Electroplating on Crystalline Polypropylene.
II. Injection Molding and Adhesion

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Synopsis

This paper describes the effect of injection molding conditions (melt temperature, mold temperature, and fill time) and etch conditions on metal adhesion in electroplated isotactic polypropylene (PP). It is found that injection molding PP homopolymer produces a lamellar surface morphology which can consistently develop after-plated peel strengths of 30 lb/in or better as measured by the Jacquet peel test. Surface etching of PP homopolymer prior to plating develops crack patterns characteristic of injection molding; a directional crack pattern is always evident in specimen surfaces crystallized under shear. The surface pattern is developed in the oxidative process by swelling of amorphous material, followed by oxidative dissolution and oxidative stress cracking. Additionally, the depth and number of the surface cracks is a function of the solvent swell and acid etch times. Crack depth increases in lamellar surfaces as the sample immersion times are increased; however, as crack depth increases, crack density decreases.

Metal-to-polymer adhesion, as measured by the peel test, represents a balance between crack depth and diminished surface strength incurred in the oxidative cracking process. Although peel adhesion usually increases with crack depth, overetching may actually reduce adhesion even though the crack depth has been increased. Any advantage from deeper cracks may, therefore, be offset by a loss in the surface strength of the polymer. Comparison of the surface and cross-sectional crack patterns in TiO$_2$-filled PP indicates that the surface morphology is similar to that of unfilled polymer. Molding conditions that produce the desired morphology are important for high peel adhesion values but appear to be less critical than in unfilled PP. A propylene–ethylene copolymer (90/10) developed 12–15 lb/in. peel adhesion—50% lower than for the filled and unfilled homopolymer when molded under similar conditions; peel adhesion in this composite system is, however, relatively insensitive to changes in molding conditions. Aging of 2–3 weeks after plating is required for maximum peel adhesion in all samples studied.

INTRODUCTION

In a companion paper[1] it was shown that polymer processing has a dramatic effect on the adhesion of plated isotactic polypropylene (PP). The variables in compression molding were related to surface morphology. Further, the oxidative cracking behavior of the surface morphologies (due to the etchant) was described in terms of crystallite orientation and crystallinity. Finally, the effect of the surface crack pattern on adhesion was discussed.

Injection molding is commercially a very attractive process for fabricating polymers into functional parts. Our objectives therefore were to identify the variables of injection molding that affect metal adhesion to PP and describe their effect on surface morphology, surface cracking behavior, and the metal–polymer interface geometry.

EXPERIMENTAL

The metal coating systems that were used to plate the PP surface were described in detail in the companion paper,[1] as were the Jacquet peel adhesion test and the microscopic techniques for studying the polymer surfaces.

Materials

Three commercially important polymers were molded:
1. Shell PP 5520 (homopolymer)
2. Avisun PP TD-253A (titanium dioxide-filled homopolymer).
3. Shell PP 7521 (propylene–ethylene copolymer, 90/10)

All materials were hot air dried in the hopper for at least 1 hr prior to molding.

Injection Molding

PP was fabricated in a $3 \times 8 \times \frac{1}{4}$ in. double-cavity plaque mold using a 12-oz Van Dorn injection molding machine. Each mold cavity was double-gated (O.D. $\frac{1}{8}$ in.). Back pressure and booster pump pressure were maintained at 0 psi, and screw speed was kept at 60 rpm while fill time, melt temperature, and mold temperature were systematically varied.

Mold release agents were avoided since some of these materials are known to interfere with the etching process.

RESULTS AND DISCUSSION

Injection Molding and Adhesion

Thermal history and shear rate represent the two major factors expected to influence crystallization during injection molding. Samples were prepared, therefore, over a wide range of molding conditions—melt temperature (198–242°C), mold temperature (4–40°C), and fill time (2.5–12.5 sec)—in several sets of systematic experiments.

Three commercially important PP modifications were examined: a homopolymer, a titanium dioxide-filled polymer, and a propylene–ethylene copolymer. Only the homopolymer was studied in detail; a representative sampling of data is given in Table I. Results obtained with the copolymer are substantially different from the other two materials and will be noted separately.

