



Synthesis of Environmental-Friendly Starch-acrylic Coating Sols by Emulsion Polymerization

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유화중합에 의한 친환경 전분-아크릴 코팅졸의 합성

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ABSTRACT : Starch is an environmental-friendly natural source, more interests are attracted to use starch for synthesis of composites and coating sols. Starch-acrylic coating sols for architectural materials were synthesized by emulsion polymerization. The structures of synthesized materials were characterized by using Infrared spectra, ¹H-NMR spectra, and physical characteristics were investigated by X-ray diffraction, foaming test, whiteness test, gloss test and tensile strength test. XRD results showed that starch in starch-acrylic copolymer matrix was in an amorphous state. Starch-acrylic emulsion was compounded with 1%, 3%, 5% foaming agent (n-pentane) and 60% CaCO₃ solution. The results showed that starch and foaming agent could increase the foamability. Tensile strength increased with the enhancement of starch and foaming agent concentration. But whiteness and gloss decreased with increase of starch and foaming agent concentration.

요약 : 전분은 친환경적인 천연자원이다. 건축 재료로서 활용 가능한 전분-아크릴 코팅졸을 유화중합으로 합성하였다. 제조된 합성물은 IR, ¹H-NMR을 이용하여 구조를 분석하였고, X-ray Diffraction, 발포 시험, 백색도 시험, 광택도 시험과 인장 강도를 측정을 통하여 물리적 특성을 조사하였다. 전분-아크릴 폴리머 매트릭스에서 전분의 무정형 상태는 XRD결과로 알 수 있었다. 에멀전을 60% CaCO₃ 수용액과 1%, 3%, 5% 발포제와 배합하였다. 그 결과 전분과 발포제의 양이 증가할수록 발포율이 증가하였다. 전분과 발포제의 양이 증가하면 인장 강도가 증가하였다. 그러나 전분과 발포제의 증가로 인해 백색도와 광택도는 감소하였다.

Keywords : wallpaper, starch, acrylic monomers, coating sol.

I. Introduction

Nowadays, most of wallpapers in the market are silk wallpapers. The main composition of silk wallpaper is poly (vinyl chloride), which could make the environment pollution due to the volatilizable foaming agent, difficult decomposition and poisonous gas-out. To protect our environment, people pay much attention to do some research on environmental-friendly wallpaper, such as natural fibre wallpaper and natural starch wallpaper. Starch is a world-wide production on earth, and has many advantages, such as renewable, low cost and biodegradability. However; pure starch is unsuitable for most uses in the industry, because of its poor mechanical properties, poor thermal properties, water absorption, and its large particle size. The modification of native starch can further change its

properties. This can be achieved in many ways. Some of these are replacement of hydroxyl groups with hydrophobic ester groups or direct grafting of polymeric chains onto the starch backbone.¹ Starch-g-poly(methyl methacrylate),² starch-g-poly(vinyl acetate),³ starch-g-poly(methyl acrylate)^{4,5} and starch-g-polystyrene^{6,7} have been successfully synthesized. In our previous works, starch-acrylic copolymer has been synthesized by emulsion polymerization and soap-free emulsion polymerization.⁸⁻¹⁰ The viscosity and particle size of emulsion increased with increasing of starch content, but decreased after adding the α -amylase as enzyme for starch. The water and alkali resistant were deduced with increasing of starch content due to the increase of hydrophilicity.

In this research, the starch was modified by direct grafting of acrylic polymeric chains onto its backbone by emulsion polymerization. The structure of starch-acrylic coating sols was investigated. The effect of starch and foaming agent content

