Vol. 13 № 4 Trans. Nonferrous Met. Soc. China Aug. 2003

Article ID: 1003 - 6326(2003)04 - 0988 - 06

Measurement of surface crystallinity of PAA and PAANa coatings and its effect on hydrophilicity of coatings①

PAN Chun-yue(潘春跃)[1], LIU Qing-quan(刘清泉)[1], XU Xian-hua(徐先华)[1], CHEN Zhen-hua(陈振华)[2]
(1. School of Chemistry and Chemical Engineering,
Central South University, Changsha 410083, China;
2. School of Materials Science and Engineering, Hunan University, Changsha 410082, China)

Abstract: The solutions of poly(acrylic acid)(PAA), poly(acrylic acid sodium)(PAANa) were coated on aluminium fins by roll coating method. The coatings with different crystallinity were obtained by varying baking time and temperature. Their surface crystallinity and surface tension were measured, and their spreading speed constant and equilibrium contact angle were tested also. The correlation of surface crystallinity, surface tension, spreading speed constant and surface hydrophilicity was discussed. It is demonstrated that surface tension and spreading speed constant increase, while equilibrium contact angle declines with increasing surface crystallinity of coatings, that is to say, the hydrophilicity of coatings is improved with surface crystallinity of coatings increasing.

Key words: PAA; PAANa; surface crystallinity; surface tension; hydrophilicity; spreading speed constant

CLC number: O 793 **Document code:** A

1 INTRODUCTION

As an important water-soluble macromolecule compound, poly (acrylic acid) (PAA) and its salts have been widely used [1]. Utilizing its fine film-forming capacity and hydrophilicity, Okoroafor et al[2], and Pan et al[3] developed a new hydrophilic paint for aluminium fin[2,3]. Hydrophilic paint for heat-exchanger of air conditioning demands little surface contact angle, so that continuous homogeneous water film can form easily, and can drain off condensed water on the surface of fin timely[4-6]. Hydrophilicity of coatings is affected by various factors such as the kinds of hydrophilic groups, concentration and distribution of hydrophilic groups, structure of coatings. Reports on this subject are rare at present time. Since components of hydrophilic paint and their structures are very complex in practice, PAA and PAANa coatings were used as researching objects so as to simplify the problem, and the relation between their surface structure and surface hydrophilicity is then studied in this paper.

2 EXPERIMENTAL

2.1 Synthesis of PAA and PAANa

Acrylic acid monomer, water, and ammonium persulfate(APS) were added into a 250 mL flask. The mixture was reacted at 80 ℃ for 3 h and PAA solution was then obtained. PAANa solution was obtained by neutralizing PAA solution with NaOH solution(2 mol/L) until pH = 7 - 8.

2.2 Preparation of samples of coatings

PAA and PAANa solutions (11%) were coated by roll coatings on aluminium fins (0.2 mm) which were degreased with degreasing agent and washed with distilled water. The samples of coatings were obtained by drying aluminium fins at different temperatures and times in blast oven. The coatings thickness was about 1 g/m^2.

2.3 Measurement of surface tension and surface crystallinity

The contact angles for distilled water and glycerine on the coatings were measured at room temperature using a contact angle tester (JLC), with a droplet technique. Water and glycerin were dropped about 10 cm above coatings and the contact angles were recorded within 30 s. The surface tension of coatings was calculated according to the method in Ref. [7].

X-ray diffraction analysis of the samples was carried out with a Japanese D/Max-313 diffractometer, using CuK$_\alpha$ radiation and with a Ni filter. The samples were scanned from $2\theta = 10°$ to $35°$ and the scanning speed was 2(°)/min.