The most definite relationship which has been observed is between peel adhesion and ΔT, $(T_{\text{melt}} - T_{\text{mold}})$ and is illustrated in Figure 1. This master curve, derived from Table I, is for samples molded at a constant shear

TABLE I
Peel Adhesion for Polypropylene[a] as a Function of
Injection Molding Variables

Molding variables				Peel adhesion[b]
Melt temp, °C	Mold temp, °C	ΔT, °C	Fill time, sec	lb/in.
212	38	174	2.5	31
212	38	174	5.0	25
212	38	174	12.5	27
212	29	183	2.5	30
212	21	191	2.5	26
212	13	199	2.5	25
212	4	208	2.5	23
240	38	202	2.5	22
240	38	202	5.0	25
240	38	202	12.5	29
240	29	211	2.5	21
200	38	162	2.5	30
200	38	162	5.0	29
200	38	162	12.5	28
200	29	171	2.5	26

[a] A homopolymer (Shell 5520) was used.

[b] Each adhesion value is an average of at least five separate peel tests. Each sample was annealed at 80°C for 1 hr and allowed to stand at room temperature for 72 hr prior to testing. A swell time of 15 min and etch time of 7 min were used for all samples.

Fig. 1. Peel adhesion of injection molded homopolymer samples plotted vs. reciprocal fill time at different ΔT ($T_{melt} - T_{mold}$) values. $T_{melt} = 198-242$°C; $T_{mold} = 4-40$°C; $1/t_f = 0.4$ sec^{-1}.

rate (denoted by the reciprocal of fill time, $t_f{}^{-1}$) of 0.4 sec^{-1}. As ΔT increases, peel adhesion values decline from a maximum of 31 lb/in. at $\Delta T = 155$°C to 20 lb/in. at $\Delta T = 202$°C.

Fig. 2. Peel adhesion of injection-molded homopolymer samples vs. fill time for three ΔT's: (Δ) $\Delta T = 162°C$; (O) $\Delta T = 174°C$; ($\square$) $\Delta T = 202°C$.

For most of the experiments, there is no significant trend between peel adhesion and t_f^{-1} (Fig. 2). Since molecular orientation is known to influence profoundly the crystallization process,[2] this indicates no significant changes in this factor for the conditions encompassed by the injection molding machine. The only definite effect is for the highest melt temperature, 240°C, where Figure 2 shows a 7 lb/in. increase in peel adhesion for a decrease in t_f^{-1} from 0.4 to 0.08 sec^{-1}.

These relationships, as expected, are complex; thus the same peel adhesion is obtained for more than one combination of melt temperature, mold temperature, and fill time. The effects are too small over the range of variables of interest to allow a complete, definite separation among the variables.

Since no major differences in surface morphology were observed, it may be presumed that the differences in adhesion are due to changes in the mechanical properties of the surface resulting, possibly, from subtle differences in the crystalline morphology or degree of crystallinity of the surface or from differences in residual stresses. Variables in the molding process are presently being examined as they affect the crystalline texture and therefore mechanical properties of the surface.

On occasion, peel tests exhibited values as high as 52 lb/in. corresponding to the removal of a "chunk" of polymer rather than to a thin continuous surface layer. In these instances, the fracture path penetrated into the bulk phase and suggests that, when the interface and surface layer strength approach that of the bulk, considerably higher average peel values may be realized.

All of the adhesion values reported above were obtained from plated samples that had been aged at least three weeks at room temperature before testing. (There is some evidence that excessive aging prior to plating—

Fig. 3. Plot of peel adhesion vs. time after plating.   Each adhesion value is an average
of at least five separate peel tests.

3–6 months—leads to a decrease in peel adhesion as a result of an increase in
surface crystallinity.)   The injection-molded samples respond to aging
(after plating) in a manner analogous to compression-molded samples.[1]
Figure 3 shows the relation of adhesion to aging in a representative sample;
adhesion values increase rapidly over the first four days and more slowly for
several weeks thereafter.

