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Fabrication of hydrophobic/hydrophilic switchable aluminum surface using poly(*N*-isopropylacrylamide)

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ABSTRACT

The quick removal of condensed water generated during operation of an automobile air conditioner is essential to prevent the growth of bacteria and fungi, which may produce odors and cause illness. Modification of an evaporator core (evacore) surface to provide superhydrophobicity is one technique that can be used to remove the condensed water. However, if the evacore surface is superhydrophobic, small water droplets can flow towards the inside of the automobile engine along with the air flowing through the air conditioner. In the present investigation, we propose an approach to fabricate an evacore surface that can be switched from hydrophobic to hydrophilic by changing the temperature. In the initial stage of air conditioner operation, the surface is hydrophilic at ambient temperature, causing water to stay on the surface. After the operation of the air conditioner, the surface becomes hydrophobic at a higher temperature, and the water rolls off the surface. To fabricate this surface, aluminum (Al) substrate was used, and it was etched by immersion in 10 wt.% hydrochloric acid (HCl) for 8 min. The etched Al substrate was coated with a functionalized poly(NIPAM-*co*-MAA) polymer by immersing in a coating solution for 1 h at 120 °C. The resulting surface is a thermosensitive hydrophobic/hydrophilic switchable Al surface, which provides a hydrophilic state under the lower critical solution temperature (LCST), 35 °C, and a hydrophobic state above the LCST.

1. Introduction

Over the past decade, research has been carried out to minimize the odor that is generated in car air conditioner evaporators. Studies have shown that the production of this unpleasant odor is due to the condensation of moisture from the air in automobile air-conditioning systems (ACS); this moisture provides a suitable environment to grow odor-causing micro-organisms [1–3]. These micro-organisms include a broad range of bacteria, protozoa and fungi, and especially, the methyl-obacterium and penicillium species, which can colonize various components within the AC parts and are the main source of malodor [4–6]. Compounds produced by these micro-organisms may be toxic and can have immunomodulating activity, which contributes to hyper allergenic responses or renders those exposed more susceptible to other micro-organisms [7]. Numerous fungi are known to produce noxious volatiles, which can have adverse effects on the health of consumers [7,8]. Some commercial products are available in the market for treatment of malodors emanating from ACSs, but these products are recommended for repeated usage due to the recurrence of the problem. Replacing the evaporator and other components requires considerable expense and is inconvenient for the consumer. Few studies have been conducted to provide a permanent solution for this problem. Therefore, a viable method for treating or preventing odors in automobile ACSs is required [9].

The evaporator core (evacore) is one of the most important parts of an automobile air conditioning system because it is where colonization of such odor producing microorganisms can occur. It is made of a vast number of thin strips of aluminum. To prevent the growth of microorganisms, accumulation of condensed water on the surface must be inhibited. Various methods have been proposed such as drying the evacore after use or making its surface superhydrophobic [10,11]. When the surface is a super hydrophobic in nature, the condensed water can be removed easily. In the present work, we hypothesized that the problem can be solved if

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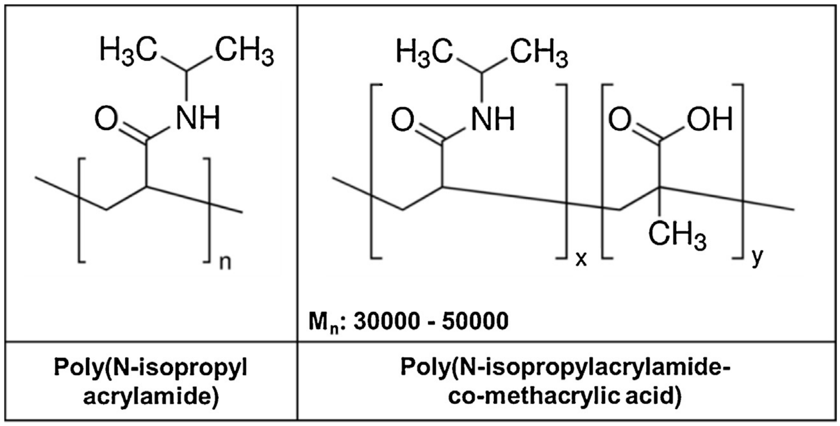

Fig. 1. The molecular structures of PNIPAAM (left) and poly(NIPAM-*co*-MAA) (right).

the accumulation and growth of the microorganisms are inhibited by reversible control of 'wettability' (i.e., the hydrophobicity and hydrophilicity) of the Al surface. Wettability is a crucial surface property that is governed by both structure (topography) and chemical composition (coatings) of the surface [12–18]. To develop structures on the surface of various substrates, 'etching' is one of the most promising and profitable approaches [19–22]. The chemical composition and behavior of the surface can be altered by coating the surface with a responsive polymer. In most cases, poly(*N*-isopropylacrylamide) (PNIPAAM) is used for switchable wettability [23–25], but the synthesis/deposition process of PNIPAAM is time consuming and inefficient. Here, we describe a commercially applicable and efficient approach to make a hydrophobic/hydrophilic switchable Al surface by using a combination of Al etching and a thermo-responsive polymer coating on the evacore. Aluminum etching provides a suitable surface structure to enhance the hydrophobicity of the surface. The poly(NIPAM-*co*-MAA) direct coating process was introduced as a thermo-responsive coating polymer instead of the conventional slow synthetic processes used for PNIPAAM. A hydrophobic/hydrophilic switchable Al surface was obtained using the proposed process, and the contact angle of the surface was measured at various temperatures.

