

Electroplating on Crystalline Polypropylene. I. Compression Molding and Adhesion

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Synopsis

A direct relationship between polymer processing and metal adhesion is evident from studies of compression-molded isotactic polypropylene (PP). Cooling rate, nature of the mold surface, and after-plated annealing are shown to affect the peel adhesion of the plated components. This report described (1) the relation of compression molding variables to polymer surface morphology, (2) the oxidative cracking behavior of the surface due to pretreatment with chromic-sulfuric acid in terms of crystallite orientation and crystallinity, and (3) the effect of surface crack patterns on adhesion.

The nature of the mold surface is the single most important variable for controlling the surface morphology of PP. Compression molding PP against oxidized aluminum or copper produces a spherulitic surface, whereas molding the polymer against Mylar or Teflon produces a transcrystalline surface. Surface etching of PP homopolymer produces sponge-like crack patterns characteristic of the morphology. Radial patterns are observed on spherulitic surfaces and random patterns, on transcrystalline ones. The various surface patterns are developed in the oxidative process by swelling of amorphous material followed by oxidative stress cracking and dissolution.

Metal-to-polymer adhesion, as measured by the peel test, may involve failure at the interface or within the polymer. Three factors are shown to be important: (a) the geometry of the interface, (b) the diminished strength of the polymer surface arising from attack by the oxidizing acid, and (c) the crystallinity of the fissured polymer surface. The highest peel values are associated with conditions that lead to deep and frequent fissuring of the polymer surface and minimum oxidative damage.

INTRODUCTION

Electroplating polymers to simulate bright, decorative metals is a technique at least twenty years old. Unfortunately, with most polymers the various proprietary processes—which involve chemical deposition of an electrically conductive metal layer on the polymer surface preparatory to electroplating—did not develop metal-to-polymer adhesion resistant to environmental factors. Plated polymers were consequently restricted to decorative uses only. Deposition of thicker coats mitigated these deficiencies but proved to be impractical for production of functional parts.

In this decade, ABS, a two-phase polymer, was successfully plated with a thin, strongly adherent metal layer. This was accomplished by acid etching of the polymer surface to remove the rubber thereby providing anchoring sites for the deposited metal.

Shortly thereafter, isotactic (semicrystalline) polypropylene (PP) was reported to develop much higher, but poorly reproducible metal-to-plastic adhesion when treated with a modified plating chemical process.

This paper describes the effect of compression molding conditions on the surface morphology of PP and the role of surface structure on metal adhesion. Optimum compression molding conditions for PP are established.

EXPERIMENTAL

The Metal Coating System

Polymers possess inherently low conductivities (10^{-22} – 10^{-10} ohm $^{-1}$ cm $^{-1}$) compared to metal (10^4 – 10^8 ohm $^{-1}$ cm $^{-1}$) and must be rendered conductive before standard electroplating techniques may be applied. One method is to chemically deposit a layer of metal uniformly on the surface. The MacDermid system was chosen for this purpose. The entire electroless deposition process, including a wash between each bath, consists of 13 separate operations the essential baths of which are outlined below.

Organic Solvent Treatment. This bath is an aqueous dispersion of turpentine and polyethers operated at $71 \pm 2^\circ\text{C}$. Samples are immersed for 15 min and then washed thoroughly with water. For plating other polymers, the chemical composition of this bath is changed, except in the case of ABS, where it is omitted entirely. The solvent swells the amorphous regions in the PP surface, making it susceptible to rapid etching.

Etchant. The etchant is an oxidizing acid bath operated at $82 \pm 2^\circ\text{C}$ and consisting of a sulfuric acid solution (approx. 20%) saturated with chromium trioxide. A commercially available fluorinated hydrocarbon, Zero Mist (The UdyLite Corporation, Detroit, Michigan), is used as surfactant. Samples are immersed for 7 min and then thoroughly washed. The etchant increases dramatically the polymer surface wettability and roughness.

Two oxidation products have been identified: carbon dioxide and acetic acid. Formation of these products arises from carbon-carbon bond cleavage which is the result of stepwise oxidation of the polymer.

The solvent treatment and etchant steps in the electroless process largely determine metal-to-polymer adhesion through formation of a complex crack pattern on the polymer surface.

Activation. An aqueous dispersion of palladium metal, formed by reduction from Pd^{2+} , is adsorbed on the roughened polymer surface where it serves as a catalyst for subsequent nickel deposition. Pd^0 is believed to be present as islands¹ rather than as a continuous film. All specimens are processed in 3.5-min cycles at $49 \pm 2^\circ\text{C}$.

