

# Preparation of Amphiphilic Acrylic Acid Copolymer and Its Application in Humidity-Sensitive Coatings

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**ABSTRACT:** A new kind of water-dispersed resin, amphiphilic acrylic acid copolymer resin was prepared by hydrophilic monomer, hydrophobic monomer, and functional monomer (diacetone acrylamide). The effect of acid value and diacetone acrylamide concentration on water solubility was investigated. It showed that the acid value should be greater than 100 mg KOH/g. The coating properties of the amphiphilic acrylic acid copolymer resin and its film were measured, which showed excellent properties in hardness, gloss, and water resistance. It was applied to prepare the humidity-sensitive coatings. The water absorption of humidity-sensitive coatings was

260%. It could increase indoor humidity or dehumidify in dry or moist environment. On the basis of scanning electron microscopy images, the mechanism of humidity-sensitive activity was also discussed. The humidity-sensitive exhibited humidity sensitivity and excellent humidity retention because fillers of porous structure combined with amphiphilic copolymer. It could be widely applied in indoor coating for controlling humidity. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3109–3117, 2011

**Key words:** amphiphilic resins; copolymerization; humidity-sensitive coatings; dehumidification

## INTRODUCTION

Indoor humidity is an important parameter to determine the occupants' perception of indoor air quality, and is also an important parameter as a cause of harmful processes that may occur on surfaces of materials, such as microbial growth. Thus, it is known that humidity has an impact on both the working efficiency and health of occupants. Moreover, the indoor humidity exhibits significant daily or seasonal variation. Materials that absorb and release moisture can be used positively to reduce the extreme values of humidity levels in indoor climates.<sup>1</sup>

The humidity-controlling materials had been studied for moisture absorption or humidity controlling.<sup>2–9</sup> The humidity-controlling materials could be prepared through composition of calcium carbonate and amorphous silica,<sup>10</sup> or zeolite powder.<sup>11</sup> The organic polymer humidity-controlling materials

contain high capacity of humidity controlling, which are used in textile industry generally.<sup>12</sup> Composite humidity-controlling materials were prepared with the mixture of different types of humidity-controlling materials and other auxiliary materials.<sup>13–16</sup>

The humidity-controlling coatings are one of the humidity-controlling materials and are different from the conventional coatings. They must have strong absorption and good water retention, which means faster response for water. They could be coated on surface to form a protective, decorative, and humidity-controlling coating. The humidity-controlling coatings are composed of the binder, porous or more layers of filler, pigment, and function additives, and could be coated on materials surface to form coating. Their humidity-controlling function, mechanism, and main raw materials are similar with the humidity-controlling materials,<sup>17</sup> whereas the method of preparation, product form, application range, construction technologies, and comprehensive properties are not the same.

In this article, a new kind of water-dispersed resin, amphiphilic acrylic acid (AA) copolymer (WDR-PAA) was prepared by hydrophilic monomers, hydrophobic monomers, and functional monomers. The effect of acid value ( $A_v$ ) and diacetone acrylamide (DAAM) concentration on water solubility was investigated. The humidity-sensitive coatings were prepared by WDR-PAA, pigments, and fillers. By measuring their basic properties, the water absorption

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**TABLE I**  
**Recipe for the Humidity-Sensitive Coatings**

Ingredient	Amount (g)
Amphiphilic acrylic acid copolymer resin	4.0
Titanium dioxide	1.5
Talc	1.0
Montmorillonite	0.5
Kaolin	0.5
Bentonite	0.5
Diatomite(CD02)	4.5
Diatomite(CD05)	2.5
Natural crystalline calcium carbonate	0.5
Precipitated calcium carbonate	0.5
Deionized water	12.0

and humidity-controlling properties of the humidity-sensitive coatings were also investigated.

## EXPERIMENTAL

### Materials

AA (Shandong Qilu Petrochemical Kaitai Industry Co.) was treated immediately before use to remove most of the inhibitor by standing over silica gel for 30 min. Methyl methacrylate (MMA) (CNPC), butyl acrylate (BA) (Shandong Qilu Petrochemical Kaitai Industry Co.), hydroxyl propyl methacrylate (HPMA) (Wuxi Yangshi Sanlian Chemicals Co.), respectively, were washed with 10% sodium hydroxide solution to remove inhibitors and then washed with deionized water to remove the residual base. The washed monomers were dried over calcium chloride. All the purified monomers were stored at  $-2^{\circ}\text{C}$  until used. Acrylamide (AM) (Tianjin Kaitong Chemicals Co.), DAAM (Wuxi Liangxi Fine Chemicals Co.), adipic hydrazide (ADH) (Wuxi Liangxi Fine Chemicals Co.), ethylene glycol monobutyl ether (Lanzhou Shuangshuang Chemicals Co.), isopropyl alcohol (Tianjin Guangfu Fine Chemical Research Institute) were of chemical pure and used as received without further purification. Azo-bisisobutyronitrile (AIBN) (Lanzhou Shuangshuang Chemicals Co.) was recrystallized in methanol before use. Titanium dioxide, talc, montmorillonite, kaolin, bentonite, diatomite (CD02), diatomite (CD05) were purchased from Guangzhou Tiantai chemical & Light Industry Co. Natural crystalline calcium carbonate and precipitated calcium carbonate were obtained from Shanghai Shuangda chemicals Co. All of fillers were industrial grade.

