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Polyolefins Journal, Vol. 4, No. 2 (2017)
DOI: 10.22063/poj.2017.1436

ORIGINAL PAPER

Evaluation of hydrophilic properties of acrylonitrile/acrylic acid copolymer films dendrigrafted with citric acid

Somayeh Akbari[1*], Niloofar Eslahi[1,2], Mohammad Haghighat Kish[1]

[1]Department of Textile Engineering, Amirkabir University of Technology, Tehran, Iran
[2]Department of Textile Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

Received: 1 November 2016, Accepted: 12 February 2017

ABSTRACT

The present study investigates the hydrophilic properties of acrylonitrile/acrylic acid P(AN/AA) copolymer films with various acrylic acid (AA) contents dendrigrafted with citric acid from zero to fourth generation numbers. It was found that the hydrophilicity of the dendrigrafted films was a complicated phenomenon. Various parameters such as intermolecular hydrogen bonding, roughness and active functional groups affected the wettability of the film samples measured via static contact angle. The results revealed that the hydrophilicity decreased with increasing the generation number owing to the steric hindrance of terminal groups. However, active functional group increased by rising generation numbers which was confirmed using zeta potential measurement. Furthermore, the percentage conversion of the reactions showed a reduction with increasing generation number and AA content which was in agreement with the reduction in wettability corresponding to the higher contact angle. On the other hand, zeta potential as well as roughness of the films increased with successive generations. **Polyolefins J (2017) 4: 213-220**

Keywords: Acrylonitrile/acrylic acid copolymer; dendrigraft; wettability; contact angle; roughness.

INTRODUCTION

Acrylonitrile-based copolymers are widely used in the production of acrylic fibers having desirable characteristics, such as high chemical resistance, strong mechanical properties, high thermal stability, and low flammability [1, 2]. However, for some applications, polyacrylonitrile fibers suffer from poor hydrophilicity and low dye uptake. In order to improve surface properties, modifications of acrylic fibers have been employed by various procedures including graft polymerization and incorporation of appropriate moieties [3-5]. For instance, acidic comonomers can improve the wettability of acrylic fibers. It was shown that by increasing the number of acidic groups through the incorporation of dendritic units, the properties improved drastically [6, 7].

During the last decade, dendritic polymers including random hyperbranched polymers, dendrigrafts, dendrons and dendrimers characterized by a highly branched structure of great regularity, a compact shape, a large number of reactive end groups, and room between the branches for taking up guest molecules have attracted considerable attention [8]. Dendrimers

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[*] Corresponding Author - E-mail: akbari_s@aut.ac.ir

can be used for surface modification of polymer materials aiming to enhance the surface properties by incorporating active groups with specific structure [9-11]. Due to their highly branched and functionalized structures, globular shapes, well-defined molecular weights and sizes, monodispersity, multivalency, and relative nonpolar interior cavities [12, 13], dendritic polymers with their intriguing physical and chemical properties are distinct from the other polymer structure. However, the multi-step synthesis and slow molecular mass growth of dendrimers is often considered to be a major drawback hindering their practical applications on a large scale [14]. In contrast to dendrimers, dendrigrafted polymers grow faster and amplify the surface group more drastically [15, 16]. Dendrigraft polymers having a multi-level branched architecture are a subset of dendrimer-like compounds with linear polymers as their initial core [17, 18]. Several promising features including the ability to interaction, entrapment and release of the guest molecules have been reported for dendrigraft structures [15, 19]. For instance, low-generation poly(amido amine) (PAMAM)-grafted carbon fibers (CFs) have emerged as new reinforcements for improving the mechanical properties of fiber composites through enhancing the surface roughness and wettability of CF [20].