Electroless. The electroless bath deposits a conductive layer of a nickel-phosphorous alloy (containing approximately 95% nickel) on the activated polymer surface in two stages. Firstly, nickel deposits on the palladium sites,¹ and secondly, the nickel-covered sites grow—nickel serves as its

own catalyst—until they impinge on their neighbors. Completion of this step leads to surface conductivities of approximately 10^4 – 10^6 ohm⁻¹ cm⁻¹. Samples are processed in 7-min cycles at $32 \pm 2^\circ\text{C}$. The conditions of all the baths in the electroless process are preferred but lie within broad limits suggested by MacDermid Company.

Copper Electroplating Bath. After the polymer surface is conductive, the sample may be metal coated using standard electroplating baths. For adhesion studies, a 2-mil-thick layer of copper is plated from an UdyLite Bright Acid Copper (UBAC) bath at 54 amp/ft² for 45 min. To avoid “burning off” the thin (0.01–0.02 mils) electroless Ni coat with the high current density, samples are first “struck” in this bath for 2 min at 15 amp/ft².

The thickness of the copper deposit must be uniform within each sample to assure reproducibility of the peel adhesion test. Uneven current density at the plating surface (cathode)—the chief cause of thickness variations—was controlled by using specially designed baffles placed on either side of the sample. Variations in the deposit were monitored by plating copper onto a clean stainless steel panel. Since the adhesion between these two metals is low, the copper foil was easily removed, and its thickness was measured. Thickness variations observed with the baffle-modified bath were ± 0.2 mils and did not affect peel test values.

Jacquet Peel Adhesion Test

Adhesion of the metal layer to the polymer is determined by measuring the force needed to pull a $\frac{1}{2}$ -in. wide strip of metal from the plated surface. The test is carried out on an Instron at a 1 in./min jaw rate separation with the peeling strip nominally vertical to the sample surface. The force, recorded on a strip chart, is reported as peel adhesion in pounds per inch of specimen width.

Peel tests were run on 3- × 4-in. plaques in the long direction; similar results obtained in the transverse direction indicated no anisotropy. Test strips were formed on each plated plaque by cutting parallel lines spaced $\frac{1}{2} \pm \frac{1}{64}$ in. through the metal to the polymer with a rotating saw. The strip end was lifted prior to testing by inserting the tip of a hot soldering iron between the metal and plastic. Specimens were secured in a specially designed test jig for the test (Fig. 1).

The Jacquet peel test, like other adhesion tests, is difficult to analyze in terms of fundamental material parameters.² Failure can occur at one of several locations: (a) in the metal layer, (b) at the metal-polymer interface, (c) in a weakened surface layer of polymer, or (d) in the bulk polymer. The failure most commonly experienced in plated PP exhibiting peel adhesion greater than 4 lb/in. occurred in a weakened polymer surface layer as evidenced by the presence of a thin layer of polymer on the peeled metal strip. Interface failure occurred in samples with lower adhesion values. In a few samples, discussed later, failure occurred partially in the polymer bulk and was associated with peel adhesion values in excess of 50 lb/in.

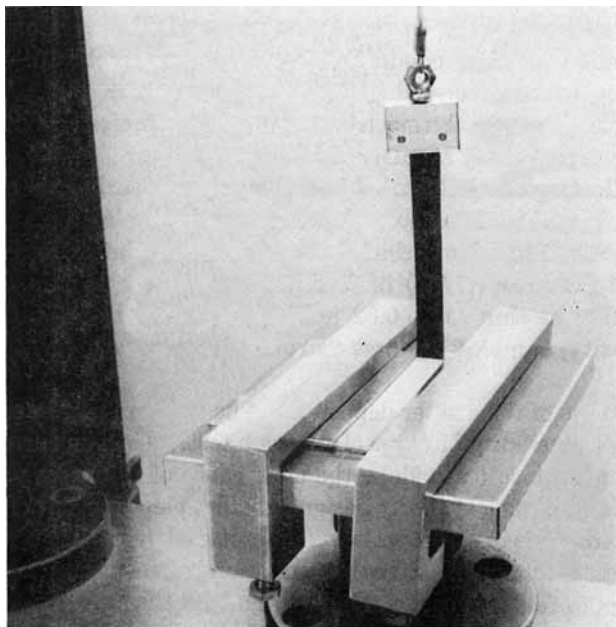


Fig. 1. The Jacquet peel test. Photograph of the sample holder which fits into the Instron.