### Preparation of WDR-PAA

Ethylene glycol monobutyl ether, isopropyl alcohol, and one half of AIBN were added to a four-necked flask equipped with a thermometer, a condenser, a mechanical stirrer, dropping funnels, and a nitrogen inlet. The mixture of monomers consisting of AA,

MMA, BA, HPMA, AM, and DAAM was added to the system at  $80^{\circ}\text{C}$  over a period of 2–3 h. Then, the rest of AIBN was added twice at intervals of 0.5 h. Then, the mixture was allowed to react for further 2 h. The viscosity and conversion rate were measured during the process. When they reached the standard, the resin was cooled to  $50^{\circ}\text{C}$ . The unreacted monomer and solvent were removed by vacuum distillation. The target pH value was adjusted by adding predetermined amounts of 25%  $\text{NH}_3\cdot\text{H}_2\text{O}$  to the resin. The WDR was obtained.

### Preparation of humidity-sensitive coatings

The humidity-sensitive coatings were prepared by the amphiphilic AA copolymer resin (WDR-PAA), pigments, fillers, and assistants such as wetting agent CF-01, fungicide YN188, dispersant agent DA-01, and defoamer agent 3016. A typical recipe used to prepare humidity-sensitive coatings is shown in Table I. First, the pigments, fillers, and coating assistants were dispersed in water with stirring. Then, the amphiphilic AA copolymer resin and ADH were added. The mixture was ground with an attritor filled with glass balls of 0.3 mm in diameter for a period of 45 min at room temperature, which afforded the humidity-sensitive coatings (WDR-PAA-C).

### Measurements of the resin

To attain quantitative and qualitative understanding of amphiphilic AA copolymer, the following measurements were made.

#### Solid content

Solid content was measured by gravimetric analysis. A certain quantity of resin was cast into a Petri dish and dried to a constant weight in a dry oven at  $75\text{--}85^{\circ}\text{C}$ . Solid content was calculated by the following equation:

$$\text{Solid content (wt\%)} = \frac{[(\text{weight of dry resin}) / (\text{weight of resin})] \times 100\%}{(1)}$$

#### Conversion

Conversion was measured by gravimetric analysis. One gram of sample was weighed, and 1 mL 5% aqueous solution of hydroquinone was added. Conversion was calculated by the following equation:

$$\text{Conversion} = W_1/W_2 \times 100\% \quad (2)$$

where  $W_1$  is the weight of nonvolatile matter in sample with adding inhibitor, and  $W_2$  is the weight of nonvolatile matter in sample without inhibitor.

### Contrast ratio

Coating was coated on two boards of which one was black and the other white (thickness of film was 30–50  $\mu\text{m}$ ), and then dried at 25°C for 24 h. The reflectivity of the black and white boards was measured with a reflectance meter (C84-III; Shanghai Anrui Automation Instrumentation Co.).

$$\text{Contrast ratio} = R_b/R_w \quad (3)$$

where  $R_b$  is reflectivity of black board and  $R_w$  is reflectivity of white board.

### Viscosities

Viscosities were measured with a NDJ-8S digital viscometer (Shanghai Balance Factory, China), using a No. 2 rotor rotating at a velocity of 60 rpm at 25°C.

### Acid value

$A_v$  was represented by equivalent amount of KOH for neutralizing 1 g of resin. The unit of  $A_v$  is mg KOH/g. The sample of resin was weighted and dissolved in ethanol. It was titrated by 0.1 mol/L of KOH–ethanol standard solution using phenolphthalein as indicator. The  $A_v$  was calculated by the following equation:

$$\text{Acid value} = V \times N \times 56.11/G \quad (4)$$

where  $V$  is the volume of standard KOH solution (mL),  $N$  is the concentration of standard KOH solution (mol/L), and  $G$  is the weight of sample (g). The molecular weight of KOH is 56.11 (GB6743-86).

### Water solubility

WDR (3 g) was dissolved in water (10 g), to stir and observe its transparency and divided into fair, good, and excellent grades according to its solubility.

### Thickness of the WDR film and coatings

Thickness of WDR and coatings were measured by micrometer screw (Chaohu City Licheng Precision Meter Co., China) as described below: three locations less than 1 cm from the edge of the upper, middle, and lower were chosen, and the average of three numerical values was taken.

