

Chemical Cleaning-Induced Surface Reorganization in Injection-Molded Polypropylene

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Abstract: Injection-molded polypropylene (PP) components are widely used in the automotive industry; however, their surface properties are strongly influenced by post-processing operations such as chemical cleaning, which may induce chemical modification or structural reorganization of the surface layers. Cleaning treatments are commonly applied prior to coating and joining operations to remove mold release agents and processing residues, but reactive chemicals and organic solvents may also modify the surface properties. In this study, the effects of alkaline (NaOH), oxidizing acidic (H_2SO_4), and organic solvent (acetone and decalin) treatments on injection-molded PP were investigated. Surface energy was determined by sessile drop contact angle measurements, surface morphology was analyzed by confocal microscopy, and chemical and crystallization changes by FT-IR spectroscopy and Differential Scanning Calorimetry (DSC). The results showed that the investigated liquids primarily acted as cleaning agents by removing weakly bound surface contaminants. At the same time, the dispersive component of surface energy increased, indicating improved exposure of the underlying PP surface. Decalin treatment caused the largest increase in surface roughness (+43%), while H_2SO_4 treatment resulted in the highest total surface energy (54.3 mJ m^{-2}). Overall, the treatments influenced adhesion-related surface properties without causing substantial chemical surface activation. On the other hand, increased crystallinity and an altered height histogram were observed due to the enhanced chain mobility and reorganization in the surface layers.

Keywords: Surface energy, reorganization, activation, roughness, polypropylene

1. Introduction

Polypropylene (PP) is one of the most favored industrial thermoplastic polymers due to its low density, favorable mechanical properties, and cost-effective processability [1,2]. It is extensively applied in automotive, packaging, and technical plastic components [3]; however, the adhesion performance poses challenges in subsequent processes such as painting, coating, and bonding due to its inherently nonpolar character and low surface energy [4,5].

A strong correlation between the surface energy and adhesion has been widely proven [6,7]. The most widespread techniques to increase the surface energy include flame, plasma, and corona discharge treatments, which increase the concentration of the oxygen-containing species on the topmost atomic layer, resulting in an increased polar component of surface energy [8–10]. Enhanced effects can be obtained with the application of adhesion promoters, too [11,12].

Injection-molded polymer parts are commonly cleaned after production to remove processing residues, mold release agents, and surface contaminants (Figure 1). Beyond their primary cleaning function, these treatments may also influence the fine surface chemistry and morphology of the polymer, particularly when reactive chemicals or organic solvents are used. Such surface modifications can significantly alter the surface energy and, consequently, the adhesion behavior of polypropylene components [13]. It has also been proven by Schuman and coworkers that if the solvent in the coating induces topographical change, good adhesion will be reached [14]. During long-term aging in detergents

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at elevated temperatures surface reorganization, blooming, morphological changes, and degradation could also be detected on PP surfaces [15].