The mechanical properties of the polymer surface and the geometry of the polymer-metal interface represent the major material factors that influence test values. Variations in peel adhesion values due to peeling speed, direction, and temperature were minimized by the test procedures and equipment described above. Reproducibility of the peel test within each sample and from sample to sample was about 1 lb/in. based on 10 samples with 6 tests per sample. All samples were aged two weeks at room temperature prior to testing.

Materials

Two commercially important polymers were molded:

1. Shell PP 5520 (homopolymer)
2. Hercules PP 6523 (homopolymer)

Both materials were dried in a vacuum oven overnight at 60°C before molding.

Compression Molding

Each sample was first melted by bringing it lightly in contact with the hot platens (0 psi) for 5 min before compression at 210°C for 15 min and then cooled to either (a) room temperature under pressure overnight (slow), or (b) 65°C under pressure in 20 min (normal), or (c) approximately 10°C without pressure in 15 sec by immersion in ice water (fast).

Mylar and Teflon films were used as received for mold surfaces. Aluminum and copper mold surfaces were oxidized as described by Schonhorn.³

Microscopy

Optical micrographs were taken with a Leitz-Panphet microscope equipped with a polaroid camera. For transmission microscopy in polarized light, samples of PP were sectioned using a Porter-Bleem Ultratome and mounted between glass slides in Canada balsam.

Plated cross sections were prepared for reflection microscopy by cutting specimens from plated plaques parallel to the extrusion direction (starting from the gate), encasing them in an epoxy resin, and carefully grinding and polishing.

Scanning electron micrographs were taken on a Stereoscan model with the cooperation of Cambridge Ltd. (through their distributors Engis Engineering, Morton Grove, Ill.) and on the JSM-2 model with the cooperation of the Japanese Electron Optics Laboratory (Boston, Mass.).

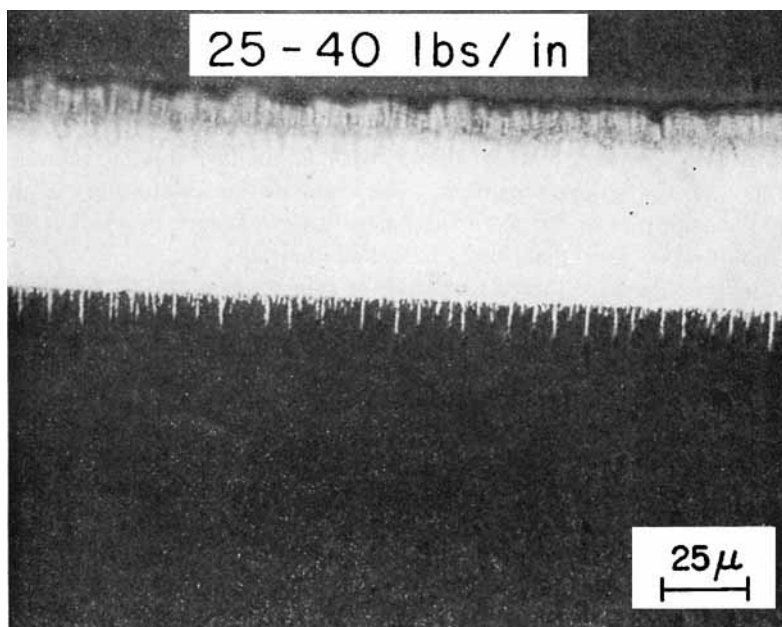
As-molded surfaces were prepared for scanning electron microscopy as follows: Samples were treated in the swellant and etchant, thoroughly washed and dried, mounted on a support, and made conductive with evaporated gold or platinum. Cross sections were encased in epoxy and carefully ground and polished prior to the above chemical treatment.

RESULTS AND DISCUSSION

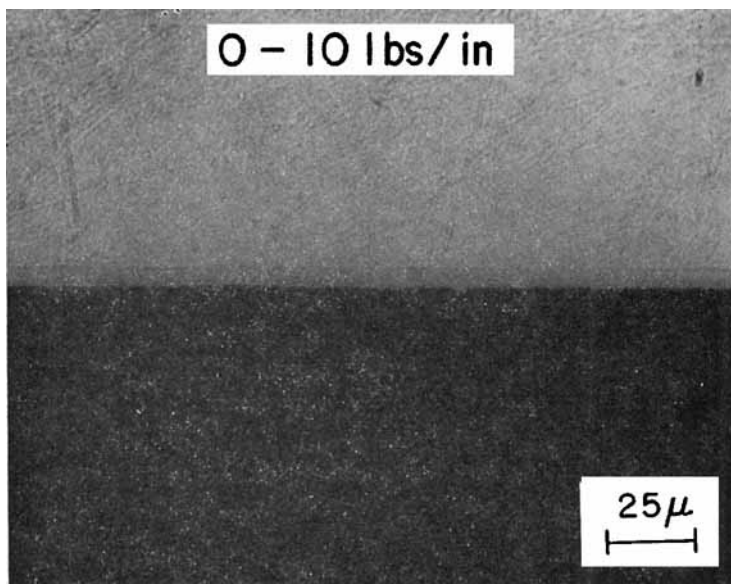
Relation of Metal-Polymer Interface Geometry to Adhesion

