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Coating of Al mould surfaces with polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), perfluoro-alkoxy (PFA) and ethylene-tetrafluoroethylene (ETFE)

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Abstract: Because of low cost, easily productivity and high thermal conductivity, aluminum (Al) moulds are preferred in the production of the polyurethane (PUR) parts. In this study, adhesion behavior and surface properties of coated materials between mould used in the production of automotive seat and PUR materials were investigated. Four different polymer types were coated on Al mould and they were characterized using contact angle, surface roughness, coating thickness, adhesion, cross-cut and SEM test methods. It was found that, PFA has the least value of surface roughness and ETFE has the highest one in the four different coatings produced. After holding period in isocyanate, decrease were measured on the angle values of all coatings. In the contact angle measurements before and after isocyanate tests, PFA exhibited the highest contact angle value.

Introduction

Polyurethanes (PURs) are used as flexible and rigid foams, elastomers and coatings. The term PUR is used to cover materials formed from the reaction of isocyanates and polyol. Flexible Polyurethane Foam (FPF) is mainly used in automotive industry as well as other various industries. Some problems can occur during the production process of FPF which are emanated by Reaction Injection Molding (RIM) process. One of these problems is sticking of the product to the mould and causing the product to damage during taking out of the product from the mould. This problem, which occurs frequently, causes extra material costs, delays on the production process and waste of workforce. Normally, the mould is used with bare aluminum and a releasing agent (e.g. paraffin wax). For every shot the releasing agent must be sprayed into the mould. Spraying with this releasing agent pollutes the total production area, so everything gets greasy. The releasing agent must be applied as a thin and uniform layer to obtain non-stick property of the surface [1, 2].

Fluoropolymers such as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA) and ethylene-tetrafluoroethylene (ETFE) are known to have excellent chemical resistance to acids, bases and solvents and they have good mechanical properties, high temperature stability, self-lubrication and non-stick properties. They are widely used in a wide range of industries, such as in aerospace, automotive, petrochemicals, medical, microelectronics and electrical industries because of their very good properties as low dielectric constant and very low surface energy. Excellent hydrophobic and anti-wear coatings on the surface of metal substrates have attracted the attention of technologists due to their ability of reducing the macro contact friction under the overall pressure and pollution on the surface of the coating [3-9].

In recent years, there has been a great deal of research interest in fabricating super hydrophobic surfaces [10, 11]. Busscher et. al. [12] studied that super hydrophobic FEP-Teflon was prepared by argon ion etching followed by oxygen glow discharge treatment of commercially available FEP-Teflon sheet material. This combined treatment yielded an increase in water contact angle from 109^0 to 140^0. FEP copolymer is also a good electrical insulation material.

The wettability of solid surfaces, governed by both the chemical composition and the geometrical microstructure of the surface, is a very important property. It is well known that PTFE is a hydrophobic material with a water-contact angle of 108^0 [13]. The contact angles of the FEP and ETFE were measured as 113^0 and 94^0 by Park et. al. [14] and Saarinen et. al. [15], respectively. Copolymers of tetrafluoroethylene with other fluorinated monomers such as hexafluoropropylene and perfluorovinylether show similar chemical and physical properties to PTFE. However they also show easy fabrication because of low crystalline. PTFE has inherent non-stick properties due to its low surface energy [16].

Miller et.al. [17] investigated the influence of film roughness on the wetting properties of vacuum-deposited polytetrafluoroethylene (PTFE) thin films using atomic force microscopy (AFM) and contact angle goniometry. It is well known that wetting of a surface by a liquid is affected by the roughness of the surface. High contact angles are believed to be due to the presence of the hydrophobic PTFE particles as well as the surface roughness of the coating. Similar results were reported by Hazlett [18] for a polytetrafluoroethylene surface and it was argued that the water contact angle changed between 108^0 and 180^0. The advancing angles measured at surface 146^0 were larger than those measured at untreated surface 94^0 performed by Veeramasuneni et. al. [19].

Ortner et. al. [20] studied surface characterization of new unused PTFE, PFA and polyvinylidenefluoride (PVDF) used with light microscopy, scanning electron microscopy, profilometry and atomic force microscopy. It has been found that in spite of higher micro-roughness, PFA exhibits the lowest nano-roughness. Terpilowski et. al. [21] measured the advancing and receding contact angles of water on Teflon plates.

