

## Crosslinkable Potato Starch-based Graft Copolymer Emulsion for Humidity Controlling Coatings

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A new kind of crosslinkable potato starch-based graft copolymer emulsion (PoSt-g-BMD) has been prepared using butyl acrylate (BA) and methyl methacrylate (MMA) as main monomers, and diacetone acrylamide (DAAM) as functional monomer. The keto-carbonyl group of DAAM in PoSt-g-BMD copolymer could react with adipic dihydrazide (ADH) at ambient temperature to form cross-linked copolymer. The PoSt-g-BMD had been characterized by the FT-IR spectra and thermogravimetric analysis (TGA). It was applied to prepare the humidity-controlling coatings (PoSt-g-BMD-C). The water absorption of PoSt-g-BMD-C was 105%. The humidity controlling properties were also measured, and the PoSt-g-BMD-C exhibited humidity sensitivity and humidity retention because fillers of porous structure combined with PoSt-g-BMD copolymer emulsion based on scanning electron microscopy images (SEM). It could be widely applied in indoor coating for controlling humidity.

**Keywords:** *potato starch-based copolymer, ambient cross-linked copolymer, graft copolymerization, humidity-controlling coating*

### 1. Introduction

In order to achieve a healthy and comfortable indoor environment, it is very important to control humidity level. Many evidences indicate that indoor humidity environment is closely related to health problems and it also affects energy consumption and the durability of the building envelope<sup>1</sup>. The humidity controlling materials that absorb and release moisture can be used positively to reduce the extreme values of humidity levels in indoor climates<sup>2,3</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<sup>4-7</sup>. The humidity-controlling coatings are composed of the binder, porous or more layers of filler and pigment<sup>8</sup>. However, almost all binders of humidity-controlling coatings were synthetic polymers that hardly decompose in the nature.

Starch, a kind of naturally abundant polysaccharide from a great variety of crops, has been used as not only food but as a kind of low cost biodegradable polymer material. Yet, the properties of starch-based materials are often responsive to the changes of the environment humidity<sup>9</sup>, temperature or pH<sup>10</sup>. In order to improve properties or expand its application field, many chemical modifications<sup>11-17</sup> of starch have been carried out through hydroxyl groups. Particularly, graft copolymerization on starch<sup>18-22</sup> gives the possibility to synthesize new highly added value materials for various applications, which were applied for the textiles, composites,

keeping the variation in the indoor climate and pH-sensitive starch hydrogels, respectively.

In this paper, A new kind of crosslinkable PoSt-based graft copolymer (PoSt-g-BMD) was prepared via graft polymerization. The keto-carbonyl group of DAAM in PoSt-g-BMD copolymer could react with adipic dihydrazide (ADH) at ambient temperature to form cross-linked copolymer. The PoSt-g-BMD had been characterized by the FT-IR spectra and thermogravimetric analysis (TGA). It was applied to prepare the humidity-controlling coatings (PoSt-g-BMD-C). The water absorption and humidity controlling function of the coatings were also investigated, and the PoSt-g-BMD-C exhibited humidity sensitivity and humidity retention.

### 2. Experimental

#### 2.1. Materials

Butyl acrylate (BA) and methyl methacrylate (MMA) were obtained from commercial sources. They were washed with dilute NaOH solution and deionized water to remove inhibitors, then dried with desiccant, respectively. All the purified monomers were stored at -2 °C before use. The potato starch (PoSt) was obtained from Lanzhou Shuangshuang Chemical Industry Co.. Diacetone acrylamide (DAAM), adipic dihydrazides (ADH), and potassium persulfate (KPS) were received analytical without further purification. Titanium dioxide, talc, montmorillonite, kaolin,

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bentonite, diatomite (CD02), diatomite (CD05), natural crystalline calcium carbonate and precipitated calcium carbonate were all industrial grade.

## 2.2. Preparation of crosslinkable PoSt graft copolymer (PoSt-g-BMD)

PoSt and water was added to gelatinization in a four-neck flask equipped with a thermometer, a condenser, a mechanical stirrer, dropping funnels for 0.5 hour at 85 °C. Then, requisite amounts of potassium persulfate (KPS) were added. After stirring 10 min, a mixture of monomers (BA/MMA/DAAM) was dropped for 4 hours, and stirred for a further 8 hours at 85 °C. The obtained emulsion was cooled to 50 °C. The target pH value was adjusted at 7-8 by adding 10% NaOH solution. Then, it was filtered through a filter of 100- mesh sieve. This afforded crosslinkable PoSt-g-BMD copolymer emulsion.