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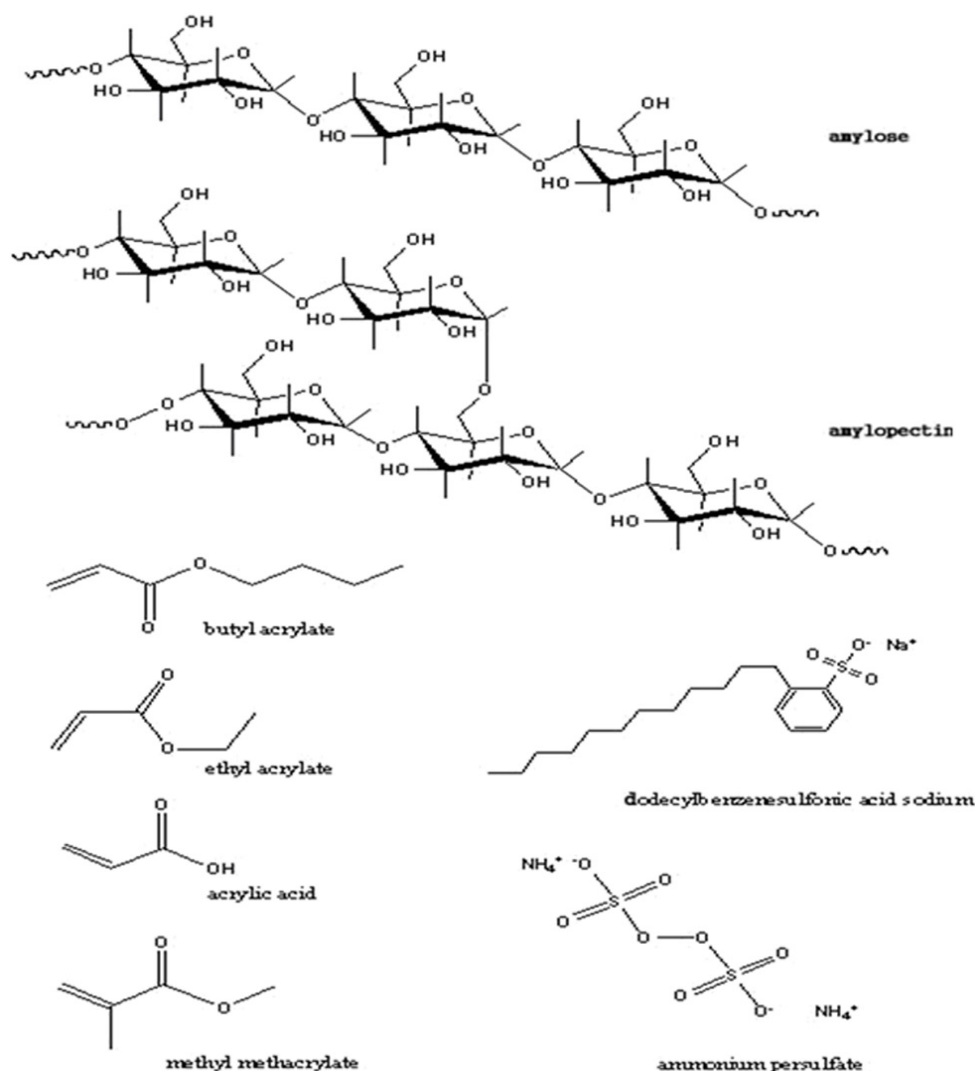


Figure 1. Structure of starch (amylose and amylopectin), monomer, surfactant, and initiator used in this study.

on foamability, whiteness, gloss and mechanical property were investigated, too. The aim of this research was to synthesize environmental-friendly starch-acrylic coating sols for architectural materials to replace the former environmental-unfriendly silk wallpapers. This research will advance the knowledge how to synthesize of wallpaper using environmental-friendly starch.

II. Experimental

1. Materials

Gencoat for corn starch was supplied from Samyang Genex Company. α -Amylase for starch dissolved enzyme was supplied from Novozymes Company. Ethyl acrylate (EA), methyl methacrylate (MMA), acrylic acid (AA), butyl acrylate (BA), dodecyl benzene sulfonic acid sodium salt 50% (DBS-Na),

ammonium persulfate (APS) and ammonia water all were supplied from Aldrich company. Other reagents and ingredients were commercially available and were used as received. The structures of experimental materials were shown in Figure 1.