The titanium dioxide-filled homopolymer and the propylene–ethylene
copolymer mentioned above were molded under conditions which produced
in the unfilled homopolymer the highest after-plated peel adhesion.   The
effects of molding variables and etch times (discussed later) on peel adhesion
are presented in Tables II and III.

TABLE II
Peel Adhesion For Filled Polypropylene[a] as a Function of
Injection Molding Variables and Etch Times

Molding variables[b]		Peel adhesion,[c] lb/in.		
$1/t_f$, sec^{-1}	ΔT, °C	7 min etch	5 min etch	4 min etch
0.67	177	25.5	26.5	22.5
0.67	186	26.0	26.5	21.5
0.14	177	26.0	26.0	26.0

[a] A titanium dioxide-filled PP (TD-253-A, Avisun) was used.

[b] Melt temperature was constant at 215°C; mold temperature varied: 38°C for
shear rates of 0.67 and 0.14 sec^{-1}, and 29°C for a shear rate of 0.67 sec^{-1}; $\Delta T = T_{melt} - T_{mold}$.

[c] Each adhesion value is an average of at least five separate peel tests.   Each sample
was annealed at 80°C for 1 hr and allowed to stand at room temperature for 72 hr prior
to testing.   A swell time of 15 min was used for all samples.

TABLE III
Peel Adhesion for a Copolymer[a] as a Function
of Injection Molding Variables and Etch Times

Molding variables[b]		Peel adhesion,[c] lb/in.		
$1/t_f$, sec^{-1}	ΔT, °C	7 min etch	5 min etch	4 min etch
0.67	162	14.5	12.5	11.0
0.67	171	15.0	12.0	11.0
0.14	162	12.5	12.0	8.5

[a] A propylene–ethylene (90/10) copolymer (Shell 9521) was used.

[b] Melt temperature was constant at 200°C; mold temperature was varied. 38°C for shear rates of 0.67 and 0.14 sec^{-1} and 29°C for a shear rate of 0.67 sec^{-1}; $\Delta T = T_{melt} - T_{mold}$.

[c] Each adhesion value is an average of at least five separate peel tests. Each sample was annealed at 80°C for 1 hr and allowed to stand at room temperature for 72 hr prior to testing. A swell time of 15 min was used for all samples.

Peel adhesion for the filled polymer, plated under optimum conditions for the homopolymer, is about 85% of the homopolymer. Inspection of Table II shows that the molding conditions for development of high adhesion in the filled material are not as important as they are in the unfilled material.

The propylene–ethylene copolymer developed 12–15 lb/in. peel adhesion (Table III)—half of that obtained for the two other polymers—when molded and plated under similar conditions.

Lamellar Surface and Interface Geometry

The surface morphology of injection-molded PP samples is nonspherulitic. A polarized light micrograph of a thin section through the surface (Fig. 4a) shows an apparently structureless layer extending 25–50 microns into the bulk; at increasing distances from the surface, a spherulitic morphology reappears. The surface layer differentiates the morphology due to injection molding from that observed for compression molding and is believed responsible for the enhanced peel adhesion values.

The presence of relatively deep, numerous, and uniform cracks filled with nickel (Fig. 4b) is observed, indicating that amorphous material[1] was present on the surface prior to acid etching and electroless nickel deposition. An ordering of the amorphous material after injection molding is suggested by the presence of surface cracks (Fig. 4c). These cracks lie transverse to the flow direction. An inspection of this scanning electron micrograph and particularly of the enlargement (Fig. 4d) shows the severity of etching.

Comparison of the surface and cross-sectional crack patterns in the titanium dioxide-filled polymer indicates that the surface morphology is similar to that found for the homopolymer.

Additional structural features—are revealed by scanning electron micrographs of an etched cross section (Fig. 4e) which disclose sheet-like bodies transverse to the flow direction and perpendicular to the surface.