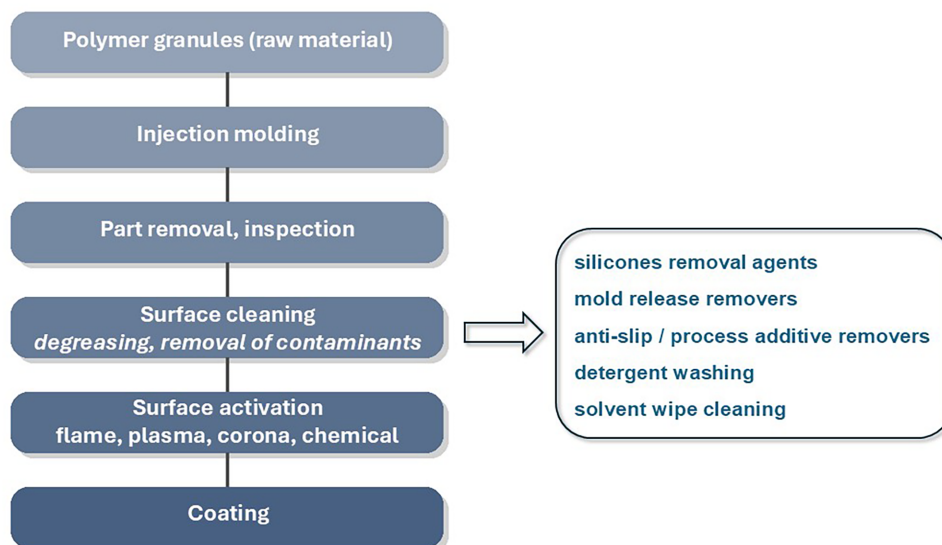


Figure 1. Procedure schematics of the injection-molded part preparation

The aim of this study is to investigate the effect of different chemically distinct cleaning liquids on the surface energy of injection-molded polypropylene parts. Acidic (H_2SO_4), alkaline (NaOH), nonpolar (decalin), and polar aprotic (acetone) liquids were selected to represent a broad range of chemical interactions with the polymer surface. Changes in surface energy were evaluated using contact angle measurements, while modifications in surface chemical composition were analyzed by Fourier-transform infrared spectroscopy (FT-IR). In addition, surface morphology was characterized by confocal microscopy to identify possible topographical alterations induced by the treatments. Crystallinity was determined by Differential Scanning Calorimetry (DSC).

By comparing the effects of these cleaning liquids, this work aims to improve the understanding of how post-processing washing steps influence the surface properties of injection-molded polypropylene. The results provide valuable insight for optimizing cleaning and surface preparation processes in applications where surface characteristics are critical.

2. Methods

NaOH , H_2SO_4 , acetone, and decahydronaphthalene (decalin) were obtained from Reanal Labor, Hungary. NaOH and H_2SO_4 were applied in concentrations of 0.1 mol dm^{-3} . $50 \times 50 \times 2 \text{ mm}^3$ test plates were prepared from Tatren HM 5046 homopolymer PP (Mol Group, Hungary) through injection molding with a Wittmann-Battenfeld Ecopower 55–130 instrument. Before treatments, the surfaces were wipe-cleaned with acetone; such samples before immersion are referred to as ‘Cleaned’. During each experiment, 3–3 plates were immersed in the liquids for 10 min (or for 5 min in the case of decalin) because of the expectedly stronger interaction of decalin with PP and the practical limitation associated with its strong and persistent odour. Uncleaned and unimmersed specimens were used as references (‘As received’ samples). After immersion, the plates were rinsed with distilled water (or with acetone in the case of decalin) and dried at 25°C for 15 min.

Surface energy components were determined through the sessile drop method and the Fowkes equation using 5 mL distilled water and ethylene glycol (Reanal Labor, Hungary) as test liquids [16,17]. Each plate was tested at a minimum of three different locations until reaching standard errors below 5%.

For chemical characterization, FT-IR spectra were recorded with a JASCO FT/IR 4600 instrument equipped with an ATR sampling station. Spectra were recorded with steps of 4 cm^{-1} in the range of $500\text{--}4000\text{ cm}^{-1}$. An average of 64 measurements was evaluated.

Surface roughness was determined with a Lext OLS5000-SAF 3D measuring laser microscope, analyzing $1280 \times 1280\text{ }\mu\text{m}$ areas with $5\times$ magnification to obtain S_a values. Sample cross-sections were also analyzed after fracture in liquid nitrogen.

The samples for DSC measurements were cut with a scalpel from the middle of the long edge of the rectangular plates, so the samples represented an increased contribution of the surface layer; however, the role of the bulk phase was still significant. DSC measurements were carried out on three samples a TA Q200 DSC equipment (TA Instruments Inc., New Castle, DE, USA) with high-purity nitrogen gas as an inert atmosphere. Two cycles were performed in the $30\text{--}300^\circ\text{C}$ temperature regime with heating and cooling at $20^\circ\text{C min}^{-1}$. Curves from the second cycle were analyzed.

X_c crystallinity ratio was determined based on (1):

$$X_c = \frac{\Delta H_m}{\Delta H_{m,100}} \times 100\% \quad (1)$$

where ΔH_m is the melting enthalpy, ΔH_{100} is the melting enthalpy of the 100% crystalline material, in this case 209 J g^{-1} [18]. Standard deviations were below 2%.

3. Results and discussion

Total surface energy and its components are presented in Figure 2. The total surface energy is the sum of polar and the dispersive components; the former arises from the polar interactions, e.g., dipole-dipole and hydrogen-bonding interactions due to the presence of polar groups on the surface, while the latter is associated mainly with nonpolar interactions, e.g., van der Waals forces, which are expected on nonpolar surfaces, such as PP. After production of the plates and cleaning with acetone, the dispersive component took the main role on the surface of the PP plates (33.78 and 32.17 mJ m^{-2} total surface energy, respectively). NaOH and H_2SO_4 improved the surface energy by enhancing the dispersive component, similarly to decalin. Polar component increase could be detected only in the case of acetone (2.65 mJ m^{-2}); however, the dispersive component was more significant here, too. Considering the experimental variability, the differences between the individual treatments were not considered significant, however.