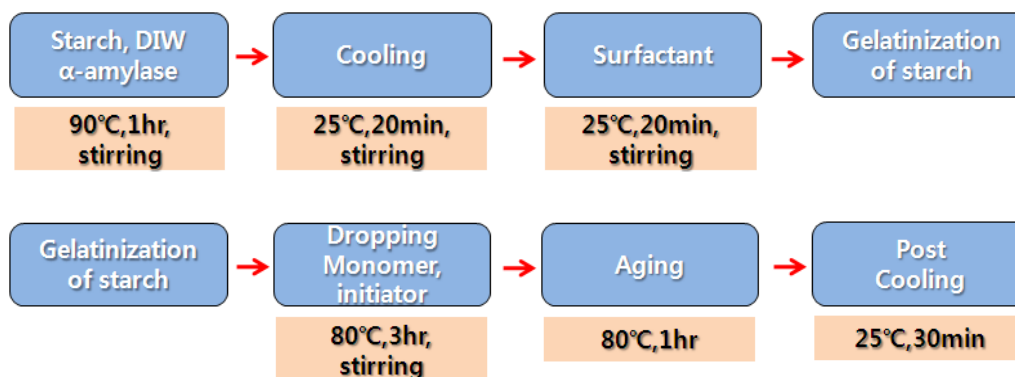
2. Preparation of Starch-acrylic Coating Sols

Starch with α -amylase aqueous suspension were gelatinized at 90 °C in a water bath for 1 hour until the starch was dissolved completely. The surfactant DBS-Na was slowly added into the suspension within 20 minutes. Grafting copolymerization was conducted with the different content (0%, 10%, 20%, 30%, 40%) starch paste, acrylic monomers and initiator APS at 80 °C for 3 hours. The recipe of polymerization was shown in Table 1. The reaction was performed under a continuous flow of oxygen free nitrogen gas. After reacting 3

Table 1. The Polymerization Recipe for Synthesis of Starch-acrylic Coating Sols

(unit: g)

Starch Content(%)	Starch Gel		Monomer				Surfactant	Initiator	pH Controller
	Starch	α -Amylase	BA	MMA	AA	EA	SDBS	APS	NH ₄ OH
0	0	0	180.0	45.86	11.64	150.5	14.35	2.37	7.41
10%	44.10	0.10	161.99	41.28	10.47	135.5	14.35	2.37	7.41
20%	88.18	0.23	143.99	36.70	9.31	120.4	14.35	2.37	7.41
30%	132.3	0.33	125.99	32.11	8.15	105.4	14.35	2.37	7.41
40%	176.4	0.43	107.99	27.52	6.99	90.30	14.35	2.37	7.41

**Figure 2.** The synthetic process of starch-acrylic coating sols.

hours, the starch-acrylic emulsion was polymerized. The synthetic process is presented in Figure 2. The emulsion was mixed with 1%, 3% and 5% foaming agent (n-pentane) and 60% CaCO₃ solution. The mixture was coated on a A4 paper with size of 210 mm×297 mm and then shifted into oven at 180 °C for 1 hour.

3. Characterization

Infrared spectra was recorded (IR-Spectrometer, BioRoad) with KBr pellets. The scans took from 2400 cm⁻¹ to 600 cm⁻¹ with an average 4 cm⁻¹ resolution.

¹H-NMR spectra were recorded on a Varian Gemini 2000 300 MHz spectrometer. For ¹H-NMR measurements, the samples were dissolved in chloroform-d₁ (FlukaChemica) with deuteration degree not less than 99.8%, in 5 mm NMR tubes, at room temperature. The sample concentration was about 1.0% by weight.

X-ray diffraction analysis was performed by using Rigaku D/MAX-2200V X-ray Diffractometer-Cu tube and Graphite Monochromator at a room temperature in a 2θ range of 0°~80°.

Foaming test was performed by Thickness Gage, FRANK Instrument. The thickness of the foaming sample was measured. All results were calculated with an average of five

measurements.

$$\text{Foamability}(\%) = \frac{\text{Thickness of coated paper} - \text{Thickness of original paper}}{\text{Thickness of original paper}} \times 100\%$$

Whiteness test was performed by Spectrophotometer, ELREPHO Instrument. Five specimens were measured and the average values were reported.

Gloss test was performed by Glossmeter ZGM1020, Zehntner Instrument. Five specimens were measured. The highest and lowest values would be abandoned and the average values were reported.

Tensile strength was performed by Tensile Tester, L&W Introduce Instrument. Five specimens were measured and the average values were reported.

III. Results and Discussion

1. Structure of Starch-acrylic Coating Sols

To investigate the effect of grafting starch on the structure of starch-acrylic coating sols, IR, ¹H-NMR spectra and XRD patterns of acrylic copolymer and starch-acrylic coating sols were obtained.