### IR spectra

The films of the amphiphilic AA copolymer were prepared by drying its resin at room temperature. Its Fourier transform infrared (FTIR) spectra were detected by Digilab FTS3000 spectrometer.

### Thermogravimetric analysis

The films of the amphiphilic AA copolymer were prepared by drying its resin at room temperature. Its thermogravimetric analysis (TGA) was performed with a Pyris Diamond (Perkin–Elmer, Waltham, MA) under the nitrogen atmosphere at a heating rate of 10°C/min from 20°C to 720°C.

### Mechanical characterization of the coatings

Coatings were prepared by the deposition of small amounts of WDR on glass plates, and these were air-dried at room temperature (25°C) for 48 h. For physical and mechanical characterization, coatings were cast on glass plates and stainless steel plates at room temperature, with a wet thickness of 100  $\mu\text{m}$ . Then, some important mechanical parameters were measured by National Standard Methods of China, such as hardness test (GB/T 1730-93), elasticity test (GB/T 1731-93), adhesion test (GB/T 1720-79(89)), gloss test (GB 9754-88), and water resistance (GB/T1733-93).

### Humidity-controlling properties

#### Humidity-increasing properties

In an artificial climate box (42L), the relative humidity (RH) was adjusted to lower than 30%.<sup>18</sup> Some coated sheets of humidity-sensitive coatings (WDR-PAA-C), previously saturated by water, were placed in the box. The curve of RH versus time was recorded.

#### Dehumidifying properties

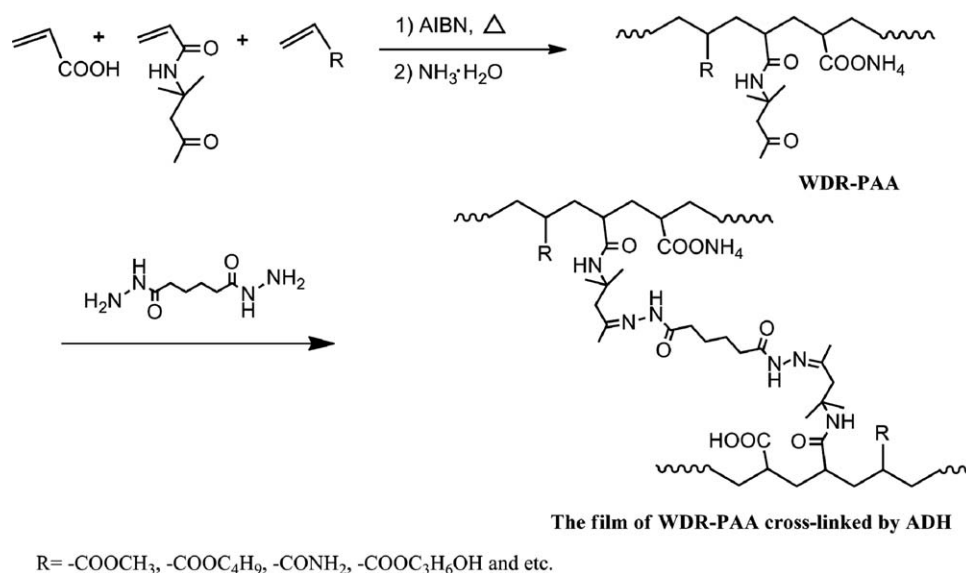
First, the RH of the artificial climate box was increased to 85% by humidifier. Then, some dry coated sheets of humidity-sensitive coatings (WDR-PAA-C) were placed in it. The curves of RH and temperature versus time were recorded.

### Scanning electron microscopy

The surface morphology was measured by JSM-7601F scanning electron microscope.

## RESULTS AND DISCUSSION

In general, the waterborne resin included water-soluble resin, water-emulsion resin, and water-dispersible resin. At first, water-dispersible resin was prepared by polymerization of monomers in polar organic solvents, and some hydrophilic group was introduced in resin chain. Then, it was dispersed in water. Water-based acrylic resin could be obtained through the copolymerization of unsaturated functional monomers, which contained carboxyl, sulfonic, amide, hydroxyl, and ether bonds, with AA



**Scheme 1** Preparation of WDR-PAA and the film of WDR-PAA cross-linked by ADH.

(ester) monomers. AA monomer was neutralized with hydroxide, organic amine, or ammonia and then dissolved in water. When the keto carbonyl was incorporated into resin, the polymer films are cross-linked through the ketone moiety using hydrazide at room temperature. The cross-linking reaction results in the formation of hydrazone moieties that form the cross-link points within the film. The result is that cross-linked films have excellent water resistance and solvent resistance. After being cross-linked, it could become room temperature curable thermosetting acrylic resin. The film properties were better than those without cross-linked films.<sup>19</sup> However, there are few reports about amphiphilic water-dispersible resin, which is used in the humidity-controlling coatings. Here, a new kind of WDR-PAA was prepared and applied in the humidity-controlling coatings for the first time.