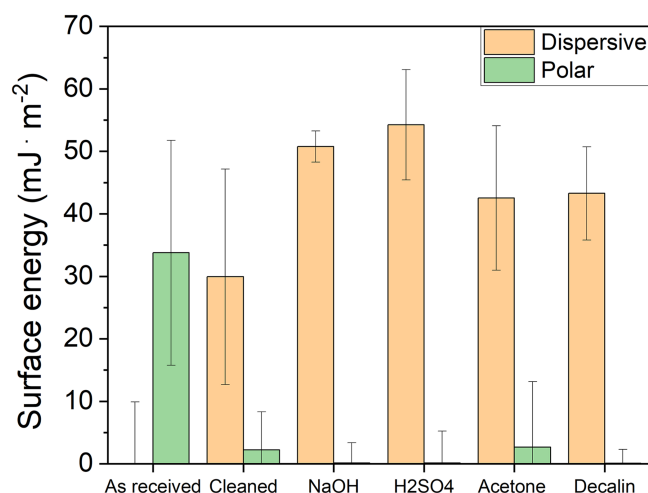


Figure 2. Surface energy components

FT-IR spectra (Figure 3) presented the characteristic peaks of PP: C–CH₃ stretching vibration at 841 cm⁻¹, –CH₃ rocking at 972, 997 and 1165 cm⁻¹, symmetric bending vibration mode of –CH₃ group at 1375 cm⁻¹, CH₃ asymmetric stretching at 2950 cm⁻¹ is related to vibration of the methylene groups. Symmetric bending of –CH₂– groups appeared at 1452, while symmetric and asymmetric stretching at 2837 and 2913 cm⁻¹, respectively [19]. Except for the wide –OH bands at around 3340 cm⁻¹ all the spectra were identical referring to macroscopically unmodified chemical structure. The attenuation of the –OH band after cleaning and its disappearance after immersion can be attributed to the removal of the surface contaminants. Acetone has been previously found to be effective in the removal of low molecular weight materials after plasma treatment, too [20]. It should be noted, however, that FT-IR probes a finite depth beneath the surface, too, thus subsurface or bulk changes cannot be completely excluded.