As shown in Figure 3, The characteristic vibrational peak

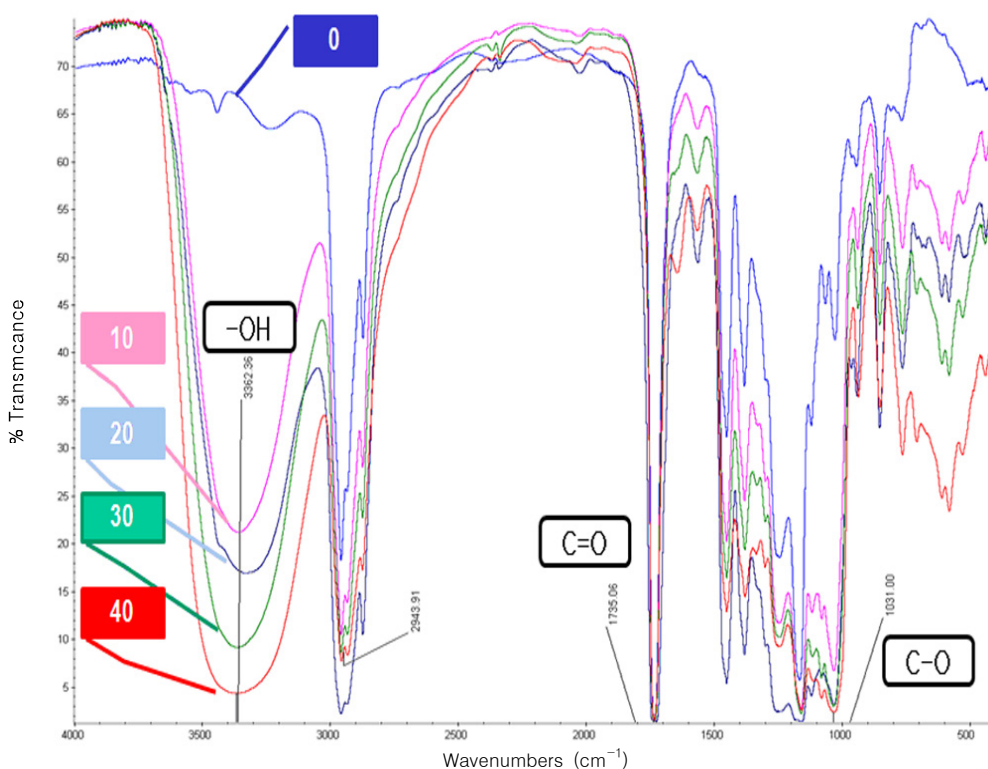


Figure 3. Infrared spectra of starch-acrylic coating sols with different content of starch.

that occurred at 1735 cm^{-1} was attributed to C=O stretching of the acrylic copolymer. For the starch-acrylic coating sols, the C-O stretching of anhydroglucose unit occurred in 1031 , 1160 and 1475 cm^{-1} . A broad peak at 3362 cm^{-1} was due to the high activity of hydroxyl groups in the starch chains. With increasing of starch concentration from 10% to 40%, there is no significant difference among them. But it seemed that the intensity of O-H peak at 3362 cm^{-1} increased with increasing of starch content.

As shown in Figure 4, This is the $^1\text{H-NMR}$ spectra of acrylic copolymer and starch-acrylic coating sols (10%). In Figure 4(a), The peaks at 0.92, 1.12 and 1.46 ppm were attributed to acrylic copolymer. After grafted by starch, the peaks at 4.47, 5.02 and 5.44 ppm were observed. It was attributed to the glycosidic group on the starch chain. The peak at 3.48 ppm showed many -OH hydroxyls on the starch chains.

From the IR and $^1\text{H-NMR}$ spectra of pure acrylic copolymer and starch-acrylic coating sols, we can conclude that the graft copolymerization between starch and acrylic monomer was successfully achieved. The grafting efficiency seems to be high, which can be confirmed by the high intensity of O-H peaks from IR spectra. The assumptive graft copolymerization mechanism was suggested in Figure 5.