### Preparation of WDR-PAA

The WDR-PAA was prepared by AA, MMA, BA, HPMA, AM, and DAAM with free-radical copolymerization. In this article, DAAM could cross-link with ADH (the second step of Scheme 1) because it contains keto-carbonyl and unsaturated bond, which can react with dihydrazide to form hydrazone. It is applied to prepare two-component water-based coatings, which may replace traditional water-based thermoplastic coating or solvent coating.<sup>20</sup> This reaction can occur at ambient temperature to form thin film of coating, which offers the advantage of fast ambient-temperature cross-linking in functionalized acrylic latex. The improvement in cross-linking density of resin was able to improve the properties of coating, which could compare with solvent-borne coatings.

### Effect of Av on water solubility

The Av is an important parameter for the water solubility of amphiphilic AA copolymer. The higher the Av, the better the solubility in water. However, the resin would be expanded infinitely and would be soluble completely in water if the Av is too high. In determining the Av of resin, the water-soluble, water absorption, water resistance, and mechanical strength properties of resin should be taken into consideration. The necessary condition of the water solubility of acrylic resin was neutralization salt formation with ammonia and other alkaline compounds.

The hydroxyl value of amphiphilic AA copolymer (WDR-PAA) was 80 mg KOH/g, the carbonyl content was 1.5%, and the Av was selected among 30 ~ 130 mg KOH/g. The water solubility parameter of WDR-PAA is listed in Table II. The hydroxyl value and the carbonyl content were calculated with amounts of monomers in polymerization. The water solubility of resin increased gradually with increasing Av. If Av was lower than 30 mg KOH/g, the resin could not be dissolved with too high turbidity value, low transparency, and poor liquidity, and the resin film was not transparent. Thus, it could not be used for water-soluble coating. If the Av of resin got to 65 mg KOH/g, it showed good water solubility with being transparent, but the surface of resin film presented blushing. It indicated that this resin could be used for water-soluble coating, but the system was unstable and easy layered. When the Av of resin was higher than 80 mg KOH/g, its water solubility would be increased to being transparent, and it could be used for water-soluble coating. Here, the resin must have water absorption; thus, the Av should be greater than 100 mg KOH/g.

TABLE II  
Effect of Acid Value (Av) of WDR-PAA on Its Water Solubility<sup>a</sup>

No.	AA (%)	Av (mg KOH/g)	Water solubility	Degrees of neutralization (%)	Turbidity value (FNU)
1	5	30	Poor	80	1682
2	7	50	Emulsion	80	570
3	10	65	Transparent	80	128
4	12	80	Clear and transparent	80	84
5	15	100	Clear and transparent	75	61
6	20	130	Clear and transparent	75	46

<sup>a</sup> Condition: isopropyl alcohol, 100 g; AIBN, 0.5%; and temperature, 85°C.

### Effect of variation of DAAM content on water solubility

As copolymer, DAAM plays multiple roles. It could copolymerize with acrylic monomers. Its keto carbonyl group could react with cross-linking agent, such as ADH. It also contains hydrophilic groups. Therefore, the effect of variation of DAAM content on the water solubility was investigated at the same Av. The result of variation of water solubility on DAAM content is listed in Table III. The water solubility of WDR-PAA was improved with increasing DAAM content from 3% to 11%, with its transparency being better, turbidity value being lowered, and viscosity being increased. It proved that amide and ketone carbonyl groups of DAAM could form hydrogen bonds with water, which increase hydrophilicity of copolymer resin.

### FTIR spectra of resin

The FTIR spectra of functional monomer (DAAM), cross-linker (ADH), WDR (WDR-PAA), and cross-linked WDR with ADH (WDR + ADH) are shown in Figure 1. In curve of WDR, a strong broad band in the range of 3200–3400  $\text{cm}^{-1}$  corresponds to stretching vibration of N–H and O–H groups. The two peaks at around 2873 and 2958  $\text{cm}^{-1}$  were ascribed to the C–H stretching vibrations of  $-\text{CH}_2$  and  $-\text{CH}_3$  groups, respectively. The bending C–H vibrations of  $-\text{CH}_2$  and  $-\text{CH}_3$  could be found near 1450 and 1390  $\text{cm}^{-1}$ , respectively. The new peak

TABLE III  
Effect of Variation of DAAM Content on Water Solubility<sup>a</sup>

DAAM (%)	Water solubility	pH	Turbidity value (FNU)	Viscosity (mPa s)
3	Fair	7	227	225
5	Good	7.5	185	243
7	Excellent	7.5	134	261
9	Excellent	7.5	84	293
11	Excellent	8	54	348

<sup>a</sup> Condition: IPA, 100 g; AIBN, 0.5%; temperature, 85°C; Av, 80 mg KOH/g; and neutralization degree, 80%.