## 2.3. Preparation of self-crosslinkable films

The self-crosslinkable films were prepared by mixing the crosslinkable PoSt-g-BMD copolymer with ADH according to the formula ratio. Then, the mixture was stirring for a period of 45 min. PoSt-g-BMD copolymer could react with ADH at ambient temperature to form the self-crosslinkable emulsion, which obtained a self-crosslinkable thin film (PoSt-g-BMD+ADH).

## 2.4. Preparation of humidity controlling PoSt-g-BMD coatings (PoSt-g-BMD-C)

The humidity controlling coatings were prepared by the PoSt-g-BMD copolymer emulsion, pigments, fillers, ADH and water. First, the pigments, fillers, and coating assistants were dispersed in water with stirring. Then, the PoSt-g-BMD copolymer emulsion 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 controlling coatings (PoSt-g-BMD-C).

## 2.5. Measurements of crosslinkable PoSt-g-BMD emulsion, film and coatings

In order to attain a quantitative and qualitative understanding of emulsion polymerization, film and coatings, further information was sought from experiments. To this end, the following measurements were made.

### 2.5.1. The conversion (C%) and graft percentage (PG%)

Firstly, Ungrafted polyMMA, polyDAAM and polyBA homopolymers were extracted by dispersing the graft copolymer in acetone that contained sufficient water to impart 25% moisture to the polymer. This mixture was stirred for 24 hours and was then centrifuged to separate insoluble graft copolymer from acetone soluble homopolymer. Two more extractions with acetone were then carried out. Supernatant and acetone-washed graft copolymer were dried in vacuum drying oven. Then, the residual homopolymers in the dried polymer product was separated by Soxhlet extraction with acetone and then glacial acetic acid for 12 hours. The conversion (C%) and

graft percentage (PG%) were calculated through following Equation 1, and 2 respectively. The calculations of C% and PG% were similar to what reported by Meshram et al.<sup>23</sup> and Song et al.<sup>24</sup>.

$$\text{Conversion (C \%)} = w_1 / w_2 \times 100\% \quad (1)$$

$$\text{Graft percentage (PG \%)} = w_3 / w_1 \times 100\% \quad (2)$$

where  $w_1$  is the weight of polymer formed extraction (g),  $w_2$  is the weight of monomer taken (g), and  $w_3$  is the weight of starch taken (g).

### 2.5.2. Solid content

A certain quantity of emulsion was cast into a petri dish and dried to a constant weight in a dry oven at 85 °C for 8 hours. Solid content was calculated by the following Equation 3:

$$\text{Solid content (wt. \%)} = (W_{DE} / W_E) \times 100\% \quad (3)$$

where  $W_{DE}$  is the weight of dry film (g), and  $W_E$  is the weight of polymer emulsion formed extraction (g).

### 2.5.3. IR spectroscopy

Fourier-transform infrared (FT-IR) spectra were recorded with the Digilab FTS3000 spectrometer. One hundred scans were collected for each sample at a resolution of 4  $\text{cm}^{-1}$  over the wavenumber region 4000-400  $\text{cm}^{-1}$ . The polymer product was separated by Soxhlet extraction.

### 2.5.4. TG analysis

The thermal gravimetric (TG) analysis was performed with the Pyris Diamond (Perkin Elmer) under the nitrogen atmosphere at a heating rate of 10°C/min from 20 to 720 °C. The polymer product was separated by Soxhlet extraction.

### 2.5.5. Scanning electron microscopy (SEM)

The morphologies of the gold-coated coatings (PoSt-g-BMD-C) were observed with the scanning electron microscope (SEM), type JSM-6701F.

### 2.5.6. Mechanical characterizations of the coatings (PoSt-g-BMD-C)

For physical and mechanical characterizations, the coatings with a wet thickness of 100  $\mu\text{m}$  were cast on glass plates and stainless steel plates, and then they were air-dried at room temperature (25 °C) for 48 hours. Important mechanical characterizations were then measured with national standard methods of China, such as, hardness, adhesion, water resistance, drying time and freezing-thawing resistance.

## 3. Results and Discussion

Starches are potential sources for a wide variety of polymers as they are renewable and ecologically friendly. Particular attention has been attached to synthesis of starch graft copolymer due to an increasing interest in the synthesis of new cost-effective polymer<sup>25</sup>. Cross-linking is a common approach to improve the performance of starch for various applications. Starch and starch products have been cross-

linked with cross-linking agents to improve the mechanical properties and water stability of starch products<sup>26</sup>.