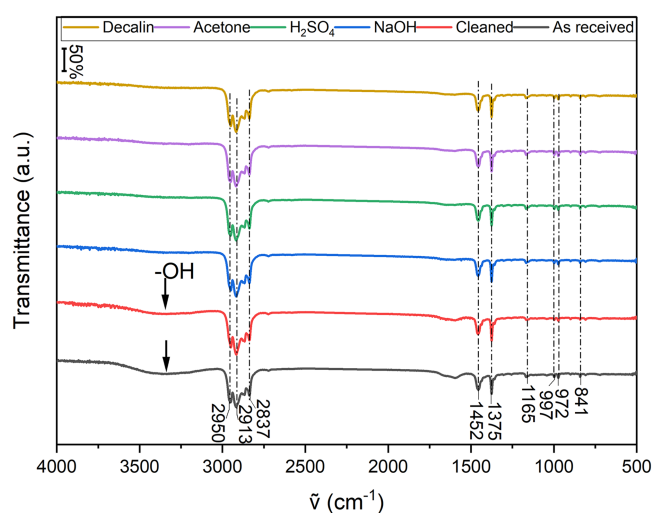


Figure 3. FT-IR spectra

DSC is sensitive to changes in the crystallite morphology of polymers and therefore was applied to detect structural rearrangements induced by the cleaning treatments. Samples were taken from the plate edges to maximize the contribution of the modified surface layer [21] was not modified by immersion in the liquids, consequently the melting and crystallization maxima were located in the regions of 163.8–164.7 and 112.8–116.4°C, respectively, while melting curves preserved their asymmetric character indicating the formation of similar crystallines in a wider size regime (Figure 4, Table 1). However, changes could be detected in crystallization ratio (Table 1). Increased X_c after decalin treatment is in agreement with the blurred surface structures obtained by microscopy and presented later, and can be attributed to the intense swelling, free chain mobility and enhanced crystal formation, as well as dissolution of surface layers. On the other hand, PP is stable against NaOH, H₂SO₄ and acetone at room temperature. In these cases the removal of additives improves the chain movements and eases the crystal formation [22]. In addition, residual ions from NaOH or H₂SO₄ can act as nucleating agents. Enhanced crystallization in any solvents and solutions is also reflected by the crystallization curves with higher peak temperatures and larger intensities (Figure 4). The increase in X_c after treatment does not necessarily imply a corresponding increase in T_m . The removal of additives and polymer swelling may increase local chain mobility, facilitating chain rearrangement and the formation of additional crystalline regions. This process can involve enhanced primary nucleation and subsequent crystal growth, while secondary crystallization may also contribute during the subsequent thermal history. Since T_m is primarily related to lamellar thickness and crystal perfection, the development of additional crystallites with relatively similar lamellar dimensions can result in a significant increase in X_c while maintaining

an almost unchanged T_m . Similar observations have been reported for modified polypropylene systems, where processing or post-treatment altered the structure without markedly changing T_m [23].

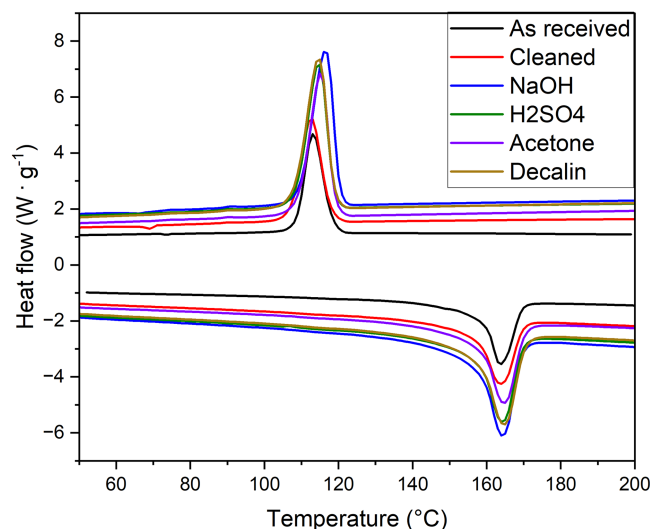


Figure 4. DSC curves

Table 1. Melting temperature (T_m), crystallization temperature (T_c) and crystallization ratios (X_c)

Treatment	T_m (°C)	T_c (°C)	X_c (%)
As received	163.8	111.9	37.7
Cleaned	163.8	112.8	39.0
NaOH	164.3	116.4	55.1
H ₂ SO ₄	164.3	114.7	48.0
Acetone	164.7	115.2	45.8
Decalin	164.7	114.7	53.5

Microscopic images are presented in Figure 5, first row. In case of Figures 5a–5d similar scratched structure was obtained due to the inhomogeneity of the mold used during production of the plates. Nonpolar decalin with higher dissolving affinity towards polyolefins induced blurred lines (Figure 5e).

The surface roughness analysis showed that most treatments slightly reduced the S_a values compared to the cleaned reference sample, indicating a smoothing effect on the surface topography (Table 2). The cleaned surface exhibited an S_a value of 1.679 μm , while NaOH, H₂SO₄, and acetone treatments decreased the roughness to 1.460 μm , 1.508 μm , and 1.452 μm , respectively. Considering the previous results and the minor alterations in S_a , this effect can be attributed to the removal of surface contaminants. The decalin-treated samples showed a significantly higher S_a value of 2.407 μm , indicating a more heterogeneous surface structure, which might be caused by surface dissolution processes.

