Hydrophobic and anti-ice properties of homogeneous and heterogeneous nanoparticle coatings on Al 6061 substrates

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Abstract- In this study, chemically homogeneous and heterogeneous nanoparticles coatings of low surface-energy materials on Al surface were investigated. Experimental work has demonstrated the existence of the heterogeneity effect on an Al surface by applying different hydrophobic functions (C-H and C-F). More precisely, for homogeneous coatings, the contact angle (CA) values were ~100^{o} while it was ~134^{o} for heterogeneous coating (HC). Contact angle hysteresis (CAH) was smaller for HC (~32^{o}) than homogeneous coatings (~46^{o} and ~56^{o}). Icing tests showed delayed ice formation and lower adhesion strength on HC. The chemical composition of the surfaces was analyzed by X-ray photoelectron spectroscopy (XPS). The scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis of the coated surfaces demonstrated the presence of a rough structure at micro/nanoscale levels on the mirror polished Al substrate.

Keywords: homogeneous coating, heterogeneous coating; contact angle (CA); contact angle hysteresis (CAH); hydrophobic; Ice Adhesion Strength; X-ray photoelectron spectroscopy (XPS); scanning electron microscopy (SEM); atomic force microscopy (AFM).

Introduction

In cold climate regions, ice and wet snow accumulations on overhead power transmission lines are sometimes the source of damage and malfunctions which may lead to mechanical line failures, insulator flashovers, etc. [1-4]. Reducing or preventing ice accumulation on exposed surfaces can be accomplished by developing ice-phobic coatings [5-8]. There is extensive research on hydro/ice-phobic properties of various nanoparticles incorporated in polymer coatings [9-12]. However, the low surface energy heterogeneous coatings (HCs) or surfaces including both hydrocarbons and fluorocarbons have drawn less attention. These types of coatings are a very attractive alternative because they show lower ice adhesion as compared to homogeneous coatings. Important papers related to this work have been published in the field of heterogeneous polymer coatings, where the authors tried to decrease ice adhesion by applying a heterogeneous effect [13-17]. Therefore, the aim of this work is to study of the heterogeneity effect on the hydrophobic and ice-phobic properties of coatings on polished aluminum alloy 6061 (AA6061).

I. Experimental procedure

Aluminum alloy 6061 composed of Al 97.9 wt.%, Mg 1.0 wt.%, Si 0.60 wt.%, Cu 0.28 wt.%, Cr 0.20 wt.% from industrial rolled sheets was cut into 5.1 × 3.2 cm samples used as substrates. Prior to coating, the plates were mechanically polished. The polished Al plates were then cleaned in acetone and distilled water each for 5 minutes. The organic polyethylene (PE) and polytetrafluoroethylene (PTFE) providing low surface energy were purchased from Good-fellow and Sigma-Aldrich® companies, respectively. A one-gram (1 g) solution of polyethylene (PE) in 50 ml of toluene was prepared as a first layer for the homogeneous coating. For HC, suspension of 1 g of dispersed nanoparticles with different surface energy such as polytetrafluoroethylene (PTFE) and Al_2O_3 in 50 ml of methanol were prepared. These suspensions were shaken by ultrasonic waves for 5 minutes followed by magnetic stirring during 20 minutes. The suspensions were used to elaborate several series of HCs on polished Al surfaces, in order to study the effect of different surface energy and surface roughness. The homogeneous and heterogeneous nanoparticle coatings were prepared using a spin-coater from Laurel (WS-400B-6NPP). Spin coating is a commonly used technique for preparing uniform thin films on flat substrates which involves the controlled precipitation from the solution of a compound on a suitable substrate while spinning with specific parameters. The spinning rate was set at 500 rpm (15 s). Upon coating, all samples were heat-treated at 70 °C in oven for 2 hours to remove residual solvents. Table 1 shows the procedure for preparing homogenous and heterogeneous nanoparticle coatings.

Table1: Detail information for prepararing homo/heterogeneous coatings.

Material	Quantity	Solvent	Method	Company	Abbreviate
PE	1 g	50 ml Toluene (at 110^{o} cc)	Spin coating	Good-fellow	PE-spin
PTFE	1 g	50 ml Methanol	Spin coating	Sigma-Aldrich	PTFE-spin
PE, PTFE	1g, 1g	100 ml Toluene	Spin coating	Good-fellow, Sigma	PE-PTFE
PE, PTFE	1g, 1g	100 ml Toluene	Spin coating	Good-fellow, Sigma	PE+PTFE

The dried samples were stored in clean Petri dishes at ambient conditions and characterization was conducted immediately after. The coated samples were characterized by measuring their hydrophobic and ice-phobic properties. The wetting characteristics reported in this study were obtained following the standard sessile drop method on a fully automated contact angle goniometer (DSA100 from Krüss) with controllable volume (4 µl) of water droplets. These measurements were performed with the Young–Laplace method. Surface topographies were studied using scanning electron microscopy (SEM, Hitachi S-4700 Field-Emission SEM with accelerating voltages from 500 V to 25 kV) to take surface images of coated samples and therefore reveal their surface characteristics. The ice-repellent performance of bare as well as prepared coatings was evaluated using a home-made centrifugal apparatus which was placed in a climate room at subzero temperature (-10^{o}C). The detail of ice preparation procedure has been described previously [9].