In the present work, PTFE, FEP, PFA, ETFE coatings have been investigated on non stick surface and with adhesive bonding to Al substrate. Change in contact angle is repeated after isocyanate treatment of the fluoropolymer surfaces. The aim of this work is to study the effect of fluoropolymer coatings, on physical, nonstick and adhesive behavior of Al surfaces.

Results and Discussion

Properties of fluoropolymer coatings and experimental results are given in Table 1. Variation of roughness of primer-secondary coatings and coating thickness depend on coating type are shown in Figure 1. Roughness value of untreated Al surface is measured as 0.96 µm and the roughness of sand blasted surface is 2.71 µm. PFA has the least roughness value of 0.29 µm.

Changes of contact angle of coatings after isocyanate interaction treatment are given in Figure 2. Among the coatings the highest contact angle value is obtained for PFA coating (107.1^{o}) and the lowest contact angle value is obtained for ETFE coating (99.2^{o}).

Tab. 1. Properties of coatings and experimental results.

Coating type	Primer roughness R_a (µm)	Coating roughness R_a (µm)	Coating thickness (µm)	Contact angle* (degree)	Contact angle** (degree)	Cross-cut test	Adhesive strength (MPa)
PTFE	-	1.47	17.00	102.50	93.00	5B	3.25
FEP	1.26	1.96	56.50	102.10	95.20	5B	0.15
PFA	1.76	0.29	49.23	107.10	102.80	5B	1.88
ETFE	2.99	3.60	90.00	99.20	83.20	3B	3.37

*fluoropolymer surfaces untreated, **surfaces treated with isocyanate

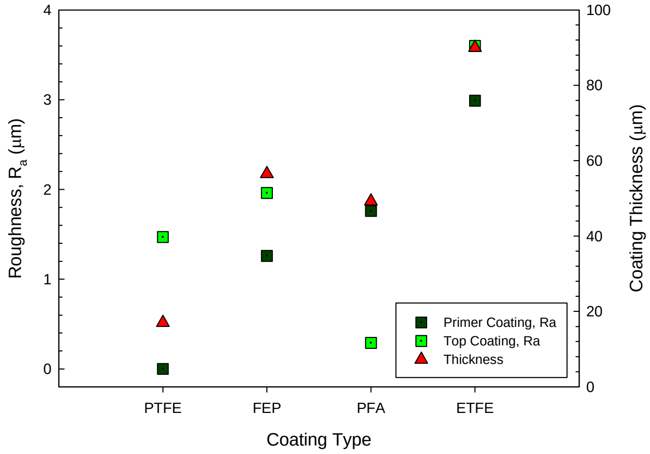


Fig. 1. Variation of roughness of primer-secondary coatings and coating thickness of top coated surfaces depend on coating type.