The use of dendritic polymers for surface modification of fibers, films and fabrics is fairly unexplored and their application is still to be optimized, particularly the dendrigraft formation on the surface. In our previous works, acrylonitrile/acrylic acid P(AN/AA) copolymers in the form of powder, film, wet spun and electrospun fibers were modified by dendrigraft formation [7, 11, 19, 21, 22]. This modification improved the characteristics of the films/fibers such as swelling/de-swelling in basic and acidic media as pH actuators, nanocarbon fiber precursors, or as active particles for loading with guest molecules [11]. The experimental results using FTIR and NMR spectroscopies confirmed the success of the recommended synthetic scheme, i.e. divergent synthetic route in a heterogeneous system. It was found that with an increase in the specific surface area, the percentage conversion increased, indicating that the topochemical reactions were prominent [21]. Besides, a decrease in the percentage conversion of the reaction was observed with increasing generation number and AA content affecting the surface properties of the copolymers [11, 19]. Thermal behaviuor of the dendrigrafted acrylic fiber was investigated, too [23]. Other parameters involved should be evaluated comprehensively to obtain the full benefits from the dendrigrafted polymers, fibers and films.

Wettability is one of the important properties of solid surfaces from both fundamental and practical aspects. It was shown that wettability is significantly affected by the surface characteristic such as chemistry, charge, hydrophilicity, topography and roughness. Among various factors, surface energy and surface roughness are the dominant factors. When the surface energy is lowered, the hydrophobicity is enhanced. The extent of wetting depends on the difference in the surface free energies of the solid, liquid, and subsequent interface [24, 25]. It is worth mentioning that hydrophobic/superhydrophobic surfaces with a very high water contact angle greater than 150° based on lotus effect are gaining ground as self-cleaning surfaces in a variety of applications because of their unique water repellency.This concept relies on the spherical droplets rolling off the surface and picking up particular dirt in their path without adhering and leaving any water droplets on the surface [26, 27]. Recently, the hydrophobicity of fluorocarbon-finished nanofibrous webs composed of electrospun poly (acrylonitrile) nanofibers was investigated from sliding angle and contact angle measurements tests [28]. Zhang et al. showed that multi-scale roughness and low energy waxes were responsible for the self-cleaning properties of bio-lotus-leaf surfaces in which the intrinsic hierarchical rough structure predominates [29].

Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact with each other; the larger the contact angle, the lower the wettability [30]. While this method has been commonly used as a criterion for the evaluation of hydrophobicity of the surface, there are a number of parameters affecting the wetting behavior including surface charge and topography. For instance, surface heterogeneity or roughness could cause variations of the contact point along the three-phase (solid-liquid-air) contact line [31]. Extensive studies have also shown that surface roughness plays a significant role in generating contact angle hysteresis [32, 33]. According to Xu et al., no self-cleaning properties were observed on a smooth hydrophobic HDPE surface, whereas the introduction of roughness enabled self-cleaning to occur, even in the presence of hydrophilic particles [34]. On the other hand, water adsorbed on the hydrophilic surfaces reduces coefficient of friction when an object slides on the hydrophobic surfaces.

Friction coefficient decreases as the contact angle increases.This is because a repulsive force is generated between water and hydrophobic surfaces owing to the surface tension of water. In fact, water droplets carry the load leading to low coefficient of friction between the surfaces, which is attributed to the low energy loss during the adhesion hysteresis process of water onto the hydrophobic surface [35].

In the present study, the hydrophilic properties of P(AN/AA) copolymer films with dendritic structure were examined and the effect of AA content and the number of generation on the wettability was evaluated with different analytical techniques such as contact angle measurement, zeta potential, FTIR and AFM. The accessibility of functional end group due to the internal hydrogen bonding was investigated by FTIR measurement. The results confirm that wettability is a complex phenomenon that is influenced by several parameters.

EXPERIMENTAL

Materials

Sodium metabisulfate, acylic acid (AA), sodium bicarbonate, citric acid (CA) and dicyclohexylcarbodiimide (DCC) were purchased from Merck, Germany. Potassium persulfate from Merck (Germany) was purified by recrystallization from methanol. The process of removing impurities by crystallization involves: dissolving potassium persulfate in hot methanol, allowing the solution to cool and become saturated with the potassium persulfate being purified, allowing it to crystallize out of methanol and isolating it by filtration.