appeared at around 1533  $\text{cm}^{-1}$  in the resin could be attributed to the N–H bending vibration of  $-\text{CONH}-$  amide group from DAAM. However, the N–H stretching vibration of this amide group that appeared at 3502  $\text{cm}^{-1}$  overlapped with the broad bands of  $-\text{OH}$  vibrations. The amide group appeared in the polyacrylate-based resin indicated that DAAM could be successfully copolymerized. Moreover, the unsaturated bond peaks in DAAM, which were exhibited at 1622  $\text{cm}^{-1}$  (C=C) and 3084  $\text{cm}^{-1}$  (=C–H), disappeared in WDR. The unsaturated bond (N=N) peak in ADH exhibiting at 1655  $\text{cm}^{-1}$  disappeared, and a peak was present at 1662  $\text{cm}^{-1}$  ( $-\text{C}=\text{N}-$ ) in WDR + ADH. It indicated that the ketone carbonyl of WDR had reacted with ADH.

### TGA of resin

TGA of WDR-PAA film (WDR) and cross-linked film (WDR + ADH) were measured. Their TG curves are given in Figure 2. It showed that WDR-PAA film started to be volatilized and decomposed at 100°C. Major weight loss appeared in the region of 300–390°C. The resin was decomposed completely

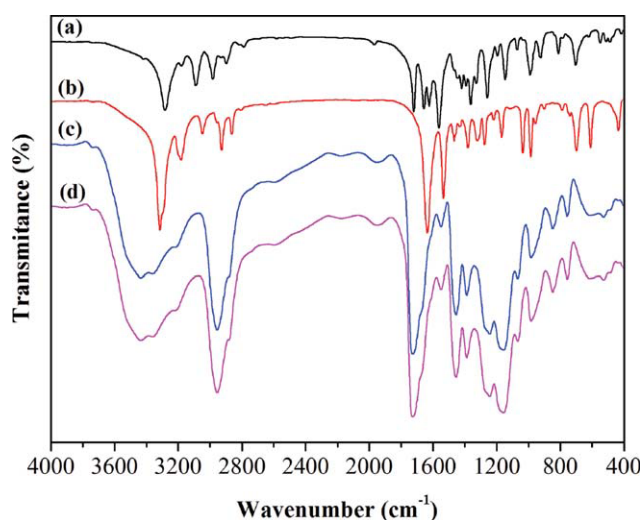
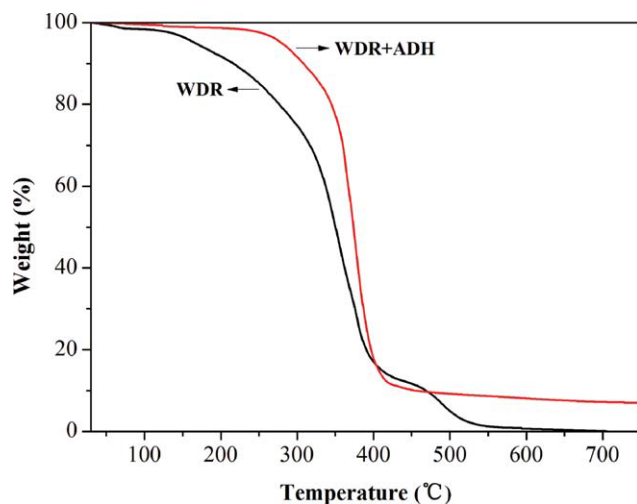


Figure 1 FTIR spectra of (a) DAAM, (b) ADH, (c) WDR, (d) WDR + ADH. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



**Figure 2** TGA data of WDR and WDR + ADH. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

at 520°C. After adding cross-linker (ADH), the cross-linked film (WDR + ADH) was more stable than thermoplastic acrylic resin. It started to be volatilized and decomposed at 220°C. Major weight loss appeared in the region of 330–420°C. It could not be decomposed completely.

### The basic properties and mechanical characterization of WDR resin and paint film

#### Properties of WDR resin and paint film

The basic properties of WDR (the amphiphilic AA copolymer) solution and its paint film were measured. The results are listed in Table IV. The smooth and transparent appearance of WDR film indicated that WDR-PAA showed good film-forming ability. The drying time, hardness, elasticity, adhesion, and other properties of WDR film came up to the standard of general indoor coatings. The high  $A_v$  and hydroxyl value showed that the amphiphilic AA copolymer resin (WDR) had water solubility. When polymer has  $-C=O$ ,  $-OH$ , and other polar groups,

it showed a greater polarity and formed hydrogen bonds with water molecules when it was soaked in water; moreover, it has highly water solubility.<sup>21</sup> The carbonyl content of the amphiphilic AA copolymer resin (WDR) was 1.5%. It showed that the WDR has cross-linking ability, and it could be used in the ambient-temperature self-cross-linking thermosetting acrylic resin.