Micrographs of the metal-polymer interface revealed structures clearly relevant to the formation of substantial adhesion. A reflection micrograph of a representative sample seen in cross section (Fig. 2a) shows a bright upper layer of electrodeposited copper and a dark lower layer of polypropylene (PP). Metal roots, 10-15 microns deep, are seen penetrating into the polymer. Peel adhesion values in samples exhibiting this complex interface geometry lie in the range of 25-40 lb/in. Adhesion values of samples having an interface geometry without noticeable penetration of the metal into the polymer (Fig. 2b) are 0-10 lb/in. In these studies, high adhesion appeared to be related to the presence of numerous, deeply penetrating metal roots. The concept that the metal layer is "keyed" into the roughened polymer surface, previously advanced⁴ for plated ABS resins, seemed applicable to plated PP.

Observed variations in interference geometry and resultant adhesion values may be related to the difference in chemical reactivities of the two plaque surfaces toward the swellant and etchant. Since it is known⁵ that the amorphous phase in PP is oxidized at a higher rate than crystalline regions, the more complex geometry may reflect a larger ratio or different organization of amorphous and crystalline material on the surface. Consequently, a study of the crystalline morphology of PP surfaces and its rela-



(a)



(b)

Fig. 2. Relation of metal-polymer interface geometry to adhesion: (a) plated sample having a complex interface geometry and 25-40 lb/in. peel adhesion; (b) plated sample having a simple interface geometry and 0-10 lb/in. peel adhesion.

TABLE I
Peel Adhesion For Polypropylene^a As a Function of Compression Molding Variables

Molding variables ^b		Peel adhesion, ^c lb/in.	
Cooling rate	Mold surface	As molded ^d	Postannealed ^e
Slow	aluminum	16	17-20
Normal	aluminum	12	17-20
Fast	aluminum	0-2	14-17
Normal	Mylar	2-3	7-8

^a A homopolymer (Hercules Profax 6523) was used.

^b Samples were compression molded at 210°C for 15 min and then cooled to room temperature under pressure overnight (slow), to 65°C under pressure in 20 min (normal) or to approximately 10°C without pressure in 15 sec by immersion in ice water (fast).

^c All samples were plated under the preferred conditions described in the experimental section. Each adhesion value is an average of at least five separate peel tests.

^d Samples were tested 1-2 days after plating.

^e Samples were heated for 1 hr at 80°C (one to two days after plating) and allowed to stand overnight at room temperature before testing.

tion to adhesion and process conditions—molding and plating—was undertaken. The effect of compression molding variables on surface morphology and on after-plated adhesion are described here, while injection molding (a more desirable process commercially) and its relation to morphology and adhesion is reported in a companion paper.⁶

Compression Molding and Adhesion

Compression molding permits samples to be prepared with a reproducible thermal history and little molecular orientation. Two variables in compression molding that can affect surface morphology are cooling rate and the nature of the mold surface.

The effects of different cooling rates and mold surfaces on after-plated adhesion are given in summary form in Table I. For each set of conditions shown, two values of adhesion are given. The "as molded" values were determined one to two days after plating, whereas the "postannealed" values were determined after the plated samples were heat treated at 80°C for 1 hr and allowed to stand overnight at room temperature.

Inspection of Table I shows that compression molding variables greatly influence peel adhesion. For plaques molded against aluminum, the smallest as-molded peel values (0-2 lb/in.) are associated with the largest cooling rates. Annealing increases adhesion in these plaques to about the same final value (14-20 lb/in.). Furthermore, samples molded against aluminum surfaces developed consistently higher adhesion compared to those molded against Mylar. Apparently, the presence of Mylar during the molding process permanently alters the polymer surface in a manner that cannot be overcome by postannealing.

The above results clearly show that (1) cooling rate, (2) nature of the mold surface, and (3) after-plated annealing affect peel adhesion values.