1,4-Dioxane and tetrahydrofuran (THF) were purchased from Lab-Scan(Lisbon, Portugal), and used as received. Acrylonitrile and dimethylformamide (DMF) from Fluka were purified by distillation before use.

Synthesis of P(AN/AA) copolymers and dendrigraft formation

P(AN/AA) copolymers containing 5, 10 and 20 mol% of AA in the reaction feed were prepared by suspension polymerization using potassium persulphate and sodium metabisulphate as the redox initiator at 60±1°C for 2 h [36]. The dried P(AN/AA) powder was dissolved in DMF (10% w/v) and filtered under vacuum. These solutions were cast into a film with a nominal thickness of 350 µm, using a film-casting device (Gardner, Germany).

Dendrigraft was synthesized according to the procedure described in the previous work [7]. In brief, the carboxylic acid of P(AN/AA) copolymer films was activated with DCC in a mixture of THF and dioxane (50:50 v/v) at room temperature for 3 h. The film was then removed and washed with pure dioxane and was allowed to hang free at room temperature. Then, these activated samples were reacted with citric acid in a mixture of THF and dioxane (50:50 v/v), for 3 h at 60±1°C to produce the G_1 product. In the succeeding reaction, G_1 was used to prepare the next product which is designated by G_2. Then, the successive compounds G_3 and G_4 were prepared. The procedures for the next generations were similar to that of G_1. Any excess of CA and dicyclohexylurea (DCU) as a byproduct could be removed by simple washing and rinsing.

For hydrogen bonding cleavage, all films were treated with 1% sodium hydrogen carbonate ($NaHCO_3$) in distilled water at 60°C for 10 min.

Analytical techniques

Fourier transform infrared (FTIR) spectra of the samples were recorded between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1} using a Nicolet 670 FTIR spectrophotometer (USA). In order to quantify the relative amounts of chemical species, the peak area ratio of the characteristic peaks was divided by the height of the peak at 2243 cm^{-1} that is characteristic of the C≡N stretching mode in AN as an internal standard [7, 36].

In order to determine surface charge density of the films, zeta potential measurement was afforded by a kinetic analyzer (Anton Paar GmbH, Austria) in clamping cell with polymethyl metacrylate (PMMA) as a reference.

Surface hydrophilicity was also determined by a contact angle of water on films according to ASTM D 724-99 test method. Digital images of a water droplet (4 µl) spreading on the sample surface were recorded by a camera, and then analyzed using the software supplied by the manufacturer.

While the contact angle of water has been commonly used as a criterion for the evaluation of hydrophobicity of the surface, this alone is insufficient for evaluation of wettability. Therefore, the topography and surface roughness of the dendrigrafted films were also characterized by atomic force microscopy (AFM), Dual ScopeTM C-26 controller model- DME Company, Denmark. Average roughness (R_a) of the prepared film is calculated from the following equation:

$$R_a = \frac{1}{S_0}\iint |Z(X,)| dXdY \qquad (1)$$

where Z(X,Y) is the elevation for a given point, Z_0 is the average of the elevation within the given area, and S_0 is the projected area of the given area [25].

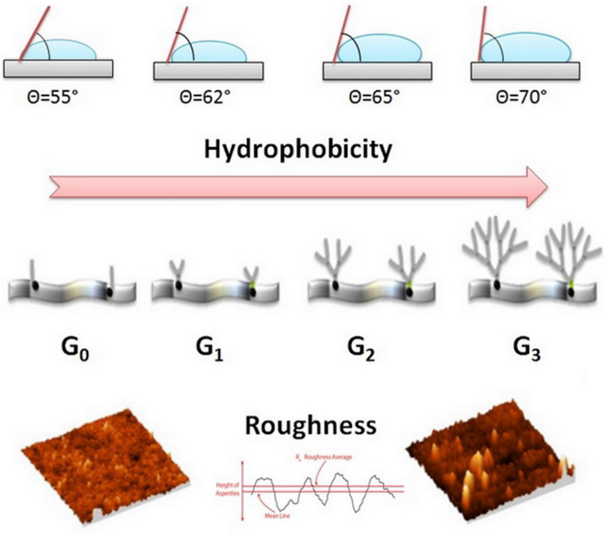
Scheme 1 represents a schematic reaction which affects the hydrophilicily of the dendrigrafted polymer.