Here, the first goal was to prepare crosslinkable PoSt-based graft copolymer (PoSt-g-BMD) that might serve as waterborne coatings, which can be cured at ambient temperature and possess good properties. The graft copolymerization was represented in Figure 1. In order to improve the properties of target coatings, PoSt-g-BMD containing diacetone acrylamide (DAAM) as functional monomer and adipic acid dihydrazide (ADH) as cross-linker, could cure fast at ambient temperature during the preparation of paint film or coatings (Figure 2). The reaction results were that form hydrazones moieties and form the cross-link points within the film, and the cross-linked films showed excellent water resistance and solvent resistance.

### 3.1. Conversion (C%) and graft percentage (PG%) of PoSt-g-BMD

We found that conversion of monomers and graft percentage of PoSt were influenced by proportions of raw

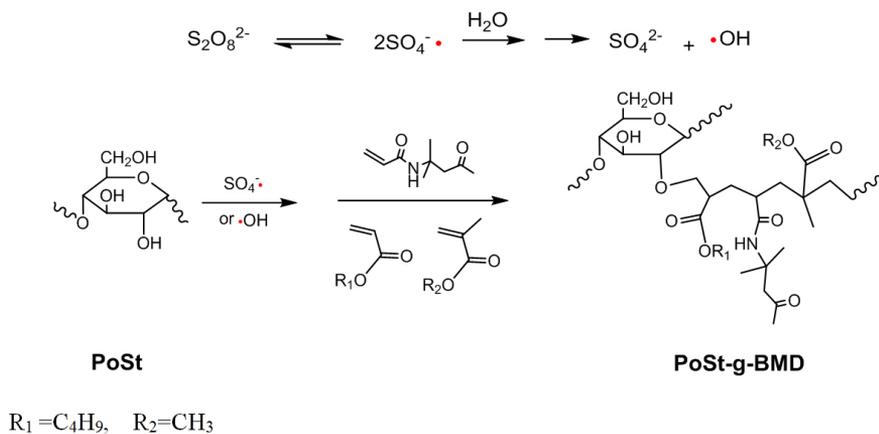
material, initiator, reaction temperature and time. These influences were investigated as follows:

#### 3.1.1. The effect of proportions of raw materials on C% and PG%

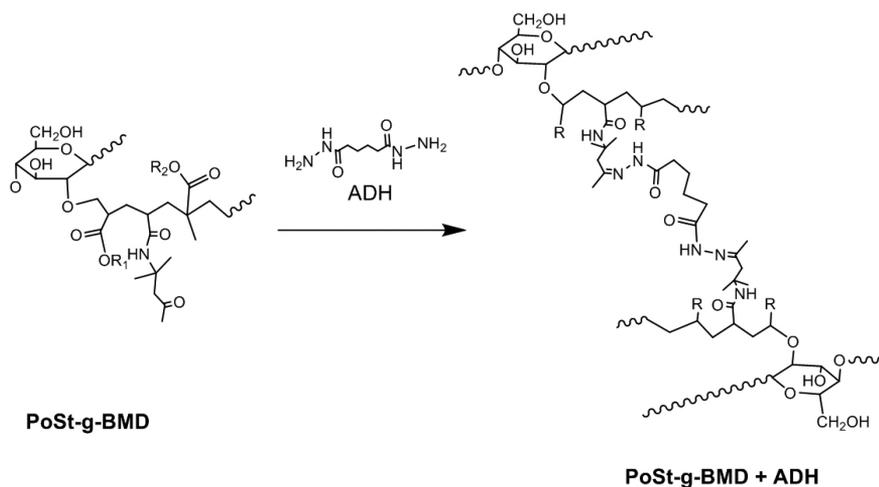
The effect of feeding ratio on C% and PG% was measured at 85°C. The results were shown in Figure 3. When ratio of PoSt to mixed monomers was less than 1:5, the monomer conversion was opposite to the graft percentage. The maximum of graft percentage (PG%) was 80% when w (PoSt) / w (Monomers) were up to 1:4. However, a further increase of the PoSt concentration had greatly reduced the C% and PG%.