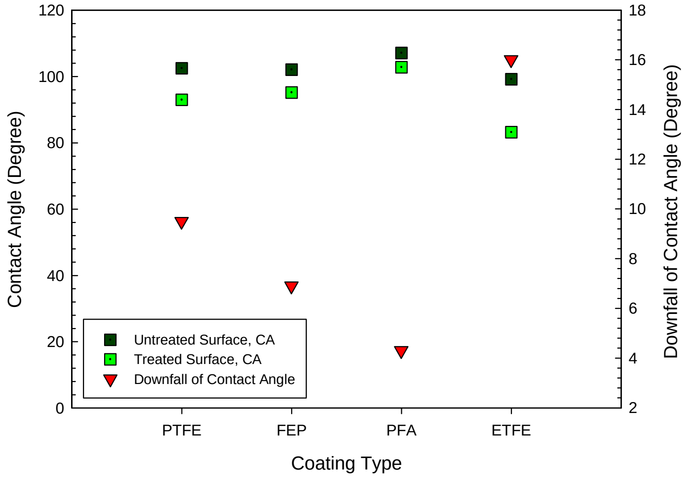
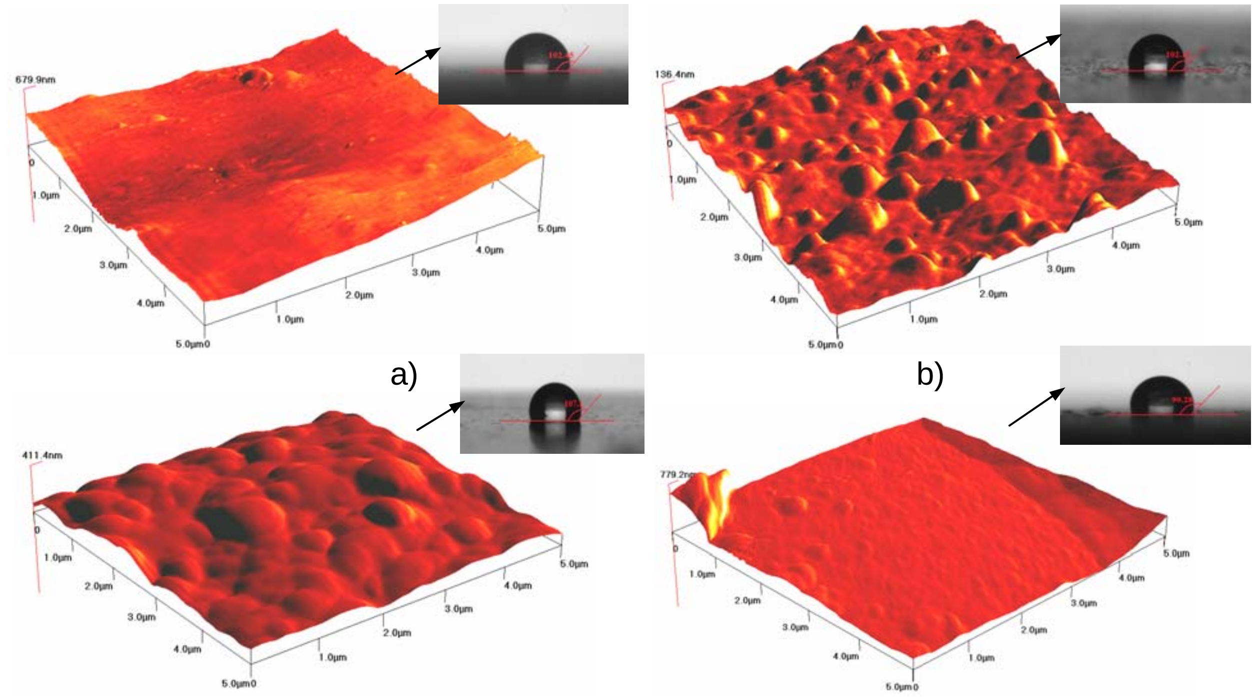


Fig. 2. Contact angles of coatings before and after isocyanate interaction depend on coating type.

This is in line with literature, Zhang et. al. [7] measured contact angle values of untreated PTFE coating between 96.8^{o} and 133.5^{o}. That is because isocyanate is a corrosive material. After the all coatings were treated with isocyanate, it was found that there is a decrease in contact angle values of all coatings. The highest loss is seen on ETFE coating with value of 16.12%. The lowest loss is from PFA coating with 1.26% value.

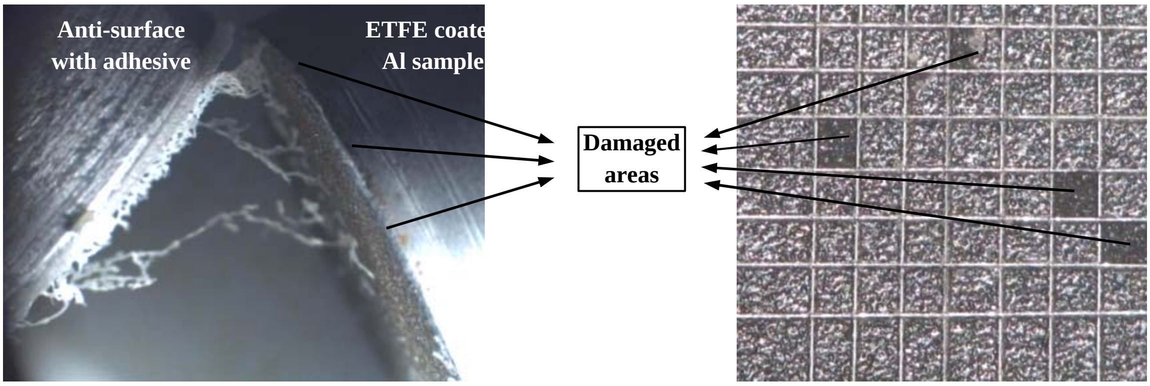


a) b)

c) d)

Fig. 3. AFM and contact angle images of fluoropolymer coated aluminum surfaces, a) PTFE, b) FEP, c) PFA, d) ETFE.

