replica of the polypropylene layer which had been detached from the corona-treated substrate with the nylon coating during the bracket peel test used to study the effect of corona duration. The micrograph shows in detail the ridges of up to  $\sim 0.5 \mu$  width, which represent periodic increases in the thickness of the layer torn from the polypropylene surface. Figure 5b shows the same effect in greater detail. Fibrils of polypropylene appear to be visible along the thicker bands.

The periodic band structure in the relatively weak surface skin (1–2  $\mu$  in thickness) of the polypropylene film may result from the particular morphology of the polymer. Commercial extruded films, such as that used in this work, are not spherulitic in structure, but are almost exclusively row nucleated. The phenomenon of row nucleation has been described by Keller and Machin,<sup>10</sup> and such a material would be expected to favor cohesive failure near the boundary of two contiguous "rows" in the relatively weak surface layer. This is consistent with our observation that



(a)

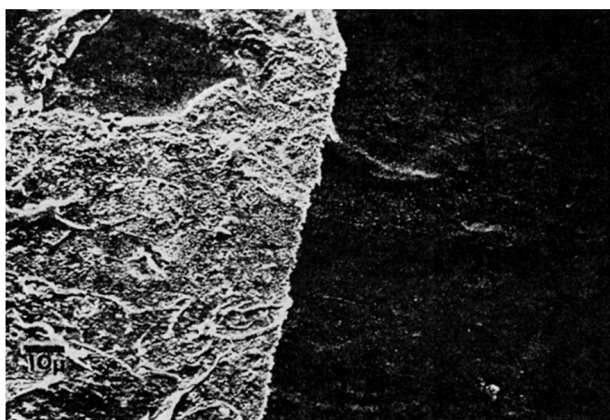


(b)

Fig. 5 (continued)

special films, prepared so as to have a spherulitic morphology, failed predominantly at the spherulite boundaries when treated under analogous conditions. This preferred failure zone may also be understood in terms of a spherulite model where imperfections such as voids, chain ends, and low molecular weight polymer are concentrated on the periphery of the spherulites.<sup>11</sup>

Cohesive failure deep within the interior of films which had previously received corona treatments is in contrast to interfacial failure of untreated film, as shown in Figure 5c. This figure shows a micrograph of the boundary between residual nylon and a nylon-free area created by peeling off the coating layer with PAA during a determination of interfacial bonding. The removal of the nylon layer exposed a virtually unaltered polypropylene surface where original surface marks could still be seen.



(c)

Fig. 5. Electron micrographs of surfaces produced by peeling: (a) and (b) detachment replicas of polypropylene surfaces formed by peeling nylon from corona treated (100 sec) surfaces (transmission micrographs); (c) scanning electron micrograph of a surface produced by peeling nylon from the right-hand side of a uniformly coated, but untreated polypropylene film.

The apparent plateau value in the bonding between polypropylene and nylon shown in Figure 4 may also be interpreted as a cohesive failure within the polypropylene substrate, and thus is not a measure of the true interfacial bonding developed between the two polymers. Nevertheless, Figure 4 does show that a brief corona exposure (less than 5 sec) with the low-powered generators employed markedly improves the nylon-polypropylene adhesion.

The marked increase in nylon-polypropylene adhesion after  $N_2$  corona treatment is somewhat surprising in view of the slight improvement in epoxy-polypropylene adhesion reported after low-pressure  $N_2$  plasma treatment of polypropylene (glow discharge).<sup>5</sup> However, the reported chemical changes accompanying the low-pressure plasma treatment<sup>5</sup> also differ significantly from the changes observed during  $N_2$  corona treatment.<sup>8</sup>

The decrease in brittleness of photo-oxidized films after corona treatment followed by nylon coating can be explained in terms of the good interfacial bonding developed on corona-treated surfaces. The photo-oxidation of polypropylene films has been shown to occur predominantly in an extremely thin surface layer.<sup>12</sup> During this oxidation, an extensive ultrastructural reorganization of the film surface occurs, producing many surface flaws.<sup>13</sup> The nylon coatings are too thin ( $\sim 0.25 \mu$ ) to directly affect the stress-strain behavior of the composite, but are capable of filling and bridging some of the surface cracks. The tenaciously bonded nylon layer produced by corona treatment can probably distribute the applied stress and prevent or retard the propagation of the surface cracks through the films. The observed improvement in the stress-strain behavior of the

oxidized polymer is similar to the reported improvement for well-bonded Mylar-aluminum-Mylar, and polyethylene-polystyrene-polyethylene composites.<sup>14</sup>