3 RESULTS AND DISCUSSION

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① **Received date:** 2002 - 06 - 10; **Accepted date:** 2002 - 11 - 06

Correspondence: PAN Chun-yue, Professor; Tel: + 86-731-8879616; E-mail: panchunyue@sina.com

3.1 Preparation of coating samples with different surface crystallinity

The surface crystallization process of polymer coatings is influenced by various factors. But there are no deep-going studies on the subject how to control surface crystallization process of polymer coatings and how to prepare samples with different surface crystallinity. In this experiment, it was found that coatings baked at different temperatures and times exhibited obviously different surface property. It was inferred that the crystallinity of coatings was different by varying thermal treating conditions. PAA and PAANa coating samples were prepared according to the thermal treating conditions provided by Table 1. The surface crystallinity of coatings was measured by X-ray diffraction. It is demonstrated that there is great difference in surface crystallinity of coatings prepared under different thermal treating conditions.

Table 1 Thermal treating conditions of PAA and PAANa coatings

Sample No	Temperature/ ℃	Time/ s
1	100	240
2	180	120
3	250	20

The crystallinity of polymer is influenced by several major factors such as chemical structure of macromolecular chain, temperature and time of crystallization, tensile stress, nucleating agent. In the experiment, the aqueous solutions of PAA, PAANa were used and there was no difference in symmetry and stereoregularity of macromolecular chain; the coatings were prepared by rolling process in the same conditions and there was no nucleating agent in the polymer solution. Hence, the surface crystallinity of PAA and PAANa coatings were influenced only by temperature and time of crystallization. The polymer molecules should have sufficient motion to allow them line up in an order so as to form three-dimensional regular aggregating structure. Segmental motion is frozen at lower temperature, on the contrary it is too violent at higher temperature, both of them are not favorable to crystallization. To improve the crystallinity of coatings, an appropriate temperature and time should be determined.

3.2 Measurement of surface crystallinity of coatings

The XRD patterns of PAA and PAANa coating samples are showed in Fig. 1 and Fig. 2.

According to standard XRD graph of aluminium, the first diffraction peak is located at $2\theta = 38.473°$. The scanning angle was determined between 10° and 35° so as to eliminate the aluminium interference on diffraction peak of coatings. As shown in Fig. 1 and Fig. 2, it can be found that a strong diffraction peak for each sample is located at $2\theta = 17°$ and other diffraction peaks are very weak. Hence, the scanning angle sector 2θ of 15°–19° was selected as the spectrum for calculating crystallinity of coatings. Based on the X-ray diffraction intensity and double-phase model conception of polymer, the diffraction integrated intensity of crystalline peak (I_c) and amorphous halo (I_a) should be determined for calculating surface crystallinity of coatings. In this experiment, a manual resolution method was conducted to separate the crystalline peak and the amorphous halo. Fig. 3 shows the representative resolution curves of X-ray diffraction graph, and the other resolution curves of X-ray diffraction graph are similar to Fig. 3. Areas of the crystalline peak and the amorphous halo were calculated by gravimetric method to obtain diffraction integrated intensity of them, respectively. The results are listed in Table 2.

Because only one crystalline peak is used for calculating crystallinity, the formula of calculating crystallinity should be given as[8]