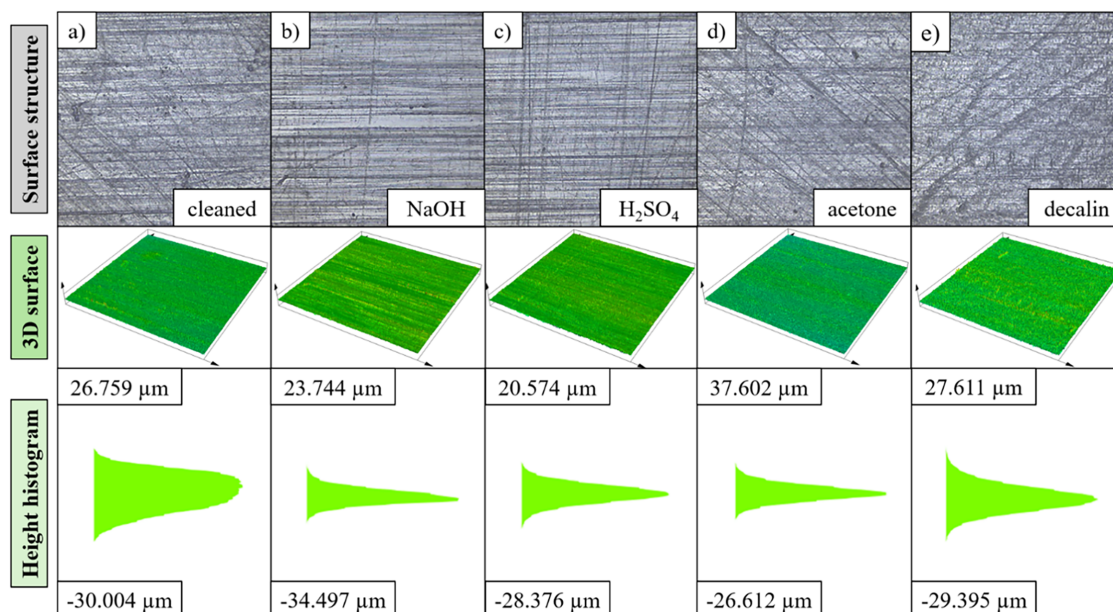


Figure 5. Images and roughness histogram obtained by confocal microscope. (a) Cleaned, (b) after NaOH, (c) H₂SO₄, (d) acetone and (e) decalin treatments

Table 2. Surface roughness results

Treatment	Sa (μm)
As received	1.60
Cleaned	1.68
NaOH	1.46
H ₂ SO ₄	1.51
Acetone	1.45
Decalin	2.41

Even in 3D plots, it is difficult to differentiate the sample surfaces (Figure 5 middle). On the other hand, a fine analysis of the height histograms showed that the cleaned sample had a similar distribution of heights, which was slightly narrowed in the case of decalin due to the most intense chain movements and smoothing to achieve a thermodynamically more stable surface. The as-received sample provided very similar results to the cleaned one. Height distribution widened in case of the other solutions and solvents; in H₂SO₄ and NaOH, the positive heights relative to the median decreased, while in acetone the average height increased due to some surface reorganization. Considering all the results, however, very short interaction with acetone during rinsing did not result in significant modification, only solvent removal. The cross-sectional micrographs after fracture in liquid nitrogen did not reveal a clearly distinguishable skin layer. Therefore, the microscopic observations did not provide sufficient evidence for a quantitative assessment of changes in skin-layer thickness (not depicted).

Comparing the surface energy and topology test results, increased surface energy is governed mainly by changes in surface chemistry. Acid treatment may remove surface species and generate more polar surface sites, increasing the polar contribution to the surface energy. Conversely, decalin-induced swelling primarily affects the surface morphology and chain arrangement and may therefore increase roughness without producing a similarly large increase in surface polarity. Submicron morphological changes may also contribute but cannot be fully resolved by the applied confocal microscopy.

It should be noted that organic solvents are environmentally unfavorable, and the decalin-treated samples retained a strong persistent odor after treatment. In addition, the use of acids and alkaline may raise environmental and material compatibility concerns. Surface activation efficiency did not overbalance this effect, however, it is important to remember that activated chain movements result in detectable modification in crystalline structure and topology.

4. Conclusions

The effects of different chemical treatments on polypropylene (PP) surfaces were investigated using contact angle measurements, confocal microscopy, FT-IR spectroscopy, and DSC. The results showed that the most significant effect of the treatments was surface cleaning, as the applied chemicals removed surface contaminants and oxygen-containing functional groups from the polypropylene surface. This was confirmed by the decrease in the polar surface energy component and the disappearance of –OH groups in the FT-IR spectra.

Only minor changes in surface roughness were observed after NaOH, H₂SO₄, and acetone treatments, while decalin caused an increase in roughness, indicating strong surface modification. However, no considerable improvement in surface energy was observed; the treatments acted primarily as cleaning processes rather than effective surface energy-enhancing modifications. Although there was no macroscopic interaction with the liquids, a reorganization in the top layers, either through swelling or removal of additives, takes place, which enables crystalline formation and topological modifications.

Abbreviations

The following abbreviations are used in this manuscript:

DSC Differential Scanning Calorimetry

PP Polypropylene

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