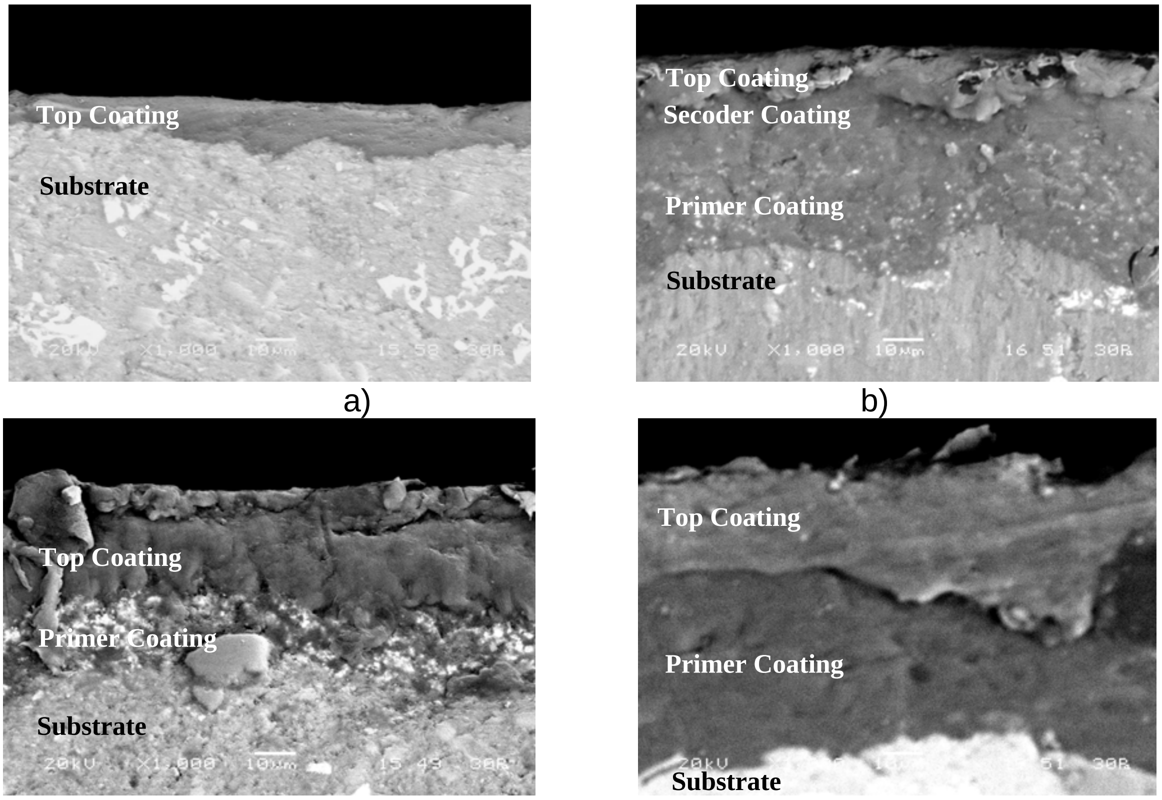
AFM and contact angle images of fluoropolymer coated aluminum surfaces are given in Figure 3a-d. The maximum peak point of PFA and ETFE coatings were found as 411.4 µm and 779.2 µm by AFM analysis, respectively. These values were similar with the one reported by Burkarter et. al. [11]. They found that the maximum peak value of 518.68 nm on the surface of PTFE coating after the surface topography analysis performed by AFM and the average value of surface roughness was 114 nm.



a) b)

Fig. 4. Stereographic images of ETFE coating, a) after ASTM C 633 adhesion test and b) after cross-cut test.

In our study, the maximum peak point of PTFE coating was found as 679.9 µm by AFM analysis at 5x5 µm^2. Riyadh et. al. [22], had produced FEP panes and inspects the AFM images at 5x5 µm^2 surface and the average value of surface roughness was 39 nm. In current study however, the maximum peak point of PFA coating was found as 136.4 µm by AFM analysis at 5x5 µm^2. Stereographic images of ETFE coating after adhesion and cross-cut tests are shown in Figure 4a-b. SEM images of cross sections of coatings are given in Figure 5a-d.



a) b)

c) d)

Fig. 5. SEM images of cross sections of coatings 1000X, a) PTFE, b) FEP, c) PFA, d) ETFE.