### Role of Corona Treatment

Interfacial adhesion has been proposed to originate in a combination of four mechanisms: (1) mechanical interlocking, (2) adsorption (mainly due to dispersion forces), (3) electrostatic attraction, and/or (4) interdiffusion.<sup>15</sup> Although adsorption has largely been favored as the dominant cause of interfacial bonding, several other effects must also be considered. The most obvious of these is the possibility of consolidation of mechanically weak surface layers on the substrate.<sup>4,16</sup> Surface topography can obviously enhance mechanical anchoring. In addition, certain types of surface structure may enhance capillary forces which would improve the wetting of a low-energy surface by a higher energy liquid, as proposed by Huntsberger.<sup>17</sup> Finally, a partially "microporous" or locally permeable surface (i.e., one with a large amorphous and microvoid content) would favor diffusion of adhesive or adhesive precursor molecules into the substrate, to create an adhesive-substrate composition gradient instead of a sharply delineated contact interface. This penetration at various sites will enhance adhesion both by increasing the effective contact area and by reducing stress concentration. The chemical nature of a surface is probably important only in determining the critical surface tension, and hence the ease of spreading of an adhesive on the surface. Chemical interaction between the surface and adhesive need only be of secondary importance, since dispersion forces alone exceed the cohesive strength of most organic polymers.<sup>18</sup>

It is not immediately obvious which of the surface changes produced by corona discharge treatment in nitrogen are responsible for the observed improvement in the bonding characteristics of the surface. We have previously reported the chemical effects of N<sub>2</sub> corona discharges on polypropylene surfaces under conditions similar to those used in the present work.<sup>8</sup> The observed changes included the formation of a surface layer of C-C unsaturation and C-C crosslinking of 200–400 Å thickness. Nitrogen appeared to behave as an inert gas, since it was not chemically incorporated into the surface in detectable amounts. The glow discharge treatment of polyethylene in helium has been shown to cause similar chemical changes and to produce surfaces which readily bonded to epoxy resins.<sup>4</sup> These latter surfaces also showed no decrease of bonding ability after bromination of the surface unsaturation and were reported to have the same critical surface tension as the untreated polymer. This last point has recently been disputed by Malpass and Bright<sup>19</sup> who observed that improved adhesion to linear polyethylene was always associated with an increase in surface energy. This increase was attributed to posttreatment air oxidation of the films.

Although  $N_2$  corona-treated polypropylene surfaces are oxygen sensitive immediately after treatment, storage for 30 min under flowing nitrogen before exposure to air (the same conditions as used in this work) was found to produce a surface which showed no detectable oxidation by ATR spectroscopy.<sup>8</sup> Similarly, posttreatment oxidation was apparently unimportant, since the wetting angle was independent of the duration of air exposure after a given  $N_2$  or argon discharge treatment. The surface energy of polypropylene does, however, appear to increase up to a maximum level during  $N_2$  corona treatment, as shown by the decrease in wetting angle with increasing corona duration (Fig. 4). Since similar decreases in wetting angle were observed with argon corona treatments, the change is not dependent on the nature of the activated gas. Surface roughness has been shown to have a marked effect on contact angle, although the relationship of Wenzel,<sup>20</sup> which indicates decreasing angle (for acute wetting angles) with increasing roughness, is an oversimplification (see, for example, Dettre and Johnson<sup>21</sup>). From a comparison of micrographs a and b, Figure 3,  $N_2$  corona treatment produces many roughly hemispherical mounds (rising to approximately 500 Å above the surface). The mounds were detectable after only 1–2 sec of treatment and increased in both size and number with increasing treatment time. After ~5 sec of treatment, roughly 10% of the surface was covered by the mounds. It is possible that these surface features cause at least part of the observed decrease in wetting angle, although some of the observed decrease may also result from chemical modifications of the surface (C–C unsaturation, or trace amounts of oxidation).