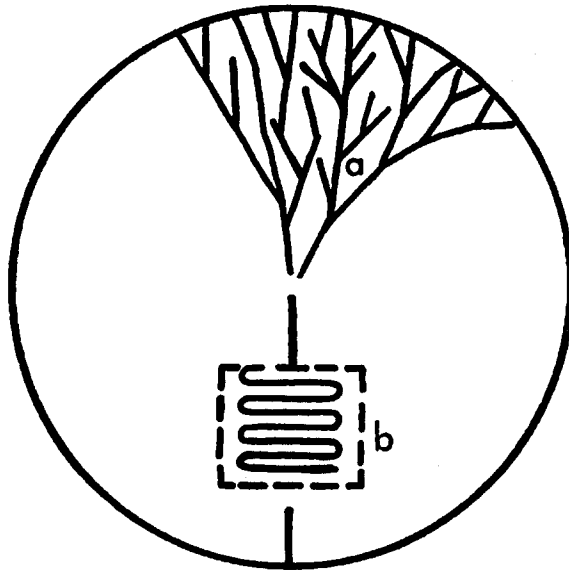


Fig. 3. Proposed structural elements of a PP spherulite¹¹: (a) branching of the lamella; (b) enlargement of a portion of a folded-chain lamella showing the chain axis perpendicular to the radius of the spherulite.

If morphology is important for adhesion, then the relationship of these variables to surface structure should be demonstrable.

Morphology of Compression-Molded PP

As is well known, the crystalline regions of unoriented semicrystalline polymer are organized into aggregates (spherulites) which consist of a nucleus and radiating fibrils readily observed by optical microscopy.

The fine structure⁷ of PP spherulites has not been completely elucidated, but the elements presented in Figure 3 will serve as a working model for the subsequent discussion. It is generally agreed that crystalline regions consist of rectangular plates or lamellae 100–500 Å thick and as large as 4 by 30 microns. These lamellae represent the fundamental structural units of the spherulite and consist of folded polymer chains. The fibrils are composed of intricate bundles of long and short lamellae tied with interconnecting polymer molecules. Tie molecules and folded chain regions together form the amorphous phase.

Spherulitic Surface and Interface Geometry

The organization of these amorphous regions on the surface and the part they play in creating a complex interface geometry is shown in the micrographs in Figure 4. These pictures are of PP molded against clean aluminum (degreased and sulfa-chromated) and cooled normally. Figures 4a and 4b are polarized light micrographs of thin sections through the surface

of an as-molded specimen and a sample after treatment in the electroless line. The first photo shows several spherulites impinging to form a smooth surface. In the latter photo electroless nickel is seen to penetrate irregularly into the polymer; the deepest cracks occur along spherulite fibrils nearly normal to the surface or between spherulites. Since the amorphous phase is being removed, this material must be organized normal to the surface in the areas of the longest cracks. As the angle between the fibril and the surface decreases, the accessibility of the amorphous phase to the etchant decreases, and so does the depth of cracks. This shows that the interface geometry is being controlled by the surface morphology.

Surface photographs of PP plaques, taken with a scanning electron microscope, show in detail the effect of etching on a spherulitic surface (Figs. 4c and 4d) and illustrate the cause of an irregular interface geometry. The oxidative process exposes the ridges of chemically resistant crystalline polymer, that comprise the familiar spherulite patterns, by dissolution of amorphous material concurrent with oxidative stress cracking.⁸ (Note that surface cracking occurs in gas phase oxidation when dissolution is not possible.) An inspection of these photographs, particularly of the enlargement (Fig. 4d), shows the sponge-like structure caused by the severity of surface etching and crack formation needed to produce substantial adhesion.

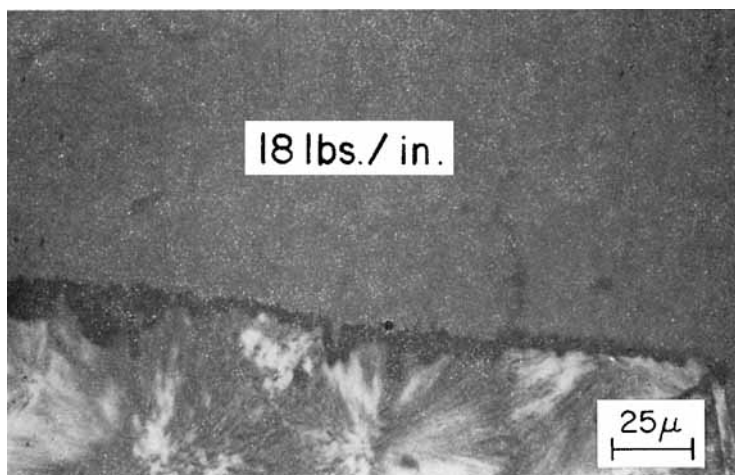
A more thorough inspection of Figure 4c shows that the etch patterns in the majority of spherulites run through the center, indicating that these spherulites were nucleated below the surface. If the centers were true spherulite nuclei, they would be highly crystalline.⁹ Two of the spherulites in this micrograph appear to be nucleated on the surface. Their centers are intact and, as seen in photographs not presented, are the highest points on the surface. The effect of a highly crystalline, chemically resistant surface on adhesion is presented in the section on transcrySTALLINE morphology.