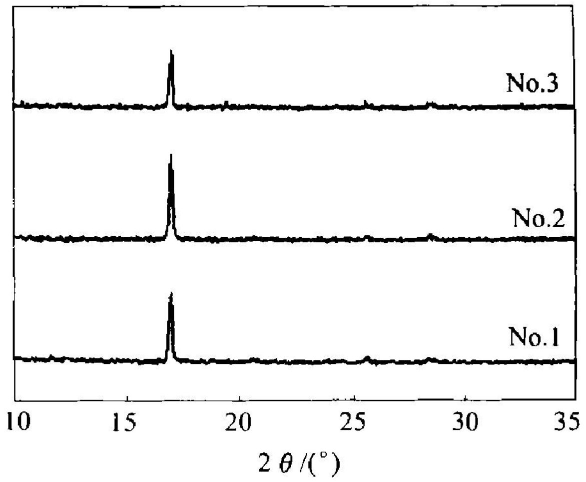

Fig. 1 XRD patterns of PAA coating samples

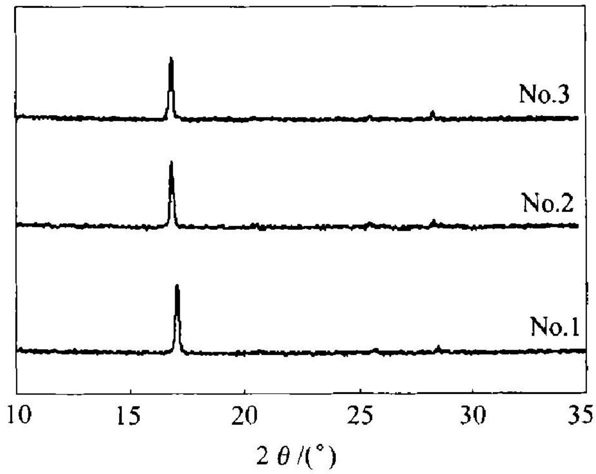

Fig. 2 XRD patterns of PAANa coating samples

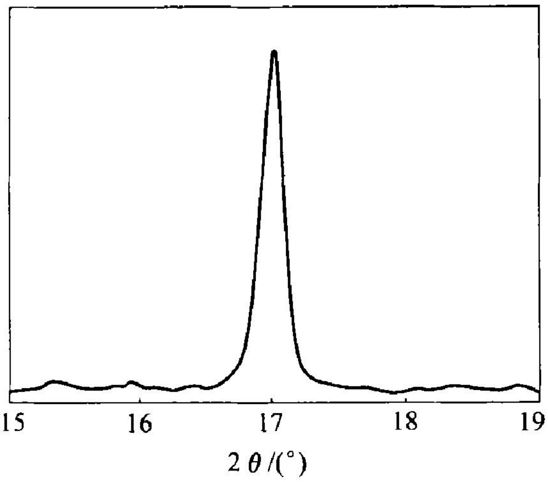

Fig. 3 Graph of resolving crystalline peak and amorphous halo

Table 2 Diffraction integrated intensity of PAA and PAANa coatings

Intensity	PAA coating			PAANa coating		
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3
I_c	50.98	64.26	44.97	49.34	38.94	37.07
I_a	25.49	35.92	31.05	24.04	23.48	26.13

$$X_c = C(\theta) I_c / [C(\theta) I_c + C_a(\theta) K I_a] \times 100\% \quad (1)$$

where I_c, I_a are diffraction integrated intensities of crystalline and amorphous moieties of sample, respectively; K is relative scattering coefficient of crystalline and amorphous moieties of per quality unit of sample, and is also defined as correction coefficient; $C(\theta)$ is correction factor of diffraction peak, including amorphous halo $C_a(\theta)$, adjusted by atomic scattering factors, angle factors and temperature factors. According to the theory of XRD,

$$1/C(\theta) = f^2 \times L \times T \quad (2)$$

where f^2 is scattering factor of all the atoms per repeating unit, and defined as $f^2 = \sum_i N_i f_i^2$, where N_i is the number of atom i per repeating unit. For example, all atom scattering factors for PAA are $f^2 = 3f_C^2 + 4f_H^2 + 2f_O^2$. The analytic expression of atom scattering factor is given by[9]

$$f_i(\sin\theta/\lambda) = \sum_{j=1}^{4} a_j \exp[-b_j(\sin\theta/\lambda)^2] + C \quad (3)$$

In Eqn. (3), the values of a_j, b_j and C are also given in Ref. [9] and θ is Bragg angle. Angle factors and temperature factors are $L = (1 + \cos^2 2\theta)/\sin^2\theta\cos\theta$ and $T = \exp[-2B(\sin\theta/\lambda)^2]$, respectively; and $2B = 10$[10]. Finally, the correction coefficient K is calculated as[11]

$$K = I_c / \sum_i I_{ic} \quad (4)$$

where I_c and $\sum_i I_{ic}$ are diffraction integrated intensity of the calculated crystalline peak and diffraction integrated intensity of all crystalline peaks which can be observed in XRD graph, respectively. Correction factors and crystallinity of coatings were calculated according to the above equations, as shown in Table 3 and Table 4.

