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Influence of Annealing and Etching on Physical and Wetting Properties of Acrylic Surface

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Abstract

The objective of this research aims to study the surface modification of acrylic for superhydrophobic applications. The acrylics were modified by annealing for 1h at 50, 75 and 100 °C. To study the effect of the etching on the surface morphology, chloroform and tetrahydrofuran (THF) with their concentration of 99.8 % v/v were used as etching acids. The annealed acrylics were then etched with THF and chloroform for 1 min. The annealing and wet chemical etching effects on morphology, optical properties and wettability can be characterized using atomic force microscopy, scanning electron microscopy, Vickers hardness tester, UV/Vis spectroscopy and water contact angle measurement. This result shows that the hardness of acrylic increases with increasing the annealing temperature. Furthermore, the wet chemical etching plays an important role in the wetting property on acrylics due to the changing of surface roughness.

Keywords: Acrylic, Tetrahydrofuran, Wettability, Annealing, Etching

1. Introduction

Polymers are often found in every materials used in our life, such as windows, lens and packaging (Kaczmarek & Chaberska, 2006; Mohajerani, Farajollahi, Mahzoon, & Baghery, 2007). Acrylic is a transparent polymer that has been used as a substitute for glass. Because it is more durable and lighter than glass (Al-Qahtani & Haralur, 2020). Annealing and wet chemical etching processes are widely used to modify the physical, mechanical and wetting properties. It is well known that the wetting property is the ability of a liquid to maintain contact with a solid surface, and it is controlled by the balance between the intermolecular interactions of adhesive type (liquid to surface) and cohesive (liquid to liquid) (Moldoveanu & David, 2017). Wet chemical etching processes that use liquid chemicals or etchants to remove materials from a wafer involve multiple chemical reactions that consume the original reactants and produce new reactants (Nayak, Islam, & Logeeswaran, 2012). In 2020, Jumrus et al. (2020) reported that annealing assisted etching technique can modified the roughness in nanoscale by reducing residual and hardness. Due to the fact that acrylic is the hardest thermoplastic polymer that softens when heated and harden upon cooling. Its effect on crystal structure, hardness, internal stresses and strength has been studied in the literature (Aadila et al., 2016). Moreover, tetrahydrofuran (THF) is one of the interesting acids which can be used to create high surface roughness (Ebert & Bhushan, 2012). The enhancement of surface roughness play an important role in superhydrophobicity (Sriboonruang et al., 2019).

In this work, we aim to modify physical and wetting properties on the acrylic surface by annealing and etching methods. Their methods were simple and low-cost to change surface roughness. Morphology, hardness and optical properties of acrylic were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), micro Vickers hardness tester and UV-Vis spectroscopy. Moreover, wetting property can be investigated using the water contact angle (WCA) measurement.

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2. Materials and Methods

2.1 Preparation

The commercial acrylic sheets (Pan Asia Industrial Co., Ltd) were cut into 10x30x1 mm^3. 2 acids (tetrahydrofuran (THF) and chloroform, 99.8% purity, RCI Labscan Ltd) with similar conditions used to compare the change on the acrylic surface. The samples were annealed under atmospheric pressure at 50°C (A50), 75°C (A75), and 100°C (A100) for 1 h. The annealed samples were then etched by the chosen acid for 1 min.

2.2 Characterization

Morphology of samples was characterized by scanning electron microscopy (SEM, JEOL JSM-IT300) and atomic force microscopy (AFM, Digital Instruments, Inc.) The Vickers microhardness (STARTECH, SMV-1000) used 0.98 N of load for annealed samples. The optical transmittance was measured by UV-Vis spectroscopy (Hitashi U-4100) from 200 to 800 nm. The wetting property was estimated by the WCA measurement using a pendant drop tensiometer with 3 µL of water droplet at five different areas for each sample.

3. Results and Discussion

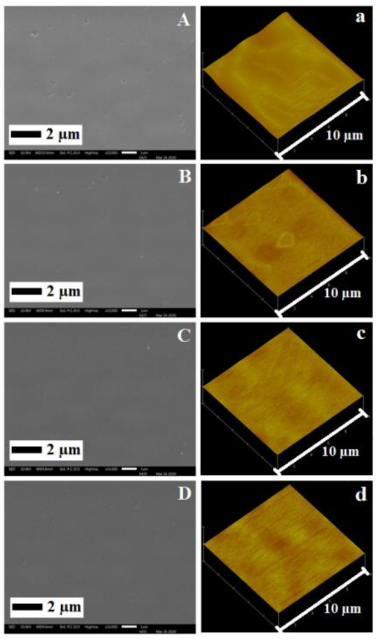

Figure 1. SEM and AFM images of, RT (A and a), A50 (B and b), A75 (C and c) and A100 (D and d).