#### The basic properties of the WDR-PAA coatings

The humidity-sensitive coatings were prepared by the amphiphilic AA copolymer resin (WDR-PAA), pigments, fillers, coating assistants, and water. The basic properties of the humidity-sensitive coatings being used in architectural indoor coatings are shown in Table V. It showed that the basic properties of the humidity-sensitive coatings had reached the standard of interior wall coatings (GB/T 9756-2001).

### The water absorption and humidity-controlling properties of the WDR-PAA coatings

Humidity is an important parameter for human health in the working and living environment, which affects our life if it is too high or too low. The best range of RH is 40 ~ 60%. When the humidity is too high (>60%), corrosion on metal surfaces, electrical insulation falling, objects mildew acceleration, serious wall condensation, deformation of wet items, and so on will occur. Extremely low (<40%) relative humidity may also cause skin chapped, resistance of respiratory system decreased, dry goods deformed, fire by static electricity happened, which will affect safety, production, life and healthy of people. Taking into consideration the effect of humidity on microbial growth, human morbidity and deterioration, and other items, Kalamees et al.<sup>22</sup> recommended an optimum humidity range: 40 ~ 60%. In this RH range, the amount of bacteria, viruses, and dust mites were least, which means that the possibility of respiratory infections, hypersensitivity, asthma, and stimulus of

**TABLE IV**  
Basic Properties of Water-Dispersed Amphiphilic Copolymer

WDR-PAA resin		WDR-PAA film	
Properties	Result	Properties	Result
Appearance	Clear and transparent	Appearance	Smooth
pH	7.5	Surface drying time (h)	1
Neutralization degree (%)	75	Hard dry time (h)	3
Viscosity (mPa s)	241	Hardness	0.42
Solid content (%)	31.34	Adhesion grade	I
Turbidity value (FNU)	46	Elasticity (mm)	1
Acid value (mg KOH/g)	130	Water absorption (%)	486
		Gloss (20°) (%)	140

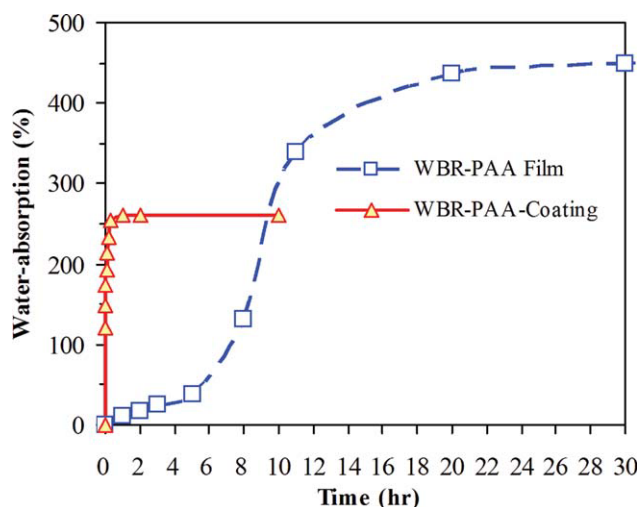
**TABLE V**  
**Basic Properties of the WDR-PAA Coating**

Properties	GB/T 9756-2001—the indoor coating standard of synthetic resin emulsion (qualified products)	WDR-PAA coating (WDR-C)
State in container	No caking, uniform after stirring	Pass
Application property	No barrier to brush spreads two times	Pass
Appearance	Normal	Normal
Drying time (h)	≤2	1
Water resistance (48 h)	No foaming, cracking, and shedding phenomena	≥2 months, normal
Freezing–thawing resistance	Does not deteriorate	Does not deteriorate
Scrub resistance	≥200 times	≥400 times
Alkali resistance (24 h)	Normal	≥2 months, normal
Contrast ratio	≥0.90	≥0.94
Adhesion grade	≤I	≤I

chemical were minimum. Therefore, it is important to control indoor humidity for production and life, especially for humid and arid regions. Here, the water absorption properties and humidity-controlling properties of the humidity-sensitive coatings were measured.

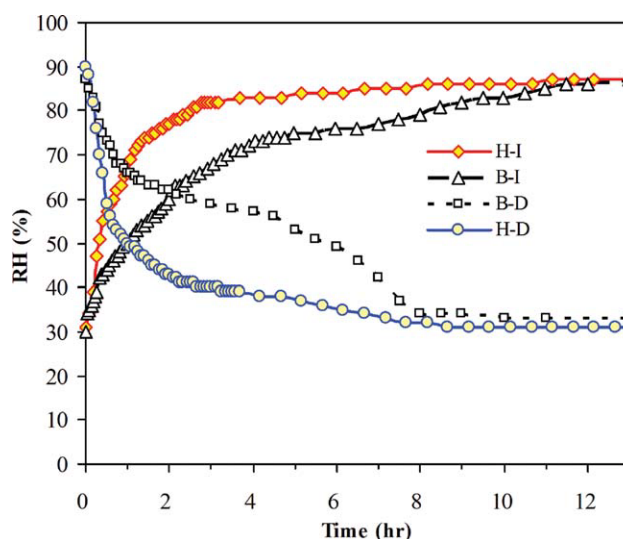
#### Water absorption properties of the WDR-PAA coatings