RESULTS AND DISCUSSION

The FTIR spectra for the dendrigrafted P(AN/AA) films (G_0 and G_4) containing 20% AA are shown in Figure 1. For the G_0 sample, there are two characteristic peaks at 1727 cm^{-1} and 1645 cm^{-1} which are attributed to the C=O stretching mode of acrylic acid and the cyclization of P(AN/AA) in the DMF solvent used in the film preparation, respectively [19]. A noticeable difference is observed for steps from zero to fourth generation in the regions of 1600–1800 cm^{-1}. After reaction of copolymer with DCC and CA to produce next generations, the cyclized structures turned into nitrile groups by protonation [7]. Therefore, the peak at 1645 cm^{-1} disappears in the spectra of G_4 film. The major absorbing bands for this sample can be seen at 2879-3100, 2945, 2242, 1730 and 1465 cm^{-1} due to the stretching of the -OH, CH_2, C≡N, C=O and bending deformation of CH_2, respectively. Furthermore, the formation of a hydrogen bonding interaction between carboxylic groups on the surface during dendrigraft formation is evident from the FTIR spectra with a band at 930 cm^{-1} for G_4 which is not observed in the G_0 product [11].

After sample treatment with $NaHCO_3$ (1%), a new peak at around 1600 cm^{-1} appears indicating the formation of sodium carboxylate group resulting from interaction of carboxylic groups in dendrigrafted copolymers with sodium hydrogen carbonate. It should also be noted that the C=O stretching of carboxylic acid groups at 1730 cm^{-1} disappears which might cause a decrease in the intermolecular hydrogen bonding. Therefore, the hydrogen bonding cleavage was occurred after reaction with $NaHCO_3$. According to Wu et al. [37], the ratio of sodium carboxylate and carboxylic acid groups affected water absorption capability of poly(acrylic acid)/montmorillonite superabsorbent composite. They found that the higher absorbent ability of sodium carboxylate was due to the ionic hydrophilic and osmotic effects. Converting carboxylic acid band appeared at 1725 cm^{-1} to carboxylate band appeared at 1576 cm^{-1} after reaction with NaOH was investigated by Yang, too [38].

Chami Khazraji et al. [24] also showed that wetting may be attributed to acid-base interactions, weak hydrogen bonding, or van der Waals dispersion forces. The extent of wetting depends on the difference in surface free energies of the solid, liquid, and subsequent



Scheme 1. Schematic representation of the effect of reaction on the hydrophilicity of the dendrigratfed polymer.

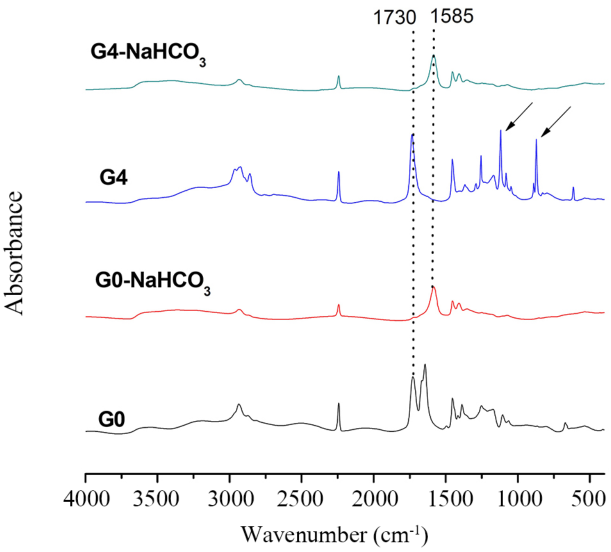


Figure 1. FTIR spectra of dendrigrafted films containing 10 % AA before and after hydrogen bonding cleavage.