#### 3.1.2. Effect of w (BA)/ w (MMA) on C% and PG%

The ratio of BA to MMA also influenced the properties of the copolymer emulsion. It was not only related to grafting percentage, but also affected the monomer conversion (Figure 4). It showed that C% and PG% increased with the increasing of the BA concentration. When the mass ratio of



**Figure 1.** The graft copolymerization of BA, MMA and DAAM on PoSt ( $R_1 = C_4H_9, R_2 = CH_3$ ).

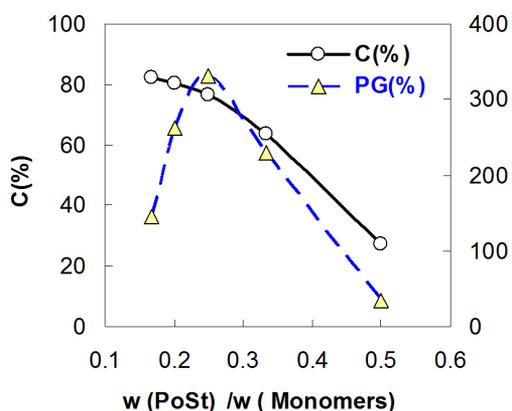


**Figure 2.** Cross-linking reaction of PoSt-g-BMD with ADH.

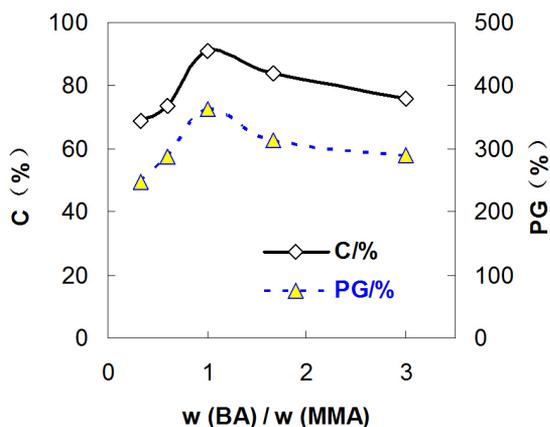
BA to MMA was 1:1, the conversion reached maximum. However, the mixed monomers (BA/MMA) concentration increased over 1:1, both the C% and PG% decreased with the increasing in BA of the monomers. This may be ascribed to the following facts. On the one hand, increasing the monomer concentration was beneficial to the diffusion of monomer molecules on the backbone, thus leading to an increasing in PG% and C%. On the other hand, the high monomer concentrations were good for the formation of accept-donor complexes between PoSt and monomers, which led to the grafting process<sup>20,24,26</sup>. Therefore, an optimum soft/hard monomer concentration of this system was 1:1.

### 3.1.3. The effect of KPS content on C% and PG%

The PoSt-g-BMD copolymers were prepared with KPS as initiator at five different concentrations (0.5, 1.0, 1.5, 2.0 and 2.5 wt.% of the PoSt) at 85°C for 8 hours. And the effect of KPS content on C% and PG% was shown in Figure 5. The conversion increased with the increasing KPS concentrations and up to a maximum at 1.0 wt.% KPS.



**Figure 3.** The effect of proportions of raw materials on C% and PG% (Cond.: w(BA) / w(MMA) = 1: 1, KPS: 1.50 wt.%, Temp: 85°C, Time: 8 hours).

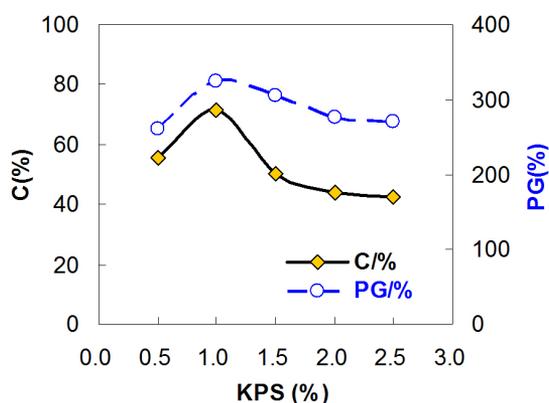


**Figure 4.** Effect of w(BA) / w(MMA) on C% and PG% (Cond.: w(PoSt) / w(Monomers) = 1: 4, KPS: 1.50 wt.%, Temp: 85°C, Time: 8 hours).

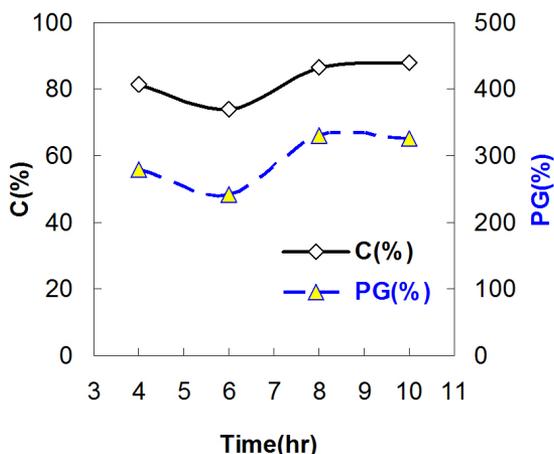
However, the C% and PG% both decreased with further increases in the KPS concentration above 1.50 wt.%, so the optimum values observed were between 1 and 1.50 wt.%. The higher concentrations of KPS produced the higher monomers conversion; but when the KPS concentration reached 2.0 wt.%, chain transfer or homopolymer formation was causing lower monomer C% and PG%.