The disjunction delamination of upper layer of the coating of ETFE from the undercoat is shown in Figure 4a. The intact part of coating at the surface was divided approximately in two equal parts. In other words, nearly half of the ETFE coating remained on the surface. Fortunately, there is no damage observed on the other coatings. According to these results; coatings except ETFE are suitable in terms of adhesive property in ASTM C633. After cross cut test, the ruptures occurred at the cages as seen in Figure 4b that with ETFE coating. The standard optimum value for adhesion durability cannot be obtained. For that reason the ETFE coating surface gets 3B (5-15% damage) value and the others get 5B (0 % damage) value (Figure 4b).

Conclusions

In present study, it was found that, PFA has the least value of surface roughness and ETFE has the highest one in the four different coatings produced. In the contact angle measurements before and after isocyanate tests, PFA exhibits the best non-stickiness behavior. Results of adhesion test indicate that ETFE coating exhibits low adhesion behavior. PFA shows the least adhesion value in the adhesion behavior test between Al surface and the coating. After holding period in isocyanate, decrease is measured on the angle values of all coatings. This result showed that isocyanate has got a corrosive effect. PFA is suggested to be used in coatings of moulds for production of the PUR. Additionally, FEP might also be considered to be used in such applications.

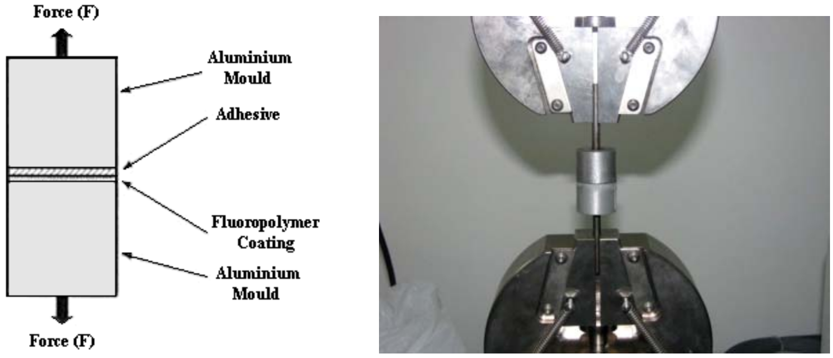
Experimental

In liquid spray coating system, nozzle diameter, gun distance and pressure were selected as 1.6 mm, 30 cm and 1.5 bar, respectively. In electrostatic deposition coating system Wagner manual gun was used. For the coating process existing voltage, current and air pressure were selected as 100 kV, 10 µA, 3 bar respectively. Coating types, drying and curing parameters of coatings are given in Table 2. Roughness and coating thickness tests were carried out on TR 200 TIME and Deflesko positector 6000 FNS model test machines, respectively. The procedures were defined by the ISO 8503-5 and ASTM D 6132 standards. Contact angle (CA) goniometry technique was performed on Krüss DSA 100. Contact angle measurements were also performed on the samples treated 360 hours in isocyanate. ASTM D 7334 and ASTM D 3359 standards were used for the contact angle and cross-cut tests, respectively. ASTM C 633 was used for the adhesion tests (Figure 6).

Tab. 2. Coating types and process parameters of coatings.

Coating type	Primer coating type	Secondary coating type	Top coating type	Drying time (min.) and temperature (ºC) of primer coat.	Curing time (min.) and temperature (ºC) of secondary coating	Curing time (min.) and temperature (ºC) of top coating
PTFE*	None	None	Grebe	None	None	10/400
FEP*	Whitford	Whitford	Whitford	5/120	10/375	10/400
PFA**	Whitford	None	Whitford	5/120	None	10/400
ETFE**	Dupont	None	Dupont	5/80	None	10/340

*liquid spray coating **electrostatic deposition coating



a) b)

Fig. 6. Application of ASTM C633 adhesion strength test a) prepared sample illustration, b) during test.

The SEM studies of the fluoropolymers were performed by using Jeol JSM-6060LV Scanning Electron Microscope. Before the SEM studies, gold coating was applied on the samples for the conductivity of the samples. AFM analysis was done with Quesant AFM analyzer and non-contact cantilever on coated samples. Stereoscopic images were investigated with Leica MZ 75 stereo microscope.

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