By analogy to studies of polyethylene crystallized under shear,[2] it is believed that (a) crystal growth is of a lamellar type and takes place at right angles to the orienting influence, (b) the lamellae form stacks of rectangular sheets parallel to the flow direction, and (c) oxidative degradation occurs preferentially in the interlamellar regions.

Depth of Crack Penetration and Adhesion

Up to this point the importance of deep, numerous, and uniform cracks in the polymer surface to peel adhesion has been emphasized. Evidence

TABLE IV
The Relationship of Peel Adhesion to Crack Depth
for Injection-Molded Polypropylene[a]

Adhesion,[b] lb/in.	Crack depth,[c] μ
>30	>15
20–26	3–12
10–15	<1

[a] A homopolymer (Shell 5520) was used.
[b] Each adhesion value is an average of ten or more separate peel tests.
[c] Crack depth determined from micrographs of plated cross sections.

presented below indicates that some qualification of this view is required. Samples chosen for this study were injection molded under the following conditions: melt temperature $210 \pm 10°C$, mold temperature $35 \pm 5°C$, and fill time 3 ± 0.5 sec; and were then plated using various combinations of immersion times in the solvent and acid baths.

(a)
Fig. 4(continued)

25 - 40 lbs / in

25μ

(b)

50μ

(c)
Fig. 4 (continued)

(d)

(e)

Fig. 4. PP lamellar surface morphology: (a) polarized light micrograph of a thin section normal to the "as molded" surface and parallel to the extrusion direction; (b) micrograph similar to (a) but taken after surface has been etched and electroless plated; (c) scanning electron micrograph of an etched surface; (d) enlargement of a fissure seen in (c); (e) scanning electron micrograph of an etched cross section normal to the surface and parallel to the extrusion direction.

(a)

(b)

Fig. 5. Micrographs from cross sections of plated samples showing the relation of crack depth to density: (a) 40 cracks/in., 3.2 microns deep; (b) 17 cracks/in., 12.5 microns deep.

Results are summarized as follows:

1. For a lamellar surface morphology obtained from injection molding, the crack pattern is always uniform; however, as crack depth increases, crack density decreases.

2. Crack depth is a function of swell and etch times only.

Fig. 6. Plots of crack depth vs. etch times for constant swell times of 5, 10, and 15 min.

Fig. 7. Plots of peel adhesion vs. etch times for constant swell times of 5, 10 and 15
minutes.   Each adhesion value is an average of at least five separate peel tests.

3. Peel adhesion is related to surface pretreatment history as well as
crack depth.

The uniform surface crack pattern on injection-molded samples is evident
from the micrographs of plated PP seen in cross section (Fig. 5).   Note also
that as crack depth increases,[3] the crack population decreases suggesting
that deeper cracks provide stress relief over greater distances.

Crack depth generally increases with etch time in a manner corresponding
to the prior amount of exposure to the organic swelling agents (Fig. 6).

Further, at a fixed etch time in the range of 4 to 7 min, crack depth is also seen to increase with the time of swelling.

Peel adhesion values cannot be predicted from crack depth alone. Although the highest values (Table IV) are associated with the deepest cracks, surprisingly good values (compared to ABS) were obtained for samples having very shallow cracks. Furthermore, moderately high values were obtained among samples exhibiting a broad spectrum of crack depth.

Oxidative damage to the surface[1] as well as crack depth is believed to play an important role in peel adhesion in a given system. (All of the peeled metal strips have a continuous film of polymer on their underside, indicating that failure occurred within a weakened polymer layer.) That these surfaces can be overetched is clearly shown by a decrease of adhesion with etch times in samples swollen for 5 and 10 min and etched for more than 5 min (Fig. 7). Any possible increase in adhesion from deeper cracks has probably been offset by the decrease in surface strength due to oxidative degradation.

A similar relationship between peel adhesion and etch time exists for the titanium dioxide-filled polymer (Table II). In general, longer etch times result in higher adhesion.

Inspection of Table III shows that the same general relationship holds for the copolymer; however, the level of adhesion in all cases is substantially lower.

References

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