The surfaces of samples prepared under "rapid cool" and "slow cool" conditions against aluminum are also spherulitic. The former condition produces small spherulites (10–30 microns in diameter) as expected,¹⁰ while the latter yields large spherulites of 150–180 microns in diameter.

The low as-molded peel values for the rapidly cooled plaques (Table I) are probably due to a decrease in crystallinity of the polymer surface. This decrease, which is a consequence of quenching,¹¹ increases the ductility of PP. Since failure in the peel test usually occurs within the polymer phase (see above), an increase in ductility is reflected in a decrease in the peel force. As observed with the more slowly cooled samples, annealing, which increases crystallinity by secondary crystallization,¹² leads to higher peel values. Since all the PP samples molded against aluminum have a spherulitic surface morphology and therefore a similar crack pattern after etching, it is understandable that the plated specimens develop about the same peel values once their crystallinities are about the same. (After annealing, all polymer specimens showed about the same density as determined with a density gradient column.)



(a)

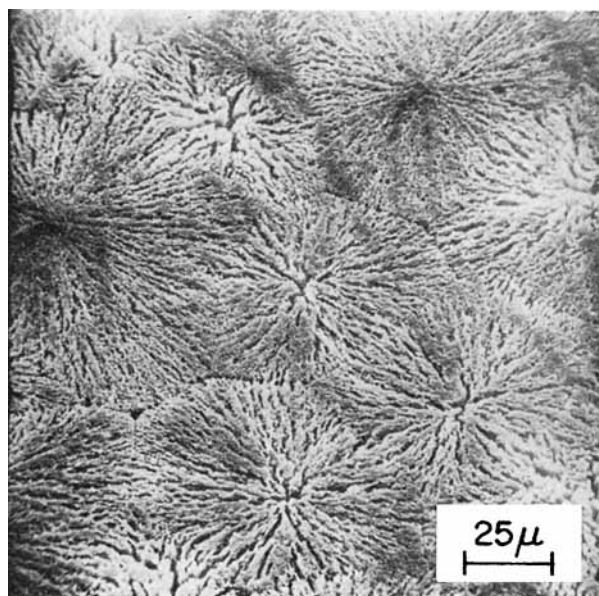


(b)

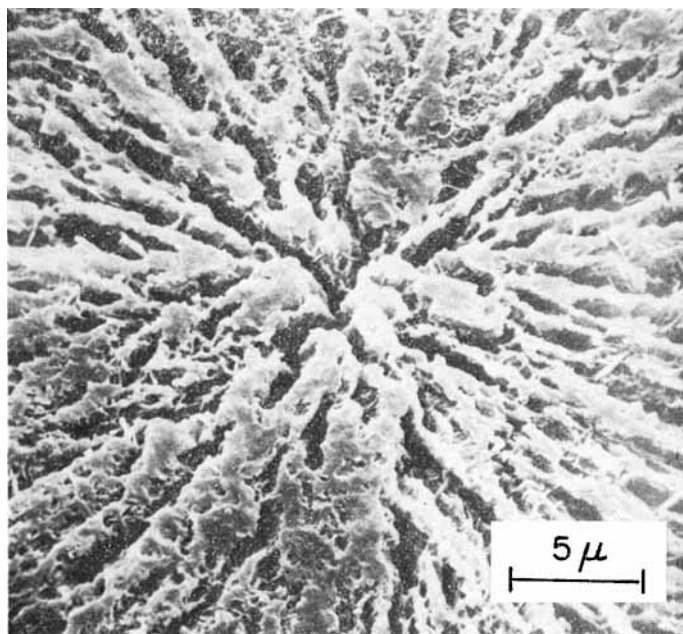
Fig. 4 (continues)

Transcrystalline Surface Morphology and Interface Geometry

The nature of the mold surface¹³ as well as the cooling rate can affect surface crystallinity in compression-molded PP. Whereas the surface morphology of PP molded against sulfa-chromated aluminum is spherulitic, it is nonspherulitic when molded against Mylar or Teflon under normal-cool conditions. The micrographs in Figure 5 show this nonspherulitic surface morphology and illustrate the effect it has on the polymer-metal interface. Figures 5a and 5b are polarized light micrographs of thin sections taken normal to the surface; 5a is the as-molded sample, and 5b is the sample after treatment in the electroless line. The first photograph shows birefringent structures that are columnated spherulites nucleated at the surface and extending into the sample from the surface. This kind of mor-