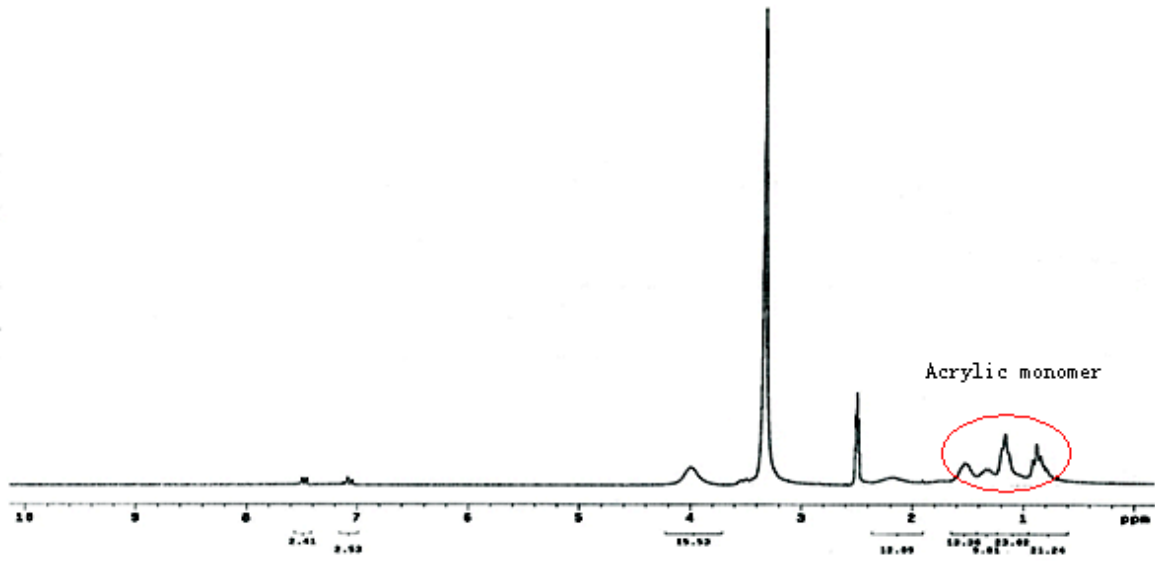
X-Ray Diffraction patterns of starch-acrylic coating sols with different content of starch were shown in Figure 6. Even

the starch content increased up to 40%, only one broad peak was clearly observed, which indicated the starch was entirely diluted and the starch was in an amorphous state. The intensity of peaks decreased with increasing of the starch content. As reported, the undiluted starch is semi-crystalline material, the XRD patterns show the five diffraction peaks of starch appearing. But once the crystals of starch in the diluted starch paste had disappeared, a broad amorphous hill is clearly observed; demonstrating that the starch dispersed in polymer matrix is in an amorphous state.^{11,12}