II. Results and discussion

Figure 1 shows the CA and CAH for the PE-spin, PTFE-spin, PE-PTFE and PE+PTFE coatings. For the homogeneous coatings PE-spin and PTFE-spin on a polished Al surface, the CA values were ~100^{o} and ~98^{o}, respectively. A significant enhancement of CA values (~134^{o}) was observed for the heterogeneous coating of PE-PTFE. In the case of HCs, the presence of PTFE nanoparticles on a PE-coated Al surface resulted in surface roughening. Therefore, to exclusively focus on the heterogeneity effect and to avoid the surface roughening, a PE+PTFE coating on Al sample was also prepared. More precisely, the PE+PTFE sample was prepared from the deposition of a mixture of PE and PTFE nanoparticles on an Al surface. This sample was only prepared to investigate the effect of the surface roughening and heterogeneity effect. As shown in Figure 1, the existence of surface roughening in case of PE+PTFE coated Al sample resulted in a bigger CA value of ~129^{o} compared to homogeneous coatings. This observation is due to surface roughening. However, the CA value of PE-PTFE (~134^{o}) was greater than that of PE+PTFE (~129^{o}). This may be due to the heterogeneity effect. Moreover, the CAH values are smaller for PE-PTFE (~32^{o}) than for homogeneous PE-spin and PTFE-immersion coatings and even for the PE+PTFE sample (~64^{o}). Therefore, a small value of CAH is the most important factor in the heterogeneity effect [14].

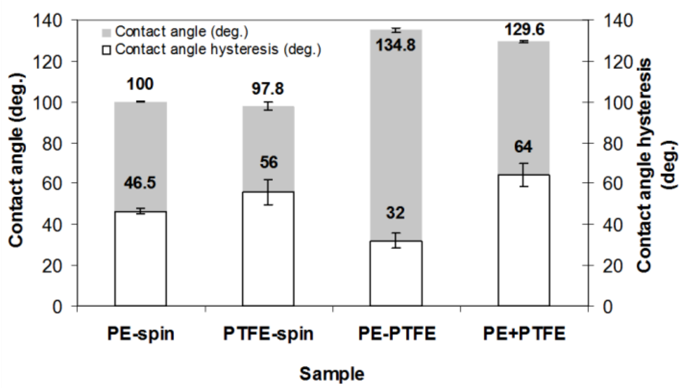

Figure 1: Contact angle and contact angle hysteresis values of homo/heterogeneous coatings.

To further support and confirm the presence of surface roughening on Al samples coated with PTFE nanoparticles, an AFM analysis was conducted. Table 2 shows the root mean square (Rms) roughness values for the PTFE-spin, PE+PTFE and PE-PTFE coatings. It is obvious that the Rms values of the PE+PTFE and PE-PTFE coatings are close together, although they are somewhat bigger for PE+PTFE than for PE-PTFE. However, the CA value of a PE+PTFE coated Al sample was smaller than what was observed in the case of a PE-PTFE coating. Meanwhile, the CAH value for a PE+PTFE coated Al sample was much bigger than that of a PE-PTFE coating. The observed difference in CAH values of such coatings was about 32^{o}. Therefore, it is possible to say that in an AFM analysis, contact angle and contact angle hysteresis measurements confirm again the effect of heterogeneity or dissimilar functions (C-H and C-F) on polished Al surfaces.

Table 2: The Rms (nm) of homogeneous and HCs samples.

Sample	Root mean square (nm)
PTFE-spin	165.5 ± 68.58
PE+PTFE	284.79 ± 173.14
PE-PTFE	239.85 ± 145

Ice adhesion tests were carried out on homo/heterogeneous nanoparticle coatings. The results showed that the ice detachment shear stress value for the HC of PE-PTFE is smaller than that for homogeneous PE-spin. Also, the ice adhesion reduction factor (*ARF*) of homogeneous and heterogeneous coatings showed that the ice adhesion strength values are ~1.13 and ~1.3 times lower than those obtained on a polished Al sample, respectively. It is worthy to mention that the shear stress values of ice detachment for the PE+PTFE sample was generally greater than that obtained on a polished Al sample. This fact is obvious from the CAH values of homogeneous PE-spin and heterogeneous PE-PTFE coatings. Since, the CAH value for the HC of PE+PTFE sample was greater than for the homogeneous and heterogeneous coatings of PE-spin and PE-PTFE, respectively. This is in agreement with the values of the shear stress of ice detachment [18]. The reason for the enhancement of CAH values in the case of the PE+PTFE compared to the homogeneous sample is the topological nature of the surface roughness, which is of prime importance in determining hydrophobicity [20-23].

III. Conclusions

In this research work, homogeneous and heterogeneous nanoparticle coatings of low surface-energy materials with hydro/ice-phobic properties were prepared by the spin coating method. The contact angle, contact angle hysteresis measurements, and AFM analysis results demonstrated the effect of heterogeneity on Al substrates. Also, the obtained results showed that the HCs prepared from dissimilar hydrophobic functions of C-H and C-F can affect the hydro/ice-phobic characteristics of such coatings. The anti-ice performance of HC, confirmed the heterogeneousity effect on Al surfaces, since the ice-phobic properties of HC improved upon those of homogeneous coatings and polished Al substrate.

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V. References

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