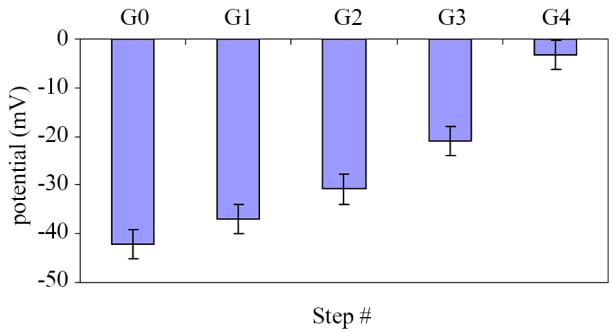

Figure 3. Increasing zeta potential of synthesized film containing 10% AA from G_0 to G_4.

beyond the first generation, only the terminal carboxylic groups at the periphery are accessible which confirms the formation of dense shell dendritic structure owing to the increased steric hindrance [15, 19]. Besides, the reduction in conversion with increasing generation is a major obstacle in the way of increasing the number of end functional groups [11].

Since wettability can be governed by surface roughness, the topography of the synthesized films containing 10% AA for G_0 and G_4 was studied by AFM as shown in Figure 4 and the calculated roughness is tabulated in Table 2. As can be seen, there is an increase in the roughness with successive generation from 13 nm in G_0 up to 31 nm in G_4, validating the obtained results of contact angle measurements. In other words, the hydrophilicity of dendrigraft structures declines with increasing step number due to the restricted mobility or steric hindrance of terminal groups. Zhang et al. [42] showed that with increasing surface roughness, the fraction of air trapped at the interface between solid surface and water increases obviously, which results in higher contact angle. Based on Wenzel modified Young's equation, contact angle θ′ on a rough surface can be determined by the following equation:

$$\cos\theta' = \gamma\frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = \gamma\cos\theta \qquad (6)$$

Table 2. Mean roughness of P(AN/AA)film containing 10% AA from G0 to G4.

Sample	Average roughness (nm)
G0	13
G1	15
G2	20
G3	27
G4	31

where r is the roughness factor, defined as the ratio of the actual area of a rough surface to the geometric projected area, γ_{SV}, γ_{SL} and γ_{LV}, respectively, denote the interfacial free energies per unit area of the solid-gas, solid-liquid, and liquid-gas interfaces [43]. In the regime of Wenzel's equation, the surface free energy of the solid part of a rough surface is r times higher than that of a flat surface and the hydrophobicity of a rough hydrophobic surface is augmented by the increase of the solid-liquid contact area. Therefore, the contact angle and its hysteresis (the difference between advancing and receding contact angles) on hydrophobic rough surfaces increase as the roughness factor increases [44]. It seems that another important factor which affects the hydrophilicity of the P(AN/AA) dendrigrafted with CA is related to the increasing roughness of the film by increasing step numbers.

CONCLUSIONS

The hydrophilic properties of P(AN/AA) film with 5, 10 and 20% of acrylic acid were evaluated after the formation of citric acid dendrigrafted in a heterogeneous system. The FTIR spectra confirmed the formation of intermolecular hydrogen bonding after dendrigraft formation, affecting the wettability of the films. The cleavage of hydrogen bonding after reaction with $NaHCO_3$ was also observed. The results of contact angle measurement showed a decline in contact

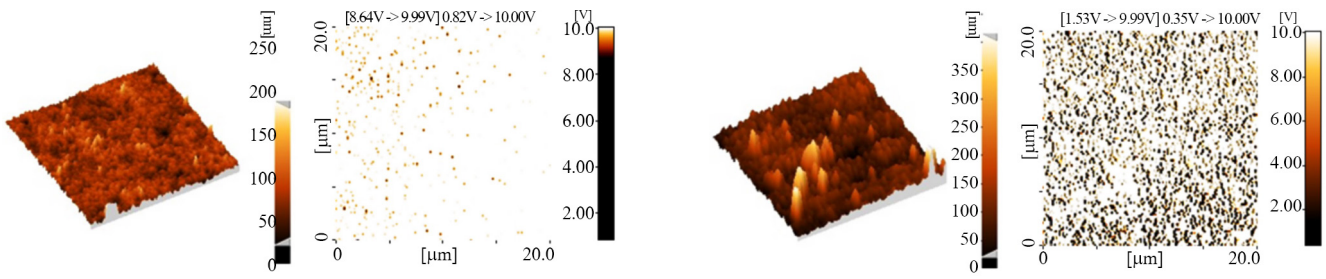

Figure 4. AFM image of P(AN/AA)film containing 10% AA: (a) G_0 and (b) G_4.

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