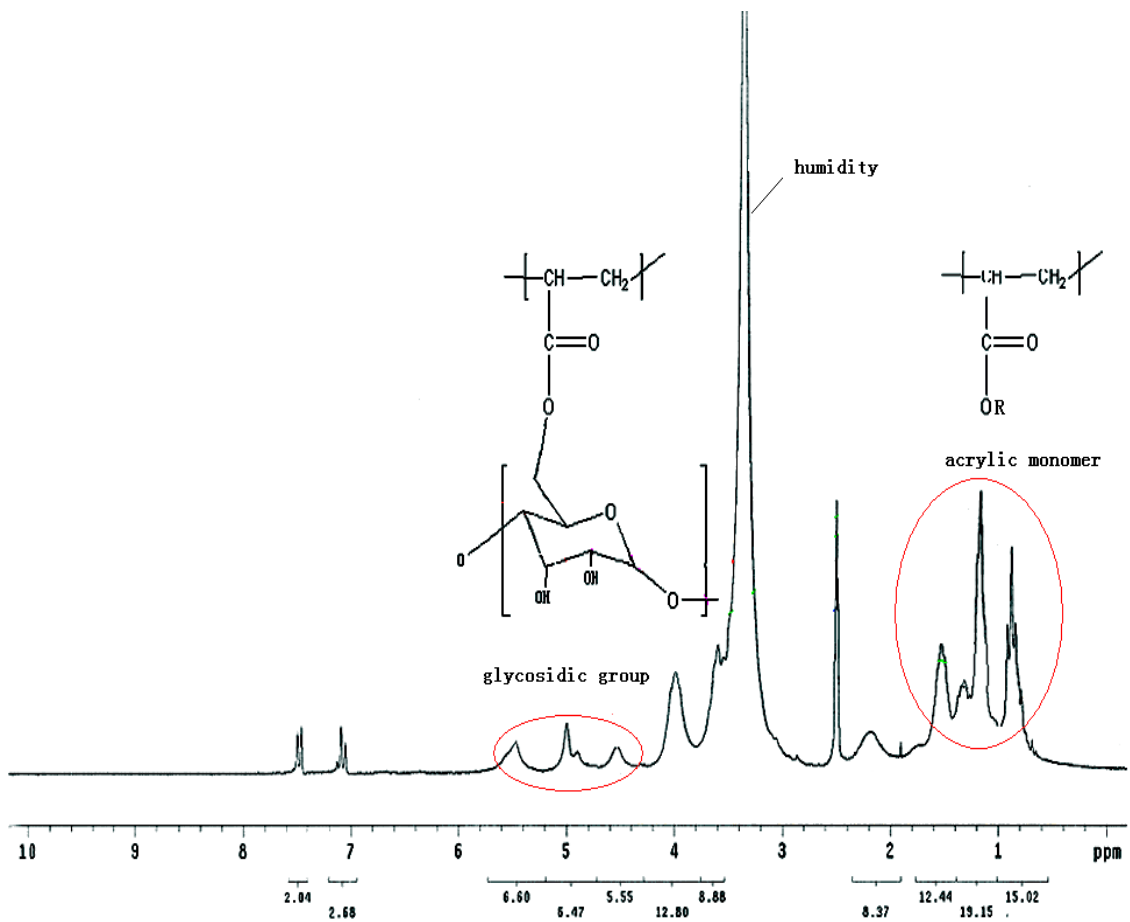
2. Foamability, Whiteness and Gloss

As the synthesized starch-acrylic coating sols is used for wallpaper, it is of practical important to discuss the foamability, whiteness and gloss. The contents of starch and foaming agent are important impact factors on foamability, whiteness and gloss. The effect of starch and foaming agent content has been studied by varying the starch content from 0% to 40% and the foaming agent content from 1% to 5%, respectively.

As shown in Figure 7, foamability has been found to increase with increasing the starch and foaming agent contents. When the contents of starch and foaming agent were respectively 0% and 1%, the foaming ratio is only 11.6%. When



(a) acrylic copolymer



(b) starch-acrylic coating sols

Figure 4. $^1\text{H-NMR}$ spectra of (a) acrylic copolymer and (b) starch-acrylic coating sols (starch content 10%).