Table 3 Calculation of correction factors and crystallinity of PAA coatings

Sample No		2θ/(°)	sin θ/λ	L	T	f^2	$C(\theta)$	K	$KC(\theta)$	X_c/%
1	C	17.23	0.097 23	86.20	0.909 8	206.06	1.039	0.96	0.997 4	66.72
	A	16.99	0.095 89	88.71	0.912 2	207.52	1.000			
2	C	17.02	0.096 05	88.39	0.911 9	207.36	1.000	0.96	0.923 6	64.20
	A	16.84	0.095 05	90.34	0.913 6	208.45	0.971 5			
3	C	17.13	0.096 67	87.23	0.910 8	206.66	1.000	0.96	0.916 1	61.25
	A	16.84	0.095 05	90.34	0.913 6	208.45	0.954 3			

Table 4 Calculation of correction factors and crystallinity of PAANa coatings

Sample No		2θ/(°)	sin θ/λ	L	T	f^2	$C(\theta)$	K	$KC(\theta)$	X_c/%
1	C	17.07	0.096 33	87.89	0.911 4	298.02	1.000	0.96	0.929 1	68.84
	A	16.86	0.095 16	90.13	0.913 4	299.66	0.967 8			
2	C	17.01	0.097 17	88.51	0.909 9	298.06	1.000	0.96	0.910 6	64.56
	A	16.72	0.094 38	91.66	0.914 8	300.70	0.948 6			
3	C	17.08	0.096 39	87.77	0.911 3	298.06	1.000	0.96	1.017 1	58.24
	A	17.45	0.098 47	83.98	0.907 6	295.45	1.059			

From Table 3 and Table 4, it can be seen that the surface crystallinities of PAA and PAANa coatings decrease with thermal treating temperature increasing. This indicates that motion of macromolecular chain is violent at higher temperature, and the conditions are unfavorable for forming three-dimensional regular aggregating structure. But there is no distinct difference in surface crystallinity between PAA and PAANa coatings.

3.3 Surface tension of coatings

According to the equation provided by Ref. [7]:

$$\cos\theta = \frac{2}{r_L}[(r_L^d r_S^d)^{1/2} + (r_L^p r_S^p)^{1/2}] - 1 \qquad (5)$$

where r_L is the surface tension of liquid; r_L^p, r_L^d are the polar and dispersive fraction of liquid surface tension; and r_S^d, r_S^p are the polar and dispersive fraction of solid surface tension, respectively. According to Eqn. (5), the polar and dispersive fraction of surface tension of coatings can be obtained by measuring contact angles of two reference liquids on coatings surface, so water and glycerin were used as two reference liquids by the authors. The pertinent parameters of reference liquids are then given by Ref. [7]. Finally, the sum (r_S) of r_S^d and r_S^p is the surface tension of coatings. The results are listed in Table 5.

Table 5 Contact angles and surface tensions of PAA and PAANa coatings

Sample		Contact angle/(°)		Surface tension/(10^3Nm^{-1})		
		Water	Glycerine	r_S^d	r_S^p	r_S
	No. 1	33	30	19.0	42.4	61.4
PAA	No. 2	43	39	18.4	36.3	54.7
	No. 3	63	46	34.9	12.6	47.5
	No. 1	13	50	0.017	99.54	99.56
PAANa	No. 2	19	50	0.169	95.8	93.25
	No. 3	27	51	0.605	83.4	83.97

As already mentioned above, it is known that there is no distinct difference in crystallinity of PAA and PAANa coatings. Nevertheless, it can be seen that the surface tension of PAANa coatings is obviously greater than that of PAA coatings from Table 5, which can be explained by strong polarity on PAANa coatings surface because of existence of sodium ion. This testifies that surface tension of coatings is firstly determined by its chemical constitution, in this case, the polarity of coatings plays a leading role in its surface tension. As for the same constitute coatings, such as PAA coatings, the surface tension increases with increasing surface crystallinity of coatings. This indicates that the surface crystallinity plays a leading role in surface tension of coatings in this case.