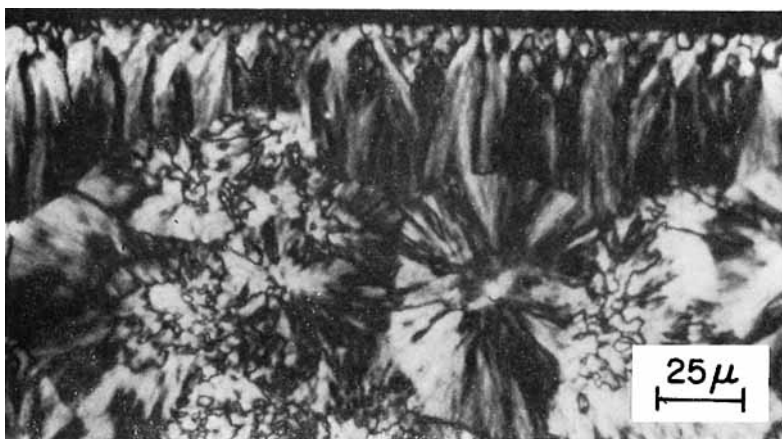


(c)

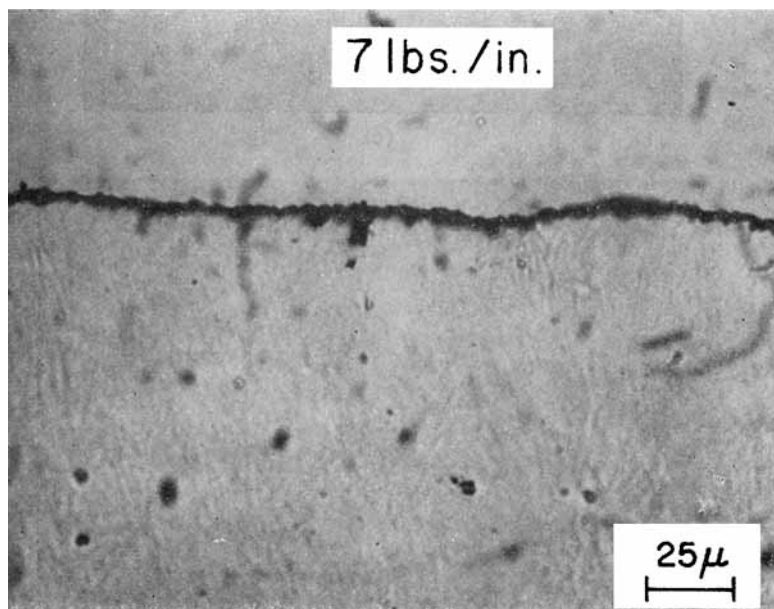


(d)

Fig. 4. PP spherulitic surface morphology: (a) polarized light micrograph of a thin section normal to an "as molded" surface; (b) polarized light micrograph of a thin section normal to an etched and electroless plated surface; (c) scanning electron micrograph of an etched surface; (d) enlargement of one spherulite seen in (c).



(a)

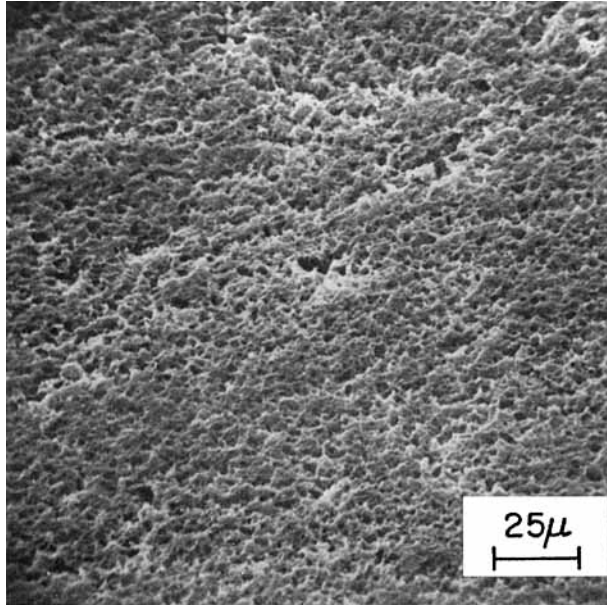


(b)