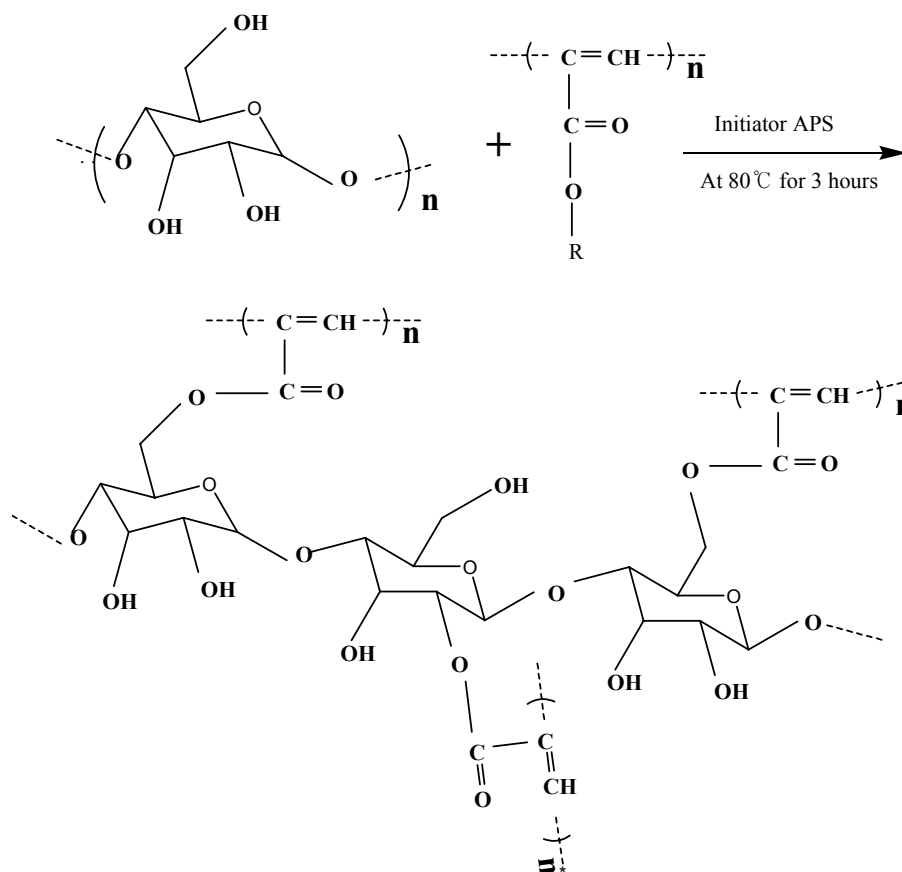


Figure 5. Assumptive graft copolymerization mechanism between starch and acrylic monomer.

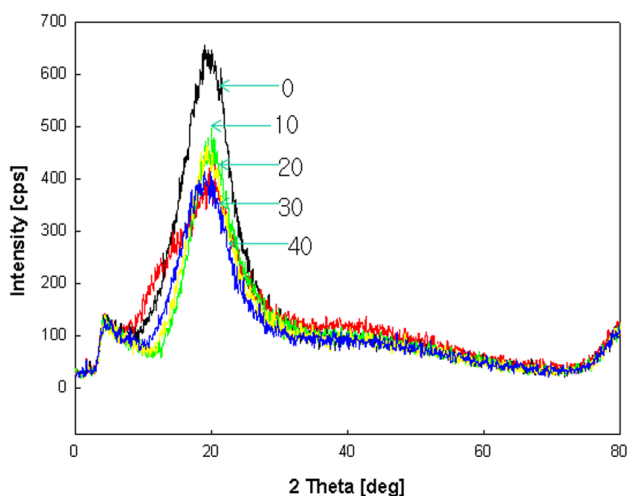


Figure 6. X-ray diffraction patterns of starch-acrylic coating sols with different content of starch.

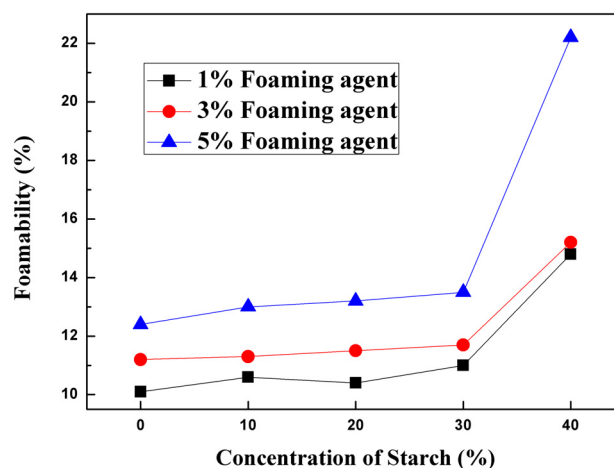


Figure 7. Foamability of starch-acrylic coating sols with different content of starch and foaming agent.

the contents of starch and foaming agent were respectively 40% and 5%, the foaming ratio reached the maximum value 22%. It is because that the there are plenty of -OH groups

on the molecule chains of starch, which greatly enhance water absorption and hydrophilicity, and then increased the foamability.

