Correlation of Near Surface Morphology of Polypropylene and Paint Adhesion Studied by Grazing Incidence X-Ray Diffraction

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Abstract
Paint adhesion on injection molded polypropylene has been found to be highly sensitive to the material used for the mold. Molds used in production are typically fabricated from steel because of its durability. For rapid prototyping or low volume production runs, molds made from a lighter, more easily machined material would offer significant advantages. To investigate the effect of the mold material on paint adhesion, samples of unfilled, high-molecular weight polypropylene fabricated in molds of differing materials have been studied using optical microscopy and grazing incidence X-ray diffraction (GIXRD). By fixing the incidence angle (limiting the penetration depth) of the X-ray beam, we were able to quantitatively compare the near-surface morphologies of samples prepared using differing mold materials. We found a pronounced variation of the crystallinity and phase assemblage with depth in all of our samples and a strong correlation between the near-surface crystallinity and their paint adhesion performance.

Introduction
Injection molded (IM) polymers have been used extensively throughout the auto industry because of their low cost and weight, and the ease with which complex shapes can be formed. Polypropylene (PP) is a desirable material because of its low cost, but is difficult to paint because of its non-polar nature. Typically, PP must first be pretreated to enhance the polarity of the surface by chemical or physical methods (UV light or flame oxidation). Chemical treatments utilize a dilute solution of a chlorinated polyolefin (CPO) as an adhesion promoter and are generally believed to partially solvate the polymer chains at the surface, allowing the CPO to penetrate and entangle before the solvent evaporates. The polar head of the entangled CPO molecules then provides sites to which the base-coat paint can adhere. The adhesion of the treated surface is a direct reflection of the solubility of the chains at the surface, which in turn, is affected by the degree of crystallinity, with amorphous PP the most easily solubilized. The process parameters (injection rate, mold temperature, pressure, etc.) and the thermal transfer
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characteristics of the mold material all affect the cooling rate of the injected PP and, hence, affect the surface crystallinity. The changes in the phase assemblage, crystallinity and texture from the surface to the core of IM-PP as a function of processing conditions and stock material (degree of tacticity) have been studied by Zipper et al. (1) using transmission X-ray diffraction at a spatial resolution of 20 microns. They found that the crystalline material was composed of the α-phase (2) (monoclinic cell; a=0.665 nm, b= 2.096 nm, c= 0.65 nm , β=99° 26’ ) and the shear-induced Β-phase (3). They also observed a skin-core variation in morphology, with the skin dominated by amorphous polypropylene and α-phase crystalline material. Their work did not consider any effects that might be introduced by varying the mold wall material.

Molds for high volume (~ 10^6 parts) production runs have been traditionally fabricated from steel because of its durability. Large, complex parts, such as bumper facias require molds that are very costly, difficult to machine and difficult to modify. For rapid prototyping and small volume production runs, alternate mold materials are very desirable to reduce cost and tooling time. Prior to adoption in a production environment, alternate mold material must be first tested to determine if the parts produced have acceptable mechanical properties and have good paint adhesion.

Test samples of IM-PP were prepared in molds made from a variety of materials to study the resulting mechanical properties of the PP and paint adhesion. Both were found to be markedly sensitive to the choice of mold material. In this report we describe our measurements of the near-surface morphology of IM-PP samples using grazing-incidence X-ray diffraction and the relationship of the morphology to the paint adhesion.

**Materials and Methods**

All samples of IM-PP were produced from a common stock of high-molecular weight, unfilled, isotactic polypropylene, Profax 6823 from Montel Polyolefins. Injection molds were fabricated to yield standard tensile test samples (ASTM D638M), a rectangular bar (11.5 cm x 1 cm x 0.38 cm) and flat disks for painting. All mold inserts were machined and polished to a mirror finish to eliminate any effects due to any variation of the surface roughness. Injection molding was carried out under identical conditions for all mold insert materials: Melt temperature = 450° F, Mold temperature = 70° F, Back pressure = 50 psi, Injection pressure = 1500 psi, Injection time = 6 s, Cooling time = 15 s, and Holding pressure = 1000 psi.

Mold inserts for this study were fabricated from P20 steel, 304 stainless steel, nickel, Alumec-89 (a low-cost aluminum alloy), 6061 aluminum, PTFE (Teflon) and a stereo-lithographically solidified acrylic resin (SLA).
Injection molded flat disks were painted by Solvay Engineered Polymers using a standard Ford Motor Company paint system for polypropylene and thermoplastic olefins, consisting of a CPO adhesion promoter, followed by a white base coat and then a clear-coat. All samples were painted together, in one batch. A standard paint adhesion test (ASTM D-3359) was performed on all samples. This method uses a "comb" of razor blades to make a cross-hatch pattern of cuts completely through the paint layer. An adhesive tape applied to the cut paint is peeled back on itself and the fraction of paint removed is used to determine the adhesion. A photograph of the tested surfaces of several of the samples is shown in Fig. 1.