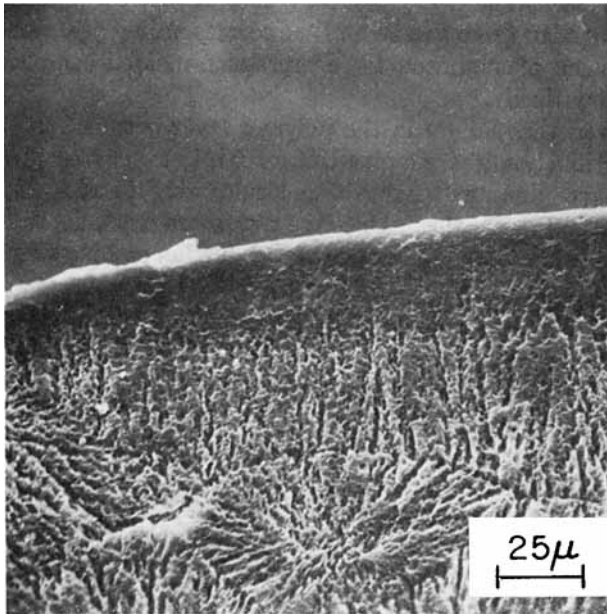
Fig. 5 (continues)

phology—transcrystallinity—has been observed in other semicrystalline polymers.¹⁴ At a depth of 50–75 microns, the morphology reverts to the spherulitic type. The dark line of electroless metal (Fig. 5b) does not penetrate into this surface as it does into the spherulitic surface (Fig. 4b).

Since it was shown previously (Fig. 4c) that spherulitic nuclei, being low in amorphous content, are chemically resistant to oxidative cracking, it is not surprising that a surface containing a high concentration of nuclei would form a relatively simple interface geometry and thus low metal-to-plastic adhesion (Table I). This crack-resistant characteristic is clearly illustrated by the shallow, pebbled texture of the etched surface (Fig. 5c).



(c)



(d)

Fig. 5. PP transcrystalline surface morphology: (a) polarized light micrograph of a thin section normal to the "as molded" surface; (b) polarized light micrograph of a thin section normal to the etched and electroless plated surface; (c) scanning electron micrograph of an etched surface; (d) scanning electron micrograph of an etched cross section normal to the surface.

As can be seen in the micrograph of the etched cross section (Fig. 5d), the layer of chemically resistant polymer extends 20–30 microns into the sample. Once this surface morphology has been formed, adhesion cannot be increased by simply increasing sample treatment times in the solvent and etchant; longer times simply erode the surface and weaken it.

Adhesion: Mechanical Keying and the Damaged Polymer Surface

Apparently, metal-to-polymer adhesion, as measured by the peel test, represents a balance between surface cracks which increase mechanical interlocking of the two components and the diminished mechanical strength of the polymer surface, both of which occur at independent rates during the oxidative process. The "keying" mechanism is clearly the limiting factor for adhesion in the Fig. 2b sample. Failure during the peel test occurred between metal and polymer; the underside of the metal strip did not show a continuous film of PP as it did for the sample in Fig. 2a. For the latter, mechanical keying was not the limiting factor. Here, the adhesion between metal and polymer was greater than the cohesion in the weakened polymer layer.

The above two micrographs (Figs. 5c and 5d), which are of plated PP fabricated by injection molding and which are discussed in detail in the companion paper, are presented here to illustrate the concept of "keying." Comparison of Figures 4b and 5b and the corresponding peel values demonstrates the same phenomenon for compression-molded samples although much less dramatically.

It is believed that failure in the polymer layer occurred in oxidatively weakened PP and not in virgin material. PP is known¹⁵ to degrade rapidly in an oxidizing medium with a loss of molecular weight and a corresponding loss of mechanical properties. Once the maximum crack depth for a given set of swell and etch times⁶ has been reached, further etching simply reduces the cohesion in an already weakened polymer.

On occasion, peel values in excess of 50 lb/in. were achieved and corresponded to the removal of a "chunk" of polymer rather than to a thin continuous film of polymer. In these instances, the fracture path is believed to have penetrated into the bulk phase and suggests that, when the interface and surface layer strength approach that of the virgin material, considerably higher average peel values may be realized.

It is concluded that substantial metal-to-plastic adhesion in the usual plating process is obtained only after a sequence of events that include (1) fabrication of a sample with a surface morphology containing substantial amounts of amorphous material, (2) formation of a deeply cracked surface by etching, (3) deposition of the electroless nickel into the cracked surface, and (4) aging of the plated samples.

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