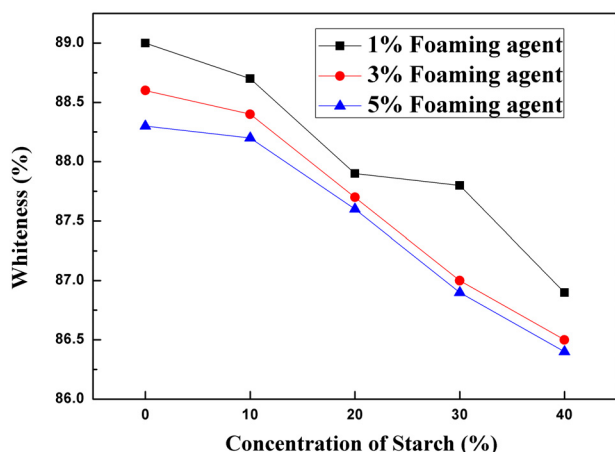


Figure 8. Whiteness of starch-acrylic coating sols materials with different content of starch and foaming agent.

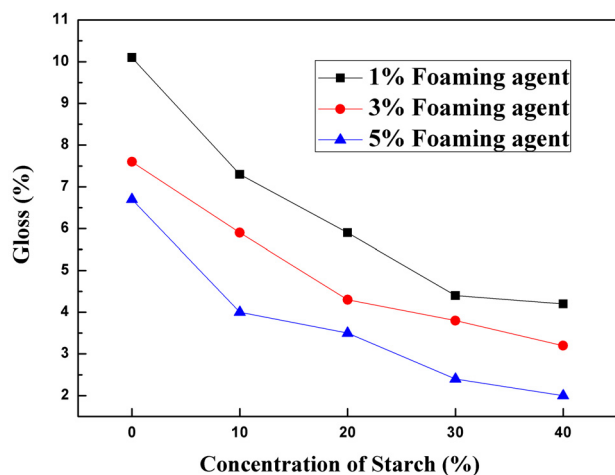


Figure 9. Gloss of starch-acrylic coating materials with different content of starch and foaming agent.

As shown in Figure 8 and Figure 9, whiteness and gloss measurements decreased with increasing of the starch and foaming agent contents. Whiteness increases as the concentration of light materials (carbonate, quartz, muscovite, kaolinite, and albite) increases, and decreases as the concentration of dark materials (especially iron oxide, clay minerals, and organic materials) increases.¹³ So whiteness measurements were strongly affected by the composition fraction of starch/calcium carbonate. The increasing of organic materials starch cause whiteness reduced. The decrease of gloss was due to surface smoothness reduction. The large particle size of starch and foaming agent also reduced the surface smoothness of starch-acrylic coating sols materials.

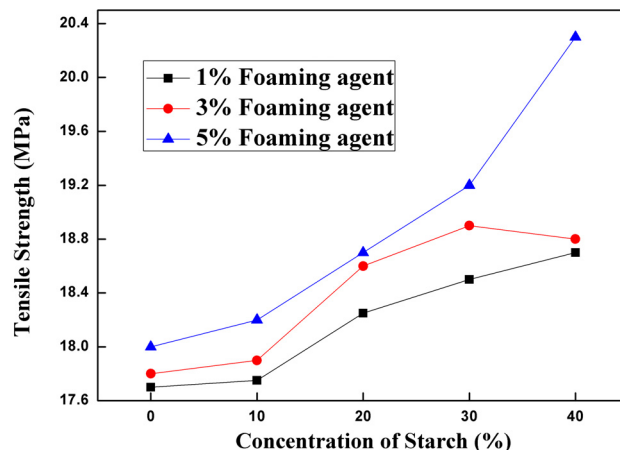


Figure 10. Tensile Strength of starch-acrylic coating materials with different content of starch and foaming agent.

3. Tensile Strength

Tensile strength curves of starch-acrylic coating materials with different content of starch are shown in Figure 10. In the foaming process, calcium carbonate acted as reinforcing filler. Tensile strength for the composition with starch 0% and foaming agent 1% was 17.7 MPa. For the composition with starch 40% and foaming agent 5%, tensile strength increased up to 20.3 MPa. Tensile strength increased with increasing of the starch content, also is increased with increasing of foaming agent content.

IV. Conclusions

Environmental-friendly starch-acrylic coating sols for architectural materials were successfully synthesized by emulsion polymerization. Starch in the starch-acrylic copolymer matrix was in an amorphous state. The foaming experiments indicated that starch and foaming agent could develop the foamability, but decreased the whiteness and gloss measurements due to the large particle size of starch. The tensile strength also improved with increasing starch and foaming agent content.

Acknowledgments

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