### 3.1.4. The effect of reaction temperature on C% and PG%

Reaction temperature also played an important role in graft copolymerization. Figure 6 showed the PoSt-g-BMD copolymer were prepared from three different reaction temperatures (70, 80 and 90 °C) with w (starch) / w (monomers) ratio of 1:4, KPS at 1 wt.% for 8 hours. The conversion increased with the increasing of reaction temperature in the range of 70-80 °C. And then conversion decreased gradually when temperature higher than 80 °C. But, the GP% also increased with increasing reaction temperatures over 80 °C. And it reached a maximum when the reaction temperature was 90°C because rate of



**Figure 5.** The effect of KPS content on C% and PG% (Cond.: w(BA) / w(MMA) = 1: 1, w(PoSt) / w(Monomers) = 1: 4, Temp: 85°C, Time: 8 hours).



**Figure 6.** The effect of reaction temperature on C% and PG% (Cond.: w(BA) / w(MMA) = 1:1, w(PoSt) / w(Monomers) = 1:4, KPS: 1.50 wt.%, Time: 8 hours).

homopolymerization was increased above 90 °C. Therefore, the optimum reaction temperature was 85 °C in this system.

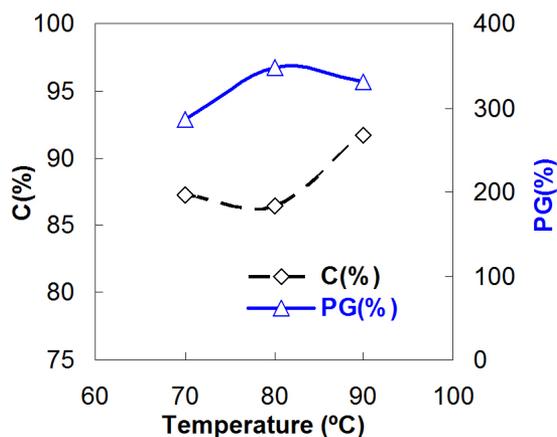
### 3.1.5. The effect of reaction time on C% and PG%

The effect of reaction time on C% and PG% of PoSt-g-BMD copolymer was determined in the range of 2-10 hours in Figure 7. It was found that C% and PG% were the highest at 8 hours. Because graft copolymerization reacted only on the surface of the starch granules, once the starch surface was fully covered with BA/MMA/DAAM, no more new BA/MMA/DAAM could attached on the starch. As a result, the reaction time longer than 8 hours that generated more BA/MMA/DAAM homopolymer and the emulsion viscosity increased. Therefore, the optimum reaction time was 8 hours in this system.

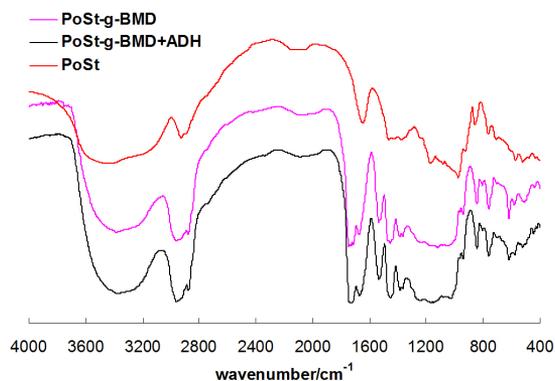
## 3.2. Structure and properties of PoSt-g-BMD emulsion and coatings

### 3.2.1. FT-IR spectra

The FT-IR spectra of the PoSt, extracted PoSt-g-BMD copolymer and PoSt-g-BMD+ADH film were shown in Figure 8. Some characteristic peaks of starch, such as -OH



**Figure 7.** The effect of reaction time on C% and PG% (Cond.: w (BA) / w (MMA) = 1:1, w(PoSt) / w(Monomers) = 1:4, KPS: 1.50 wt.%, Temp: 85°C).