interface. It is expected that the hydrophilic groups produced in different steps of the reaction affect the contact angle of water on the film. The results of contact angle measurement for different generations G_n(n=0-4) of P(AN/AA) films containing 5, 10 and 20% AA are illustrated in Figure 2. It is obvious that there is a decline in contact angle by increasing acrylic acid content for G_0 to G_3. However, for G_4, maximum hydrophilicity is observed for the film with 5% AA. Furthermore, expanding dendrigraft procedure from G_0 to G_3 gives birth to an increase in contact angle, indicating more hydrophobic surface. With increasing step number, it is expected that hydrophilicity would increase owing to the increasing amount of carboxylic acid groups. However, the opposite trend is obtained which might be attributed to the steric hindrance and intramolecular hydrogen bonding confirmed by FTIR analysis. Another probable reason for the decrease in wettability (increase in contact angle) is also proposed to be due to the low values of the percentage conversion [7].

To show the relative quantity of these groups, the theoretically expected hydrophilic group ratio (R_n) was defined as the ratio of the number of hydrophilic groups in each step (N) to the average molecular eight of the repeating units (MG_n) using the following equations:

$$MG_n = MG_{n-1} + \alpha \times b \times \times 3^{n-1} \tag{2}$$

$$N = b \times c \times R^n \tag{3}$$

$$R_n = \frac{N}{MG_n} \tag{4}$$

where is the generation number, is the molecular weight of grafted C_A unit, is the content of AA in copolymer, and is the percentage conversion in each step determined from NMR data [7]. The calculated parameters are also summarized in Table 1. The change in the molecular weight of the polymer is a crucial point in these reactions. As can be seen, the molecular weight (MG_n) increased considerably with increasing step number (n). On the other hand, there is a decreasing trend in conversion (C) by increasing generation which is in agreement with the reduction in wettability corresponding to the increase in contact angle in Figure 2. This reduction in percentage conversion can be attributed to the restricted motions and activities of the reacting groups that essentially exist in the solid phase synthesis [19]. Similarly, Janorkar et al. [39] and Walters et al. [40] suggested a modified method for achieving a higher conversion. In addition, the conversion percentage of the reactions decreases with the increase in AA content. According to de Gennes et al. [41], the reason probably arises from the congestion-induced de Gennes densed packing. With increasing acrylic acid content, the steric hindrance is increased and the percentage conversion is decreased.

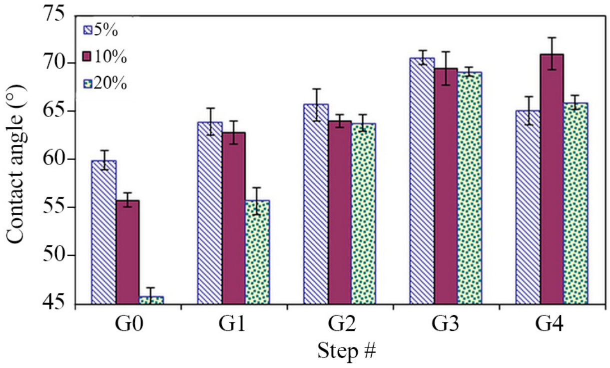


Figure 2. Contact angle of films containing 5, 10 and 20% acrylic acid from G_0 to G_4.

The zeta potential of the prepared suspensions is reported in Figure 3. The negative values of zeta potential for the synthesized films are attributed to the presence of anionic carboxylic acid groups. It is expected to have a decrease in zeta potential with higher generation due to the growing number of carboxylate groups on the surfaces through the formation of dendritic structures. However, the zeta potential increases with successive generations from G_0 to G_4. With the increase in the molecular weight of dendrigrafted films

Table 1. Comparison of the ratio of hydrophilic sites for dendrigrafted P(AN/AA) films from G_0 to G_4.