The water-absorption ability and rate of WDR-PAA film and its coatings (WDR-PAA-C) were measured (Fig. 3). It indicated that WDR-PAA film exhibited high water absorption ability, which could get to 471% percent after absorbing for 30 h. However, the water-absorption capability of WDR-PAA-C was lower, near 260%, whereas its water-absorption rate was very fast, which got to 90% about 10 min, and close to be saturated about 20 min. This means that

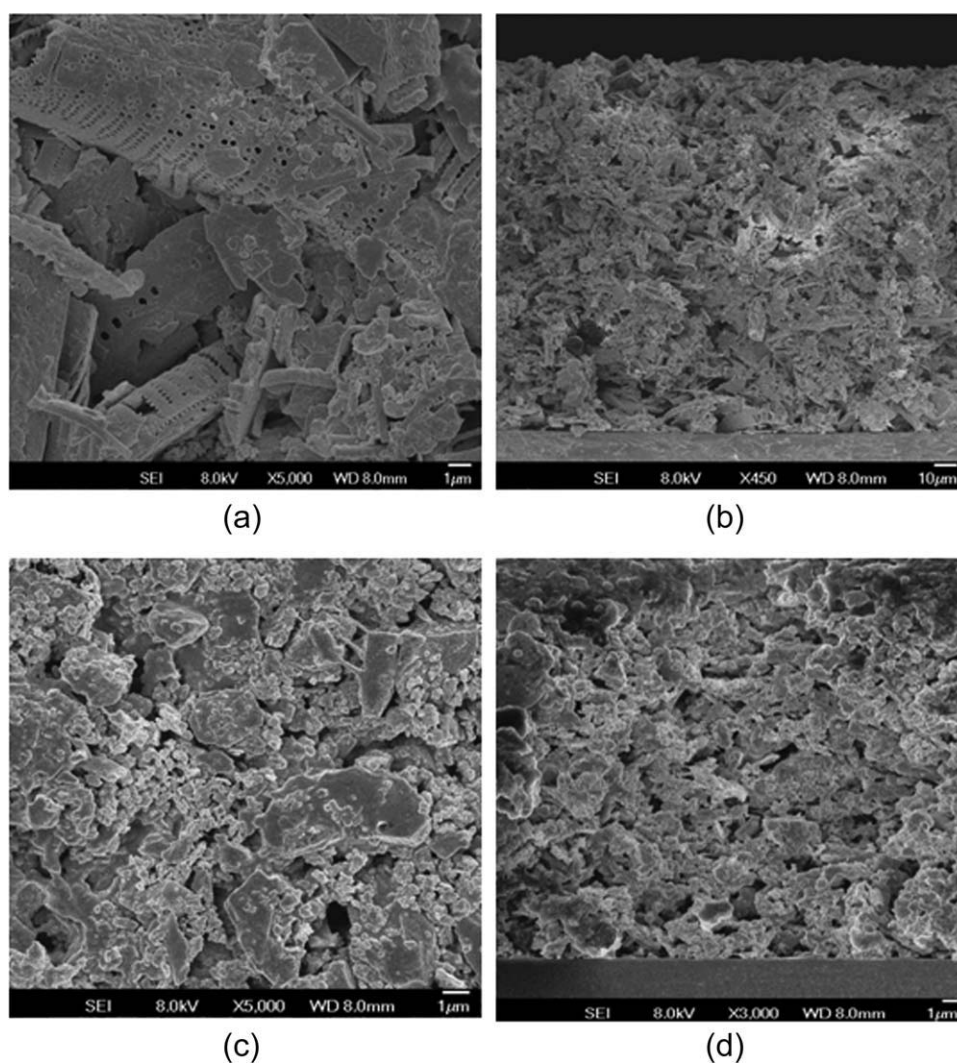


**Figure 3** The water absorption rate of WDR film and WDR-PAA coating. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

WDR-PAA-coating is a kind of the humidity-sensitive coatings that can easily absorb water. We consider the reason is as following: the WDR-PAA film was less porous than that of WDR-PAA-coating. WDR-PAA film could gradually be water-swollen in water because the carboxyl groups of WDR formed hydrogen bonds with water molecules when it was soaked in water. First, there was a chain elongation process in water. The water absorption rate of resin was soared after 5 h when the chain elongation was finished. The water absorption rate of resin was close to saturated in 20 h. The compact property of resin was decreased, and the surface area increased when the porous and multilayer fillers were added into coatings, and the chain elongation time was



**Figure 4** The dehumidifying and humidity-increasing properties of WDR-PAA-C. H-I, humidity increasing with moist coatings; B-I, blank (humidity increase under water); H-D, humidity decreasing with dry coatings; and B-D, blank without coatings. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5** Scanning electron microscopy images of the WDR-PAA coatings (WDR-C) and general indoor coatings. (a) WDR-C, surface; (b) WDR-C, cross-section; (c) conventional indoor coatings, surface; and (d) conventional indoor coatings, cross-section.

shorter. Thus, the water absorption rate of the humidity-sensitive coatings was fast, which was a combined action of resin and fillers.