**Figure 8.** FT-IR spectra of PoSt, PoSt-g-BMD and PoSt-g-BMD + ADH copolymer.

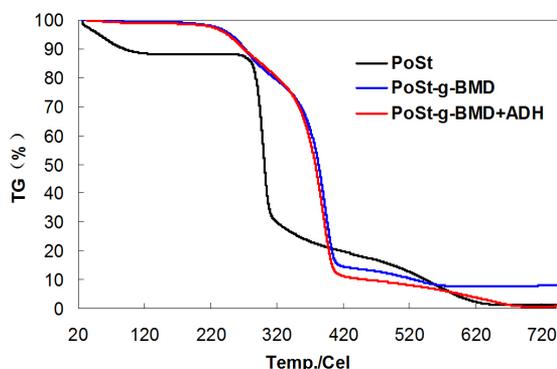
stretching vibration and C-O stretching vibration appeared at 3600  $\text{cm}^{-1}$  and 1647  $\text{cm}^{-1}$ . The peak appeared near 1530  $\text{cm}^{-1}$ , 1545  $\text{cm}^{-1}$  and 1734  $\text{cm}^{-1}$  in the PoSt-g-BMD could be attributed to the -OH bending vibration, C=O stretching vibration and  $\text{COO}^-$  symmetric stretching vibration. However, the N-H stretching vibration of this amide group appeared at 3511  $\text{cm}^{-1}$  and overlapped with the broad bands of -OH vibrations. The amide group in the PoSt-g-BMD indicated that DAAM had been successfully copolymerized. The characteristic absorption of the C=C bond at 1640  $\text{cm}^{-1}$  and the =C-H bond at 1423  $\text{cm}^{-1}$  in DAAM disappeared; it indicated that the monomers had polymerized. Moreover, ADH of the -N-H ( $\text{NH}_2$ ) stretching vibration at 3319  $\text{cm}^{-1}$  and DAAM of ketone carbonyl (-C=O-) stretching vibration at 1747  $\text{cm}^{-1}$  all disappeared, which indicated that DAAM cross-linked with ADH at ambient temperature.

### 3.2.2. Thermo gravimetric analysis (TGA)

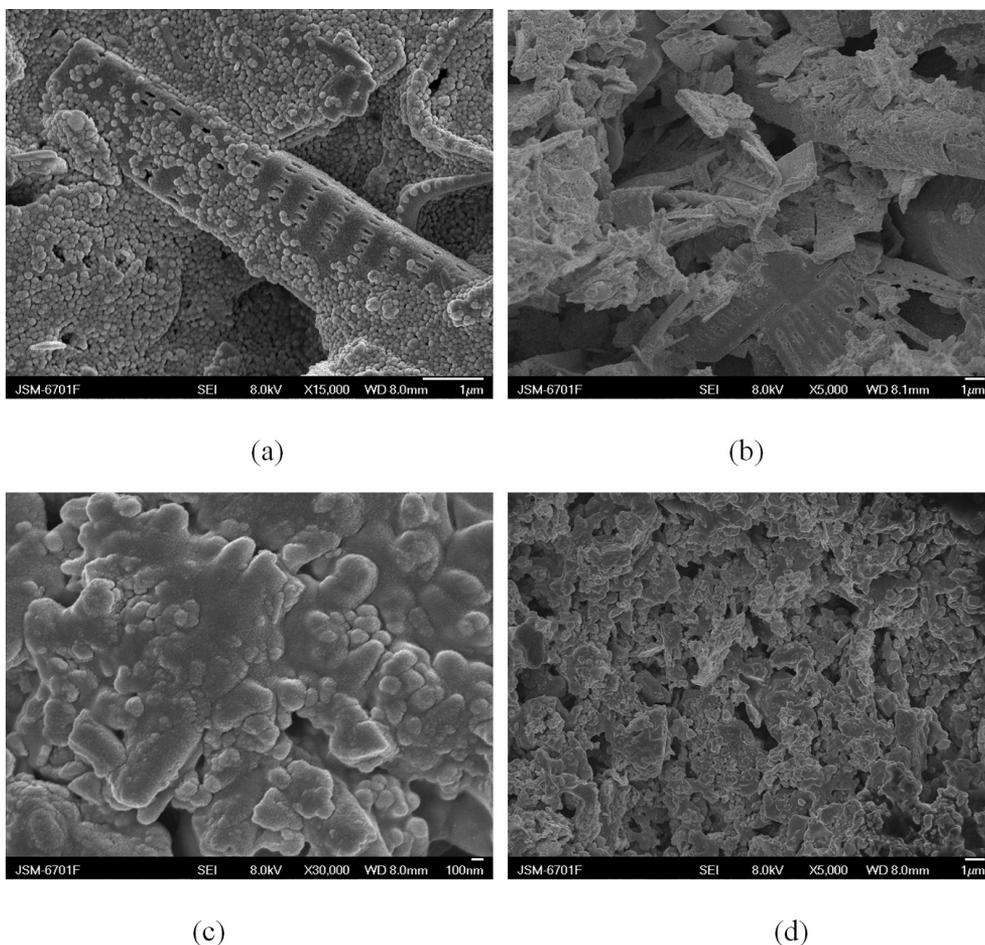
The thermo gravimetric curves of PoSt, extracted PoSt-g-BMD copolymer and PoSt-g-BMD+ADH film were shown in Figure 9. The curves of PoSt, PoSt-g-BMD and PoSt-g-BMD+ADH showed that their first weight loss in the range of 20 °C to 180 °C was due to the loss of physically absorbed interlayer water. It can be seen the PoSt began to decompose at 280 °C and decomposed completely at 495 °C. However, the PoSt-g-BMD and PoSt-g-BMD+ADH began to decompose at 400 °C and decomposed completely at 520 °C. It can be concluded that PoSt-g-BMD grafting copolymer emulsion and PoSt-g-BMD+ADH grafting copolymer had much higher thermal stability than pure PoSt.