2. Materials and methods

In this experiment, aluminum 3003 alloy (Al: Al 96 wt.%, Mn 1.5 wt.%, Fe 0.7 wt.%, Si 0.6 wt.%, Zn 0.1 wt.%, Cu 0.2 wt.%, remainder 0.15 wt.%, Dongwon Systems, Korea) coupons with dimensions of 30 × 30 × 0.2 mm were used as substrates. Poly(*N*-isopropylacrylamide-*co*-methacrylic acid) (poly(NIPAM-*co*-MAA), M_n: 30,000–50,000, Sigma-Aldrich, USA) random copolymer was used as a polymer material. The molecular structures of PNIPAAM and poly(NIPAM-*co*-MAA) are shown in Fig. 1.

The experimental process is divided into two parts: etching of the Al surface and polymer coating the etched Al surface. The surface of the substrate became rough due to chemical etching, and a functional polymer was applied using a surface reaction. The Al substrates were ultrasonically cleaned with acetone to remove organic contaminants and residual dust particles from their surfaces, and they were then rinsed with deionized water (DIW). The clean samples were dried on a hot plate at 100 °C for 3 min prior to etching. Dried Al substrates were etched by immersion in 10 wt.% hydrochloric acid (HCl) (OCI Company, Korea) for different intervals of time ranging from 1 to 8 min followed by rinsing with DI water. After the surface etching step, functionalized poly(*N*-isopropylacrylamide-*co*-methacrylic acid) (PNIPAAM-*co*-MAA) was applied by immersing 8 min etched Al substrates in a coating solution. These samples were kept in a convection oven (OV-02, JEIO TECH, Korea) for 1 h at 120 °C. After the polymer coating, the substrate was rinsed with ethanol followed by DI water to remove the unreacted polymers. The polymer was dissolved in an ethanol/DIW mixture (1:1 ratio) at a concentration of 2 wt.%.

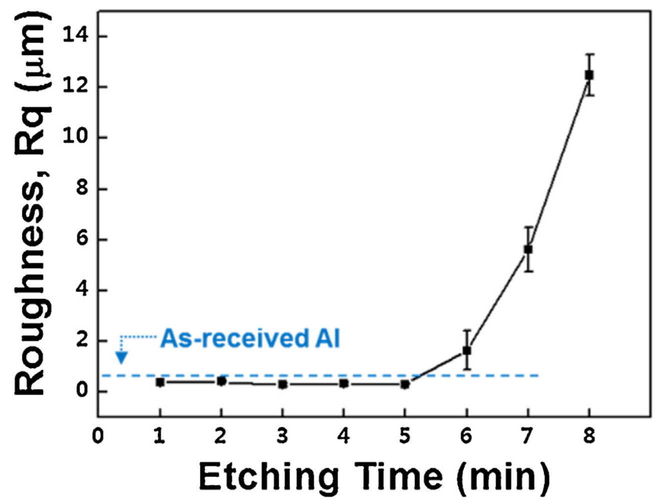

Fig. 2. The roughness values of the etched Al surface as a function of the time.

The poly(NIPAM-*co*-MAA) coated Al surface was characterized by measuring static/dynamic contact angles using a contact angle analyzer (Phoenix 300, SEO, Korea) with a heating and tilting stage. The static contact angle was measured for 100 s after the water droplet came into contact. Surface morphology was observed using a confocal 3D microscope (μ-surf, Nanofocus, Germany) and field-emission scanning electron microscopy (FE-SEM, MIRA3, TESCAN, Czech). An FT-IR spectrometer (iS50, Thermo Fisher Scientific, USA) was used to analyze the PNIPAAM film surface.

3. Results and discussion

3.1. Surface etching with HCl

Random microstructures were fabricated on the Al surface using a chemical wet etching process with a 10 wt.% HCl solution. Fig. 2 shows the roughness values of the etched Al surface with respect to the etching time. The roughness values calculated from surface topography images which were obtained by confocal 3D microscope. Three different places were used on Al substrate to measure and presented with average RMS roughness and standard deviation in Fig. 2. The roughness of the as-received Al surface was 0.66 μm.