During adsorbing water, the thickness of the WDR film increased (by 350%), whereas the WDR-PAA-coating was little changed (increased by 2%) because the porous and multilayer filler with a huge specific surface and pore volume afforded expansion space for volume expansion of water-absorbent resin. Thus, the WDR-PAA coating was better if it was used in indoor coating in humidity controlling.

#### Humidity-controlling properties of the WDR-PAA coatings

The amphiphilic AA copolymer resin (WDR-PAA) was applied to prepare the humidity-sensitive coatings (WDR-PAA-C). Its humidity-controlling properties were investigated in an artificial climate box.

First, dehumidifying activity of the humidity-sensitive coatings was measured. In the artificial climate box, RH of which was higher than 85%, six pieces of dry coated sheets were placed in one side of the box. There are eight vent holes in walls connecting the box to outside, which was like windows of room. Outside RH was lower than 35%, which simulated the dry weather. The relationship between RH and time in the artificial climate box, which was dehumidified by dry coated sheets, is shown in Figure 4. The curve H-D showed dehumidifying activity of WDR-PAA-C. The blank experiment (B-D) was measured by withdrawing the coated sheet. The results showed that the RH could be decreased by WDR-PAA-C from 85% to 60% within 0.5 h, and decrease from 85% to 40% within 4 h. However, it needed 4 h for decreasing RH from 85% to 60% if the box is empty, decreasing from 80% to 40% within 7 h. It was concluded that the WDR-PAA



coatings showed excellent dehumidification, and it was a good humidity-controlling coating.

The humidification of the WDR-PAA-C was also measured. Six pieces of coated sheets, which had been saturated by water, were placed in the artificial climate box whose RH was lower than 30%. The relationship between RH and time in the artificial climate box is shown in Figure 4. H-I is the curve of humidity increasing activity of WDR-PAA-C. The blank (or control) experiment (B-I) was measured by replacing the coated sheet with a dish-like glass vessel filled with water, the area surface of which was similar with the former coated sheets. The results showed that the RH could be increased more than 60% within 1 h by water-saturated coated sheet. This means that the absorbed water in the humidity-sensitive coatings was easily released into air, and the specific surface area of the humidity-sensitive coatings was bigger than a dish-like glass vessel because it has porous and multilayer fillers. In dry room, the traditional methods to increase RH are keeping a basin of water or watering on floor. It is a great step that the wall was coated by such kind of humidity-sensitive coatings. The increasing humidity becomes easy by watering wall occasionally.

#### The surface morphology of the WDR-PAA coatings

The surface and cross-section morphology of the humidity-sensitive coatings (WDR-PAA-C) and the general commercial indoor coatings are compared in Figure 5. The cross-section and surface of the WDR-PAA-C are shown in Figure 5(a,b). It indicated that the coating surface was loose as coralliform. This mean that its specific surface area was large, which contained more porous channels and interstice. Thus, the water, moisture, and gas could pass through the coating freely. It was also a proof that it has good water absorption. The WDR-PAA-C had good water absorption, high water absorption speed, and good water and gas permeability. The general commercial indoor coating is shown in Figure 5(c,d). This coating surface was more compact as gravel accumulation. Its specific surface area was low, which contained less-porous channels and interstice. Thus, its water and gas permeability was poorer than the humidity-sensitive coatings.

The reason was that the humidity-sensitive coating was composed of the amphiphilic AA copolymer resin, which added porous and multilayer fillers. The coating structure was loose like coralliform. The filler particles were parceled by water-absorbent resin. They were all water-absorbent materials. Porous filler with a huge surface area and pore volume afforded expansion space for volume expansion of water-absorbent resin. Thus, the water and gas permeability of the humidity-sensitive coatings was

good. Because of the humidity-sensitive property, this WDR, amphiphilic AA copolymer could also be used in antifog coating, anticondensation coatings, and insulation coatings.

## CONCLUSIONS

The WDR-PAA was successfully prepared. It was applied to prepare the humidity-sensitive coatings. The water absorption of humidity-sensitive coatings was 260%. It could increase indoor humidity or dehumidify in dry or moist environment. The humidity-sensitive coatings exhibited humidity sensitivity and excellent humidity retention because they had porous structure with a huge surface area and pore volume, which afforded expansion space for volume expansion of water-absorbent resin. It could be widely applied in indoor coating for controlling humidity.

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