### 3.2.3. The basic properties of the PoSt-g-BMD copolymer

The PoSt-g-BMD copolymer would be used in architectural indoor coatings. Moreover, the mechanical stability, viscosity, solid content, drying time, freezing-thawing resistance (3 times) and storage stability (3 months) of the emulsion reached the standards of Chinese indoor coating standards of synthetic emulsion (GB/T1720-79(89)). Then, some important mechanical parameters were measured by national standard methods of china, such as hardness test (GB/T 1730-93), adhesion test, gloss test (GB 9754-88), and water resistance (GB/T1733-93) It



**Figure 9.** Thermo gravimetric analysis (TGA) of PoSt, PoSt-g-BMD and PoSt-g-BMD+ADH copolymer.



**Figure 10.** SEM images of PoSt-g-BMD-C and traditional interior wall coatings ((a) Surface of PoSt-g-BMD-C; (b) Cross Profile of PoSt-g-BMD-C; (c) Surface of traditional interior wall coatings; (d) Cross Profile of Traditional interior wall coatings).

showed that the basic properties of the humidity-sensitive coatings had reached the standard of Chinese interior wall coatings standards.

#### 3.2.4. The basic properties of the PoSt-g-BMD-C

The PoSt-g-BMD-C was prepared by the PoSt-g-BMD copolymer, pigments, fillers, ADH and water. The coatings with a wet thickness of 100  $\mu\text{m}$  were cast on glass plates and stainless steel plates, and air-dried at room temperature ( $23 \pm 2$   $^{\circ}\text{C}$ ) for 48 hours for physical and mechanical characterizations. Then, some important mechanical characterizations were measured by national standard methods of China, such as contrast ratio, hardness test (GB/T 1730-93), adhesion test (GB/T1720-79(89)) and water resistance (GB/T1733-93). It showed that the basic properties of the humidity-controlling coatings had reached the standard of Chinese interior wall coatings standards.

#### 3.2.5. The morphology of the PoSt-g-BMD-C coatings

In order to verify the suggested humidity controlling mechanism of PoSt-g-BMD-C, the surface and cross-section morphologies of the crosslinkable humidity controlling PoSt-g-BMD coatings (PoSt-g-BMD-C) and

traditional interior wall coatings were measured by scanning electron microscope (SEM) in Figure 10. As shown in Figure 10a, b, the surface attached starch particles and cross-section of PoSt-g-BMD-C presented lots of holes and voids in microstructure. Furthermore, it indicated that the coating surface was loose as coralliform. This meant that its specific surface area was large, which contained more porous channels and interstice. Thus, water, moisture, and gas could pass through the coating freely. And it was also a proof that it has good water-absorption<sup>4</sup>. The PoSt-g-BMD-C had good water absorption, high water absorption speed, and good water and gas permeability. The morphologies of traditional interior wall coating were shown in Figure 10c, d. This coating surface was more compact due to its 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 controlling coatings. The reason was that the humidity controlling coatings were composed of the crosslinkable PoSt-g-BMD copolymer emulsion, which added porous and multilayer fillers. The filler particles were parceled by PoSt-g-BMD grafting copolymer. They were all water-absorbent materials. Porous filler with a huge surface

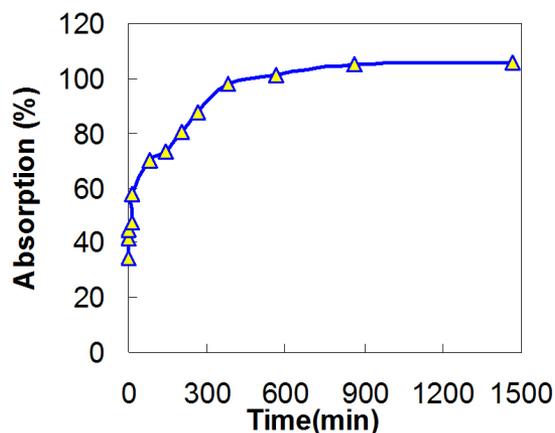


Figure 11. Water absorption rate of PoSt-g-BMD-C.