Schonhorn and Hansen<sup>4</sup> have attributed the improvement in adhesive bonding after glow discharge treatment of various polymers to an improvement in surface cohesion of the substrate, that is, a chemical consolidation of weakly bound material present as a thin surface skin on the extruded polymers. The consolidation of a weakly cohesive surface layer by corona-induced crosslinking may also be of importance in adhesion to polypropylene.<sup>22</sup> This effect, however, appears to be supplemented by several additional, interrelated factors. For example, the drop in contact angle during treatment facilitates the spreading of sebacyl chloride on polypropylene surfaces. Similarly, the observed concurrent changes in surface topography may affect both contact angle and "mechanical anchoring."

The corona-produced mounds (Fig. 3b) may result either from massive surface erosion to expose resistant domains, from the deposition of molecular fragments ablated from the surface by the discharge, or from local fusion of small discrete areas. The first two possibilities appear unlikely in view of the early appearance of the mounds (detected after 1 to 2 sec of exposure), the negligible weight loss after prolonged treatment, and the fact that preliminary results indicate the absence of similar objects after glow discharge treatment of the polymer. The mounds may be associated with the "condensed" spark discharge which occurs during corona treatment, even between large, flat electrodes. The mounds may originate

from local fusion caused either by the recombination of many ions and electrons in discrete regions<sup>23</sup> or by a direct heating with the plasma streamers constituting each spark discharge. The mounds then probably indicate the presence of relatively disordered, low-density regions (created by the rapid thermal quenching which must follow fusion) in a matrix of unaltered polymer. The simultaneous crosslinking of the surface which occurs during corona treatment<sup>8</sup> could also impede extensive reversion of the zones to the initial state.

In addition to improving surface wettability, the mounds may present regions of enhanced permeability through which nylon chains can grow or diffuse and ultimately key the nylon coating onto the polypropylene. Together with the crosslinking of the surface skin, this keying effect may be largely responsible for the vast improvement of surface bonding after the N<sub>2</sub> corona treatment of polypropylene. The extensive interpenetration of the two polymers at these contact points may well produce a total interfacial bond strength comparable to that which would be developed if complete wetting occurred.

Published work tends to support some of the points discussed above. Microscopic surface roughing has been reported to occur during the corona treatment of cellulose.<sup>8</sup> Malpass and Bright<sup>19</sup> have suggested that the glow discharge treatment of linear polyethylene may cause an increase in surface amorphous content which leads to an associated increase in surface penetration by the adhesive molecules. Garnish and Haskins<sup>22</sup> have observed that exposure of polypropylene surfaces to trichloroethylene vapor leads to an extremely rough, highly bondable surface, despite an observed decrease in the critical surface tension. This observation tends to support the contention that surface wettability is not an indispensable prerequisite for adhesive bonding.

## CONCLUSIONS

Corona treatment has been shown to greatly improve the adhesive bonding between the inherently incompatible polymers nylon 6 10 and polypropylene. Although polypropylene film substrates alone have been discussed, the observed effects can be expected to take place for fiber, yarn, and fabric substrates. The effects of corona treatment on fabrics and films formed from various polymers have been studied and will be reported elsewhere.<sup>24</sup>

The observed improvement in adhesive bonding is believed to be partially attributable to the chemical consolidation of weak surface layers. However, changes in surface topography which appear to result from the spark nature of the corona discharge might possibly improve the micro-wetting of the treated surface and play an important role in interfacial adhesion. This latter possibility is being further investigated by a comparison of the physical and adhesive properties of polymer films that have been activated by either glow or corona discharges or by solvent

vapors. Finally, it is possible that all of the C-C crosslinking and unsaturation detected by IR ATR spectroscopy on N<sub>2</sub> corona-treated surfaces<sup>8</sup> occurs in the mounds visible in Figure 3a. If this were the case, then improvement in adhesive bonding owing to weak layer consolidation, to wettability increase, and to interpenetration of the coating and film could all be ascribed to mound formation.

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