Meanwhile, Table 5 shows that the contact angle of water on PAA coatings is greater than that on PAANa coatings, and so is the surface tension. As for the same constitution coatings, the contact angle of water decreases with surface tension increasing, that is to say, the hydrophilicity of coatings is improved. This demonstrates that the surface tension has an important effect on the hydrophilicity of coatings.

We hope that the contact angle of water on the hydrophilic paint can decline as much as possible in practice. The above mentioned results show that when the surface constitution of coatings is identical, the higher surface crystallinity is beneficial to increasing the surface tension and improving the hydrophilicity of coatings. Hence, in thermal treating technology, it is necessary to optimize the thermal treating conditions so as to improve the hydrophilicity of hydrophilic paint as much as possible.

3.4 Spreading process of water on coatings surface

In order to improve the hydrophilicity of hydrophilic paint, it is really important to research spreading process of water on coatings surface. Initial contact angle of water, spreading speed and equilibrium contact angle on the coatings surface are all determined by interactions between water and coatings surface. It is demonstrated that the contact angle of water on the PAA and PAANa coatings surface decreases with time increasing. Two plots of contact angle versus time are given in Fig. 4 and Fig. 5.

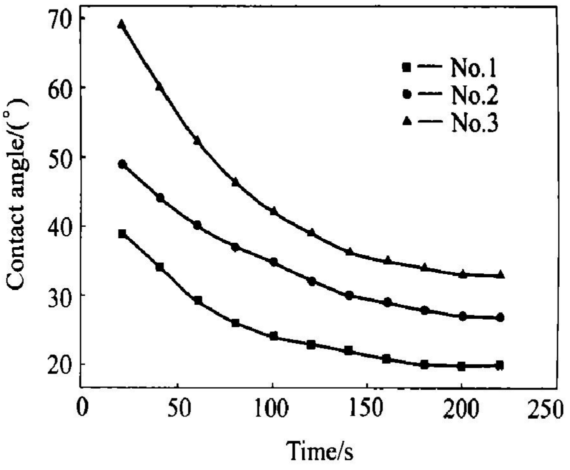

Fig. 4 Plots of contact angle on PAA coatings vs time

The relationship between contact angle(θ) and time(t) is given by the following equation[7]:

$$\cos\theta_t = \cos\theta_\infty[1 - a e^{-ct}] \qquad (6)$$

where θ_t is the contact angle at time t; θ_∞ is the contact angle in infinite time; a and c are constant and the spreading speed constant respectively. Eqn. (6) can be converted into the following expression:

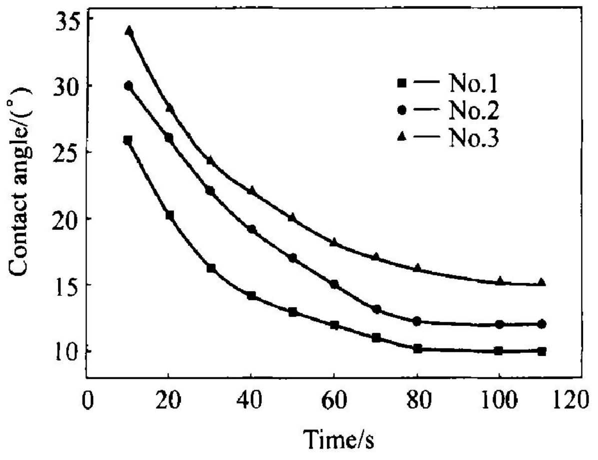

Fig. 5 Plots of contact angle on PAANa coatings vs time

$$\ln(1-\cos\theta_t/\cos\theta_\infty) = -ct + \ln a \qquad (7)$$

Two plots of $\ln(1-\cos\theta/\cos\theta_\infty)$ versus t are illustrated in Fig. 6 and Fig. 7. The spreading speed constant c, deduced from the slope of the obtained curves, is reported in Table 6.