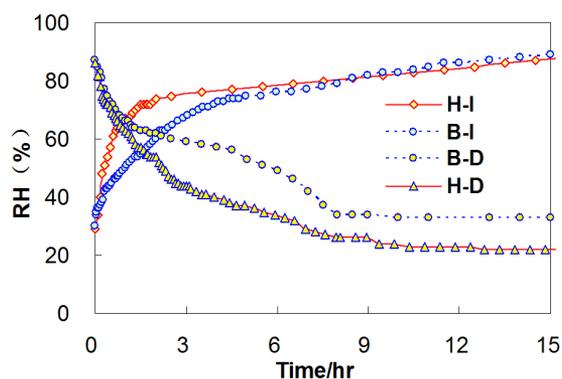


Figure 12. The dehumidifying and humidity increasing properties of the PoSt-g-BMD-C (H-I: Humidity increasing with moist coatings, B-I: Blank humidity increase, H-D: Humidity decreasing with dry coatings; B-D: Blank without coatings).

area and pore volume afforded expansion space for volume expansion of PoSt-g-BMD grafting copolymer. Therefore, the PoSt-g-BMD-C with the better performance of humidity controlling and PoSt was a natural raw material.

### 3.3. Water absorption and humidity controlling function of PoSt-g-BMD coatings

#### 3.3.1. Water absorption properties of the PoSt-g-BMD-C

The coatings were cast on glass plates with a wet thickness of 100  $\mu\text{m}$ , and they were air-dried at room temperature ( $23 \pm 2$  °C) for 48 hours, and then weighed the glass plate and sample. Then dipped into the distilled water at  $23 \pm 2$  °C and weighed at regular intervals. The water absorption and water absorption rate of PoSt-g-BMD coatings were measured. In Figure 11, it indicated that the water absorption rate of PoSt-g-BMD coatings was very fast, which got to 80% about 15 min, and was close to be saturated about 9 hours, which could get to 105%. Meanwhile, during adsorbing water, the thickness of the PoSt-g-BMD-C had

no change as the porous and multi-layer filler with a huge surface area and pore volume afforded expansion space for volume expansion of humidity controlling coatings.

#### 3.3.2. The humidity controlling behaviors of PoSt-g-BMD-C

The humidity controlling properties of PoSt-g-BMD coating were investigated in an artificial climate box according to reference Wang et al.<sup>6</sup>, Song et al.<sup>7</sup>. The dehumidifying activity of the humidity controlling coatings was measured. In Figure 12, the curve H-D showed dehumidifying activity of humidity controlling coatings. The blank (or control) experiment (B-D) was measured by withdrawing the coated sheet. The results showed that the relative humidity (RH) decreased from 90% to 40% within 3 hours. It could keep RH below 30% for more than 8 hours. However, it needed 7 hours for decreasing RH from 90% to 40% if the box was empty. It was concluded that the humidity-sensitive coatings showed excellent dehumidification. Meanwhile, humidification of the humidity controlling coatings was measured. A piece of coated sheet whose area equaled with that of the glass vessel, which had been saturated by water, was placed in the artificial climate box which RH was below 30%. H-I is the curve of humidity increasing activity of the humidity controlling coatings. The blank experiment (B-I) was measured by replacing the coated sheet with a dish-like glass vessel (diameter: 15 cm) which was filled with water. The results showed that the RH increased over 60% within 1.2 hours by water saturated coated sheet, which was similar to keeping water in it. That meant the humidity controlling property of coatings prepared by crosslinkable PoSt-g-BMD-C was excellent. And it could be used in interior walls for humidity controlling.

## 4. Conclusions

The crosslinkable PoSt-based copolymer emulsion (PoSt-g-BMD) was synthesized by graft copolymerization. The grafting polymers onto starch were confirmed by both FT-IR and TGA. The PoSt-g-BMD containing diacetone acrylamide (DAAM) as functional monomer and adipic acid dihydrazide (ADH) as cross-linker, could cure fast at ambient temperature during the preparation of paint film or coatings. The emulsion was used in interior wall coatings for controlling humidity, and could increase indoor humidity or dehumidify in dry or moist environments. The obtained coatings had good humidity-sensitivity and humidity-retention. This emulsion is a promising candidate for indoor wall coatings which could be widely used to control humidity.

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