n	5 % AA				10 % AA				20 % AA			
	MG_n	N	L	R_n	MG_n	N	L	R_n	MG_n	N	L	R_n
0	54.16	0.06	-	$10^{-}\times1.13$	54.80	0.09	-	$10^{-}\times1.72$	55.91	0.15	-	$10^{-3}\times2.74$
1	67.37	0.11	60.69	$10^{-}\times1.65$	64.85	0.14	51.61	$10^{-}\times2.26$	66.10	0.14	32.33	$10^{-3}\times2.24$
2	75.24	0.11	20.78	1.51	75.98	0.16	19.08	2.13	75.24	0.13	9.67	1.77
3	82.20	0.10	6.13	1.23	79.95	0.06	2.26	0.73	92.45	0.25	6.07	2.72
4	98.98	0.20	3.98	1.99	90.10	0.15	1.93	1.64	126.30	0.56	4.49	4.41

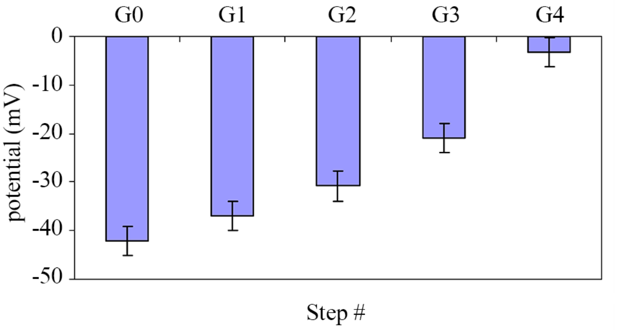


Figure 3. Increasing zeta potential of synthesized film containing 10% AA from G_0 to G_4.

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

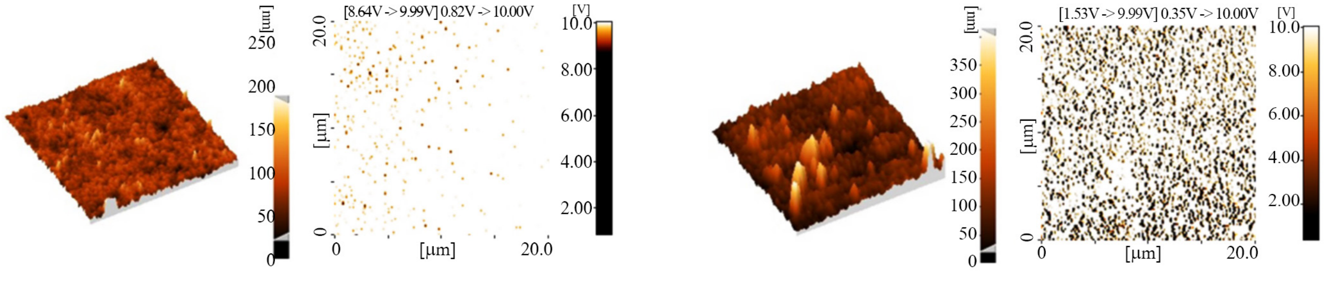


Figure 4. AFM image of P(AN/AA)film containing 10% AA: (a) G_0 and (b) G_4.

angle by increasing AA content. However, there was a reduction in wettability with increasing the generation number owing to the steric hindrance of terminal groups, resulting in the low values of the percentage conversion of the reaction of dendrigraft formation on the surface. In fact, the decreasing trend of conversion with increasing generation number was a major obstacle in the way of increasing the number of functional groups. Furthermore, the zeta potential increased with successive generations from G_0 to G_4, validating the formation of dense shell dendritic structure. Another important factor affecting the hydrophilicity was also related to the increasing roughness of the film with step number from 13 to 31 nm. The results confirm that wettability is a complex phenomenon that is influenced by several parameters.