Figure 1 shows SEM and AFM images of the acrylic surface after annealing with different temperatures. The surface roughness of all samples slightly changes in the nanoscale, as measured by AFM but not significantly in SEM. The surface roughness of bare acrylic (RT) is 5.024 and annealed acrylics at A50, A75 and A100 are 0.706, 0.447 and 0.344 nm, respectively. It has been reported that annealing at a temperature lower than the transition glass temperature (T_g = 105°C) plays an essential role in the reduction of surface roughness (Aadila et al., 2016).

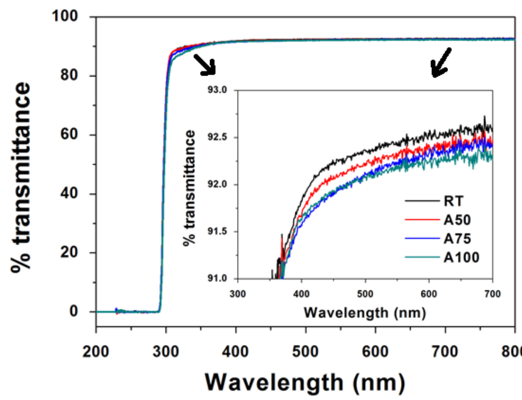

Figure 2. The spectra of transmittance after annealing at different temperatures.

The transmission of the samples with the wavelength from 200 to 800 nm is exhibited in Figure 2. Interestingly, the high transparency of the bare and annealed acrylics in the UV and visible regions is observed. This is because a small roughness change does not exceed the wavelength of incident light (< 100 nm), as indicated by the Mie scattering effect (Zhang et al., 2017).

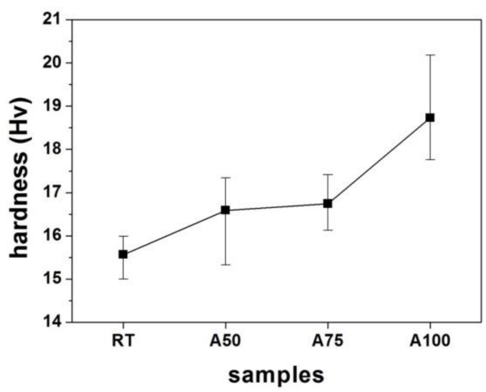

Figure 3. Micro-vickers hardness evolution after annealing at different temperatures.

The variation of micro-vickers hardness as a function of annealing temperature from room temperature to 100°C is shown in Figure 3. The hardness increased from 15.6 to 16.6, 16.8, and 18.7 Hv with increasing the annealing temperature from RT to 50°C, 75°C and 100°C, respectively. This is in good agreement with Khodabakhshi et al. result (Khodabakhshi, Kazeminezhad, Azarnush, & Miran, 2011). Interestingly, the hardness was increased with increasing the annealing temperature lower than T_g of acrylic due to the gentle and independent vibrations in acrylic molecules (Wu et al., 2013). Whereas annealing temperature higher than T_g shows a decreasing of hardness due to rapid grain growth in acrylic.

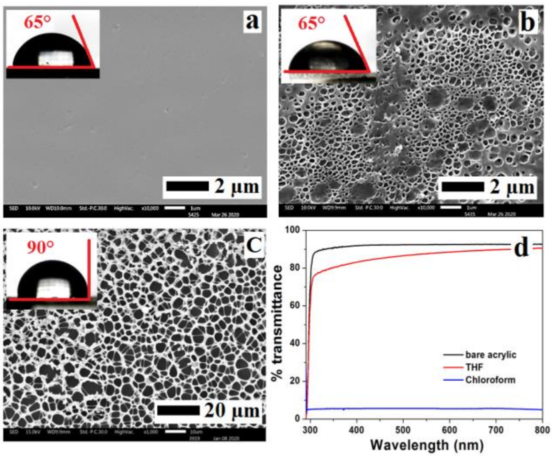

Figure 4. SEM images of (a) bare acrylic, (b) etched with THF, (c) etched with chloroform, and (d) transmittance spectra.

Figure 4 (b and c) shows the morphology of acrylic substrates for the etching of two different acids between THF and chloroform used, as affected by the increasing of surface roughness. The surface of bare acrylic is very smooth, with a WCA of 65°, as shown in Figure 4 (a). Although the surface morphology of the etched acrylic changed by THF but did not change in WCA (Figure 4 (b)). This is due to the THF etching is uncontrolled in the reaction and the roughness on the surface, as confirmed by figure 4 (d). Whereas the WCA of etched acrylic by chloroform increased to 90° (Figure 4 (c)). The chemical reaction of chloroform is better than THF due to its low boiling point, which affected to surface roughness (Kim et al., 2017). The molecular structure on the etched surface leads to a change in the WCA and their adhesion force (Hiratsuka, Emoto, Konno, & Ito, 2019). However, chloroform has highly hazardous acid and the average transmittance spectra is reduce to 5% which is compared to the spectrum of the THF etched sample of 83%, as seen in Figure 4 (d) (Yeh, Wu, Huang, Lee, & Jeng, 2019).