![Paint adhesion scratch test of painted disks of PP from different molds.](image)

Optical microscopy was used to examine polished and etched (4) cross-sections to reveal the surface-to-core crystalline morphology. Etching was performed on the epoxy potted sections using a mixture of equal parts of benzene, chloroform and xylene at 80° - 85° C, and performed in repeated 20-30 s treatments to avoid overheating (total etch time = 3 minutes). Several examples of the optical micrographs are shown in Fig. 2. The morphology visible in samples prepared using this technique was also visible in a second set of thin samples microtomed from IM-PP samples (no etching) and viewed under crossed polarizers.

Grazing incidence X-ray diffraction was used to study the phase assemblage of IM-PP with depth from the surface. Samples (1cm long) were cut from the rectangular bars with the narrow (0.38 cm) face used as the sample surface. To limit the influence of surface roughness, the incidence angle was restricted to a minimum of 0.5°. The divergence of the incident beam was limited to ~1/10 the incidence angle. Copper radiation was used in a Scintag PTS 0-2θ diffractometer. Two examples of diffraction patterns are shown in Fig. 3. Measured patterns were profile fitted over the entire angular range to account for both the crystalline peaks and the amorphous phase. The
amorphous fraction of the scattered intensity was determined by the ratio of the fitted area of a broad peak centered near 16° 2θ to the total area under the whole pattern. An estimate of the α-phase crystallite size was obtained from a Scherrer analysis (5) of the FWHM of its (110) peak (assuming only particle size broadening). The results of this analysis are shown in Fig. 4.

Results
Adhesion testing of the painted surfaces indicates that the samples molded into stainless steel and P20 steel had the best adhesion, while samples molded into PTFE and acrylic had very poor adhesion. Aluminum molds also produced samples with very poor adhesion, while a nickel molded sample was more similar to the steel molded samples.

Fig. 2. Optical micrographs (100X, Nomarski contrast) of polished and etched cross sections of IM-PP.

Optical microscopy of the samples in cross-section shows that all samples have a region of spherulitic crystallites below the surface, with varying amounts of low-contrast material at the surface. Metallic molds all produced samples with extensive ranges (up to ~ 600 microns) of this
low-contrast material, while the PTFE and acrylic molds with much narrower ranges (~100 microns). Spherulitic grains were the largest in the samples formed in non-metallic molds.

Fig. 3. Diffraction patterns collected at 0.5° incidence angle for samples of polypropylene molded against 6061-aluminum and PTFE. Indices displayed above are for the α-phase; those shown below are for the β phase. The amorphous fractions for the cases shown are: PTFE, 12%; 6061-Al, 42%.

A comparison of grazing incidence diffraction data collected at an incidence angle of 0.5° (Dpenetration ~ 23 microns) indicates a strong variation of the amorphous fraction near the surface, with the predominant crystalline peaks assigned to the α-phase (Fig. 3). The nonmetallic molds produced the smallest fraction of amorphous material, while the steel molds produced the highest amorphous fractions. Additional peaks in the diffraction pattern for the sample molded against PTFE can be assigned to the β-phase. The α-phase crystallite size has a strong negative correlation with increasing amorphous fraction. In general, the diffraction results are consistent
with the paint adhesion tests. The notable exception are samples produced in aluminum containing molds. In these cases our estimate of their amorphous fraction indicates that they should be comparable to samples from steel molds, yet they are clearly both poor performers in the paint adhesion test.

Fig. 4. Mean α-phase crystallite size and amorphous phase percentage determined from the GIXRD obtained at an incidence angle of 0.5° (D_{penetration} ~ 23 microns). The superimposed line is a guide for the eye, illustrating the expected decrease of crystallite size with increasing amorphous fraction in the samples.

Conclusions
We have studied the effects of different mold wall materials on the paint adhesion and near-surface morphology of samples of injection molded polypropylene. Optical microscopy reveals a change in morphology of the samples from the outer surface to the core, but does not lend itself to a quantitative analysis. X-ray diffraction patterns collected in grazing incidence confirm that the outer skin of the molded parts contain significant amounts of amorphous polypropylene, with increasing fractions of crystalline polymer at greater distances from the outer surface. The appearance of amorphous material at the surface of IM pieces is expected, and is the result of quenching of the melt on the cold wall of the mold. The core of the IM piece cools more slowly
(limited by the thermal conductivity of the mold wall material), and results in larger, more
perfect crystallites (primarily $\alpha$-phase). The appearance of the $\beta$-phase is the result of
crystallization of the PP under shear during injection. A comparison of the diffraction patterns
collected at the lowest incidence angle used (0.5°), indicates a good correlation between that
amorphous fraction at the surface and the paint adhesion, with the exception of samples molded
in aluminum molds. The crystallite size for all samples decreases with increasing amorphous
fraction, in a fashion consistent with a growth of amorphous material at the expense of the
crystalline phases. These two results in conjunction with the paint adhesion tests suggest that
poor paint adhesion of samples produced in aluminum molds is the result of a surface
contaminant (not present in sufficient quantities to be observed in our diffraction experiments)
that interferes with the adhesion promoter. Further studies of the aluminum molded samples
using other surface sensitive techniques are continuing.

References
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