The spreading speed constant and equilibrium contact angle are two important parameters reflecting hydrophilicity of coatings. As can be seen in Table 6, the spreading speed constant of water on PAANa coatings is greater and the equilibrium constant angle is smaller compared to PAA coatings. This indicates that water is easy to spread on the PAANa coatings because of its higher surface tension. As for the same constitution coatings, the spreading speed constants increase and the equilibrium contact angles decline with the surface crystallinity increasing.

Table 6 Spreading speed constant c of PAA and PAANa coatings

Parameter	PAA coating			PAANa coating		
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3
c/s^{-1}	0.023 3	0.020 7	0.019 1	0.059 7	0.051 8	0.039 6
Equilibrium contact angle/(°)	20	27	33	10	12	15

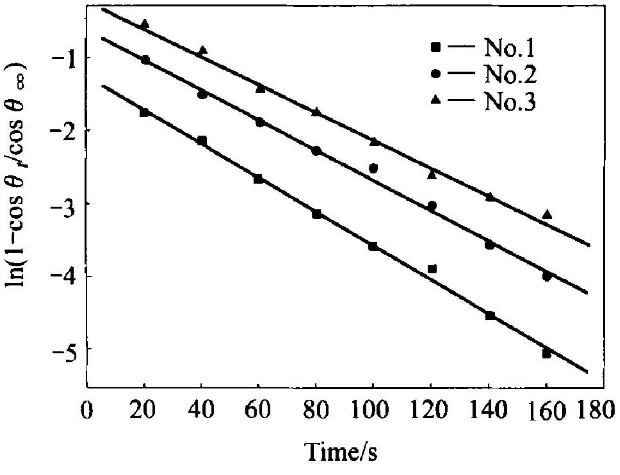

Fig. 6 Kinetics of water spreading on PAA coatings

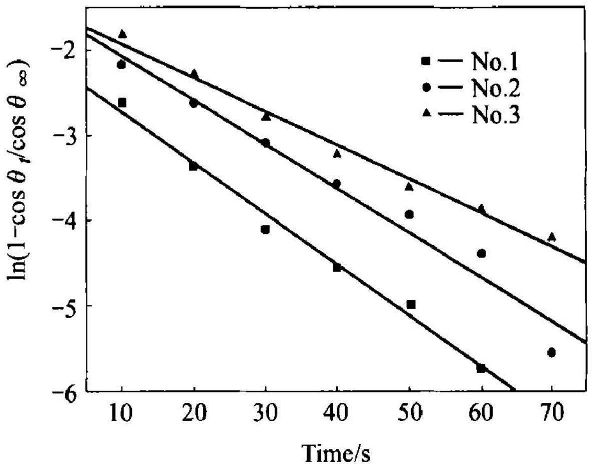

Fig. 7 Kinetics of water spreading on PAANa coatings

4 CONCLUSIONS

1) When the chemical constitution of coatings is different, such as PAA and PAANa coatings, the surface tension is obviously different in spite of no distinct difference in their crystallinity, because there is strong polarity on PAANa coatings surface due to the existence of sodium ion. This demonstrates that the surface tension of coatings is firstly determined by its chemical constitution, in this case, the polarity of coatings plays a leading role in its surface tension.

2) When the chemical constitution of coatings is identical, such as PAA coatings, the surface crystallinity decreases with thermal treating temperature increasing, leading to surface tension declining. Hence, this shows that the surface crystallinity has an important effect on surface tension in this case.

3) The surface tension and spreading speed constant increase, and equilibrium contact angle declines with the surface crystallinity of coatings increasing, that is to say, the hydrophilicity of coatings is improved with the surface crystallinity of coatings increasing.

ACKNOWLEDGEMENT

The authors would like to thank the support of Huabei Aluminium Corporation, Ltd.

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(Edited by YUAN Sai-qian)