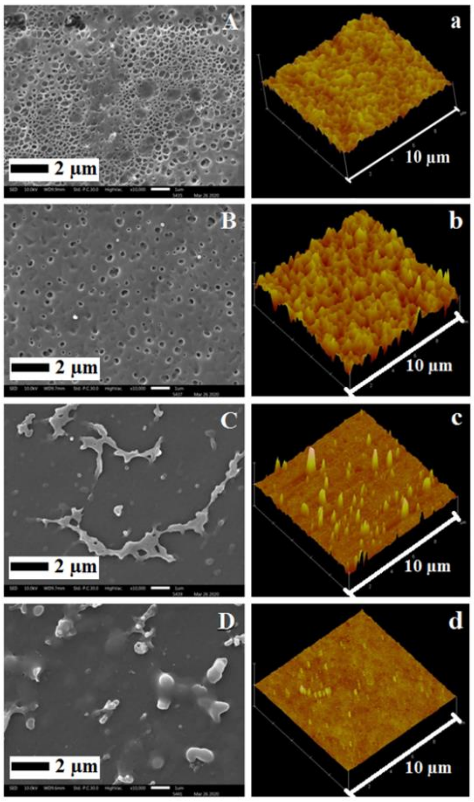

Figure 5. SEM and AFM images of, (A and a) bare acrylic (RT-THF), (B and b) annealed and etched (A50-THF), (C and c) annealed and etched (A75-THF), and (D and d) A100-THF.

The SEM and AFM images of THF etching samples are shown in Figure 5. The bare acrylic (RT-THF) surface roughness is 10.355 nm, while the roughness of the annealed and etched samples (A50-THF, A75-THF and A100-THF) are 26.691, 8.778 and 2.461 nm, respectively. It is noted that the annealed samples at room temperature (RT) rapidly etched while etching ability was decreased with the annealed samples at a higher RT. This result is in good agreement with the microhardness result (see in Figure 3).

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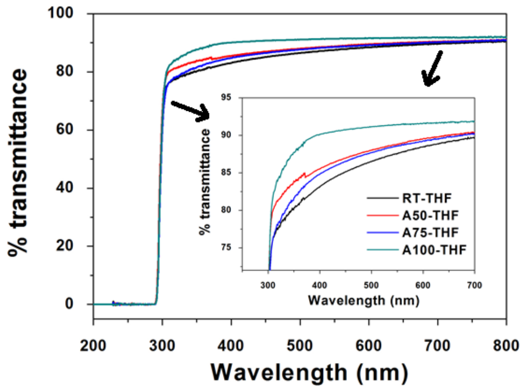

Figure 6. Transmission of the etched samples after annealed at different annealing temperatures.

The optical property of the annealed and etched samples is shown in Figure 6. From the figure, the sample A100-THF exhibits the highest transmittance because the surface roughness is the lowest. Interestingly, the sample A50-THF shows high transparency, although (Figure 6) it has the highest surface roughness. Thus, the transmittance not only depends on surface roughness in the micro-scale but also on the changing of morphology in the nano-scale, as shown in the AFM images (Figure 5 (a-d)). This is in good agreement with our previous paper (Jumrus et al., 2021). It is noted that THF etching creates both micro and nano-roughness on the acrylic surface, which depends on the hardness after annealing.

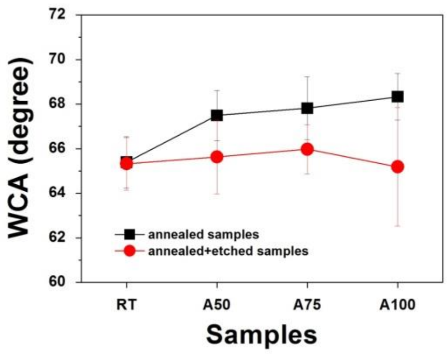

Figure 7. Variation of WCA after annealing in different temperature and etching.

Figure 7 shows the wettability of the samples. The annealed samples have a WCA that is slightly increased with increasing of the annealing temperature. This can be indicated that the annealing has direct effect on leaving some hydroxyl ions from the surface and lead to improving surface stability (Wu, Xu, Yang, & Zhang, 2016). However, some low surface energy will be eliminated from the annealed acrylic that was etched with THF. This is due to the annealed and etched acrylic's WCA not changing significantly.

4. Conclusions

Facile wet chemical etching techniques and annealing were modified using the wetting property of the acrylic surface. The annealing temperature and acid for etching are the main factors explaining the transparency and optimum surface roughness. These developments result in the creation of superhydrophobic applications. The acrylic materials are valuable because they are lighter than glass, but they also impact weather-resistant and have high transparency. This is an alternative material which can be used as a substitute for glass in the future.

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Conflict of Interest

The authors would like to declare that there is no conflict of interest in this paper.

Ethical Approval

Not applicable.

Publication Ethic

Submitted manuscripts must not have been previously published by or be under review by another print or online journal or source.

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