REFERENCES

1. Sen K, Bahrami SH, Bajaj P (1996) High-performance acrylic fibers. J Macromol Sci Poylm Rev 36: 1-76
2. Abdouss M, Mousavi Shoushtari A, Majidi Simakani A, Akbari S, Haji A (2013) Citric acid-modified acrylic micro and nanofibers for removal of heavy metal ions from aqueous media. Desalin Water Treat 52: 7133-7142
3. Jia Z, Du S, Tian G (2007) Surface modification of acrylic fiber by grafting of casein. J Macromol Sci Pure 44: 299-304
4. Matama T, VazF, Gubitz GM, Cavaco-Paulo A (2006) The effect of additives and mechanical agitation in surface modification of acrylic fibres by cutinase and esterase. Biotechnol J 1: 842-9
5. Abdolahifard M, Bahrami SH, Malek RMA (2011) Surface modification of PET fabric by graft copolymerization with acrylic acid and its antibacterial properties. ISRN Org Chem 2011: 1-8
6. Bajaj P, Sreekumar T, Sen K (2001) Effect of reaction medium on radical copolymerization of acrylonitrile with vinyl acids. J Appl Polym Sci 79: 1640-1652
7. Akbari S, Kish MH, Entezami AA (2008) Copolymer of acrylonitrile/acrylic acid solid surface film dendrigrafted with citric acid. Polym Int 57: 846-853
8. Akbari S (2013) The application of dendritic materialin textile engineering. Sci Bull Escorena 7: 11-28
9. Klaykruayat B, Siralertmukul K, Srikulkit K (2010) Chemical modification of chitosan with cationic hyperbranched dendritic polyamidoamine and its antimicrobial activity on cotton fabric. Carbohyd Polym 80: 197-207
10. Bashar MM, Khan MA (2013) An overview on surface modification of cotton fiber for apparel use. J Polym Environ 21: 181-190
11. Barzegar RR, Akbari S, Kish MH (2013) Dendrigraft with citric acidon acrylonitrile/acrylic acid copolymer electrospun fibres. Polym Int 62: 1767-1776
12. Caminade A-M, Laurent R, Majoral J-P (2005) Characterization of dendrimers. Adv Drug Deliv Rev 57: 2130-2146
13. Kresge C, Leonowicz M, Roth W (2001) Dendrimers and dendrons. Concepts, Syntheses, Applications. VCH: Weinheim.
14. Voit B (2000) New developments in hyperbranched polymers. J Polym Sci Pol Chem 38: 2505-2525
15. Njikang GN, Gauthier M, Li J (2008) Sustained release properties of arborescent polystyrene-graft-poly (2-vinylpyridine) copolymers. Polymer 49: 5474-5481
16. Gauthier M, Moeller M (1991) Uniform highly branched polymers by anionic grafting: Arborescent graft polymers. Macromolecules 24: 4548-4553
17. Gauthier M (2007) Arborescent polymers and other dendrigraft polymers: A journey into structural diversity. J Polym Sci Pol Chem 45: 3803-3810
18. Teertstra SJ, Gauthier M (2004) Dendrigraft polymers: Macromolecular engineering on a mesoscopic scale. Prog Polym Sci 29: 277-327
19. Akbari S, Kish MH, Entezami AA (2011) Copolymer of acrylonitrile/acrylic acid film dendrigrafted with citric acid: Host/guest properties of dendrigraft/dye complexes in relation to acrylic acid content. Iran Polym J 20: 539-549
20. Gao B, Du W, Ma Q, Zhang R, Wang C, Zhang J (2016) Effects of grafting low-generation poly (amido amine) onto carbon fiber surface by in situ polymerization on the mechanical properties of fiber composites. High Perform Polym: https://doi.org/10.1177/0954008316658534

21. Akbari S, Kish MH, Entezami AA (2010) Modification of acrylonitrile/acrylic acid copolymer films and fibers by dendrigraft formation. Polym Int 59: 1550-1557
22. Abdouss M, Mousavi Shoushtari A, Majidi Simakani A, Akbari S, Haji A (2014) Citric acid-modified acrylic micro and nanofibers for removal of heavy metal ions from aqueous media. Desalin Water Treat 52: 7133-7142
23. Akbari S (2016) Thermal analysis of acrylonitrile/acrylic acid copolymer dendrigrafted with citric acid. J Text Polym 4: 27-36
24. Chami Khazraji A, Robert S (2013) Self-assembly and intermolecular forces when cellulose and water interact using molecular modeling. J Nanomater 2013: 10.1155/2013/745979
25. Miwa M, Nakajima A, Fujishima A, Hashimoto K, Watanabe T (2000) Effects of the surface roughness on sliding angles of water droplets on superhydrophobic surfaces. Langmuir 16: 5754-5760
26. Fürstner R, Barthlott W, Neinhuis C, Walzel P (2005) Wetting and self-cleaning properties of artificial superhydrophobic surfaces. Langmuir 21: 956-961
27. Li S, Huang J, Ge M, Cao C, Deng S, Zhang S, Chen G, Zhang K, Al-Deyab SS, Lai Y (2015) Self-cleaning cotton: Robust flower-like TiO_2@cotton fabrics with special wettability for effective self-cleaning and versatile oil/water separation (Adv. Mater. Interfaces 14/2015). Adv Mater Interfaces 2: 10.1002/admi.201570068
28. Sadeghi P, Tavanai H, Khoddami A (2017) Hydrophobicity of fluorocarbon-finished electrospun poly (acrylonitrile) nanofibrous webs. J Text Inst 108: 189-195
29. Zhang M, Feng S, Wang L, Zheng Y Lotus effect in wetting and self-cleaning. Biotribology 5: 31-43
30. Yuan Y, Lee TR (2013) Contact angle and wetting properties. In: Surface science techniques. Bracco G, Holst B (Eds), Springer, 3-34
31. Kubiak K, Wilson M, Mathia T, Carval P (2011) Wettability versus roughness of engineering surfaces. Wear 271: 523-528
32. Krumpfer JW, McCarthy TJ (2010) Contact angle hysteresis: A different view and a trivial recipe for low hysteresis hydrophobic surfaces. Faraday Discuss 146: 103-111
33. Gao L,McCarthy TJ (2006) Contact angle hysteresis explained. Langmuir 22: 6234-6237
34. Xu QF, Liu Y, Lin F-J, Mondal B, Lyons AM (2013) Superhydrophobic TiO_2–polymer nanocomposite surface with UV-induced reversible wettability and self-cleaning properties. ACS Appl Mater Interfac 5: 8915-8924
35. Pawlak Z, Urbaniak W, Oloyede A (2011) The relationship between friction and wettability in aqueous environment. Wear 271: 1745-1749
36. Bajaj P, Paliwal D, Gupta A (1993) Acrylonitrile–acrylic acids copolymers. I. Synthesis and characterization. J Appl Polym Sci 49: 823-833
37. Wu J, Lin J, Li G, Wei C (2001) Influence of the COOH and COONa groups and crosslink density of poly(acrylic acid)/montmorillonite superabsorbent composite on water absorbency. Polym Int 50: 1050-1053
38. Yang CQ (1991) Characterizing ester crosslinkages in cotton cellulose with FT-IR photoacoustic spectroscopy 1. Text Res J 61: 298-305
39. Janorkar AV, Luo N, Hirt DE (2004) Surface modification of an ethylene-acrylic acid copolymer film: Grafting amine-terminated linear and branched architectures. Langmuir 20: 7151-7158
40. Walters KB, Hirt DE (2007) Synthesis and characterization of a tertiary amine polymer series from surface-grafted poly (tert-butyl acrylate) via diamine reactions. Macromolecules 40: 4829-4838
41. de Gennes P-G, Hervet H (1983) Statistics of "starburst" polymers. J Phys Let 44: 351-360
42. Zhang J, Han Y (2008) A topography/chemical composition gradient polystyrene surface: Toward the investigation of the relationship between surface wettability and surface structure and chemical composition. Langmuir 24: 796-801
43. Wenzel RN (1949) Surface roughness and contact angle. J Phys Chem 53: 1466-1467
44. Tsai P-S, Yang Y-M, Lee Y-L (2006) Fabrication of hydrophobic surfaces by coupling of Langmuir-Blodgett deposition and a self-assembled monolayer. Langmuir 22: 5660-5665