

## Effects of water-soluble cellulosic polymers on coating development and quality

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### ABSTRACT

Recently, 'environmentally friendly' has gained more importance for paper industry than before. In this study, a water-soluble biodegradable polymer produced from cellulose was applied as a coating constituent. The polymer applied was cellouronic acid with almost all primary alcohol groups at C-6 oxidized selectively to carboxyl groups. The influences of several water-soluble polymers, i.e., cellulosic polymers including cellouronic acid, starch and polyvinyl alcohol, upon binder migration and coating characteristics were studied. Infrared spectra and energy dispersive X-ray analysis of scanning electron microscopy exhibited that the binder latex was distributed uniformly across the coating containing cellulosic polymers in the thickness direction. These effects were not observed with starch or polyvinyl alcohol. Coatings containing cellulosic polymers provided good coating surface properties, that is, high porosity and high light scattering efficiency, which can lead to good printability. Biodegradable cellulosic polymers are capable to give both good recyclability and good printability to coated paper.

**Keywords:** *Binder migration, Cellouronic acid, CMC, Coating, Starch, Water-soluble polymer*

### INTRODUCTION

Binder migration meaning that binder latex concentrate near the top surface of coating layer occurs occasionally in a drying process for coated paper. Binder migration may harm significantly coating surface properties such as porosity and optical properties, and printability. Binder migration is affected by many factors; base paper properties, coating color compositions, wet coating structure, coating application method,

etc. It was reported<sup>1,2)</sup> that starch formulated in coating colors induced binder latex migration. In this study, the effect of water-soluble cellulosic polymers formulated as a coating additive on binder migration was studied and compared with the effect of other water-soluble polymers, i.e., starch and polyvinyl alcohol. A water-soluble biodegradable cellulosic polymer, polyglucuronic acid (cellouronic acid) sodium salts, was also applied as a coating additive.

## **EXPERIMENTAL**

### **Water-soluble polymer samples**

Cellulosic polymers used were anionic polymers with carboxyl groups, i.e. cellouronic acid and carboxymethyl cellulose (CMC), and nonionic polymers, i.e., hydroxyethyl cellulose (HEC) and hydroxypropyl cellulose (HPC). Cellouronic acid with almost all primary alcohol groups at C-6 oxidized selectively to carboxyl groups (Fig. 1) was prepared from regenerated cellulose with 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-NaBr-NaClO systems<sup>3)</sup>. Its degrees of substitution and polymerization were about 1.0 and 55, respectively. Six grades of sodium salt types of CMC (Finnfix 5, 30, 300, Noviant, Finland and Cellogen PL15, WS-A, FSB, Dai-ichi kogyo seiyaku, Japan) with different degrees of substitution or polymerization were used as shown in Table 1.

Three kinds of starch, i.e., starch phosphate (P-140, Oji Cornstarch, Japan), oxidized starch (Ace C, Oji Cornstarch, Japan) and TEMPO-oxidized starch prepared from commercial oxidized starch (Ace C) with TEMPO-NaBr-NaClO systems, and amylopectin were compared. These were compared also to polyvinyl alcohol (PVA110, Kurare, Japan) as a synthetic water-soluble polymer.

### **Coating**

The coating colors at 50 wt% solids containing the water-soluble polymers were prepared. One pph of each water-soluble polymer were added separately to 100 pph of precipitated calcium carbonate (Brilliant-15, Shiraishi kogyo, Japan) in slurry with 10 pph of carboxylated SB-latex (LX407G, Nippon Zeon, Japan) as a binder. Viscosity of the coating colors diluted to 25 wt% solids was measured using a Brookfield viscometer. All measurements were performed at a fixed shear rate of  $132\text{ s}^{-1}$  at 23 °C for 5 minutes. The coating colors at 50 wt% solids were drawn down on a PET film ( $140\text{ g/m}^2$ ) with a wire bar (No. 14). The coat weight ranged around  $18\text{ g/m}^2$ . The coatings on a film were dried immediately for one minute using a hot-air dryer.

### **Binder migration**

Attenuated Total Reflection (ATR) measurements using an infrared absorption spectrometer (MAGNA-IR 860, Nicolet) were performed to determine the binder latex content near the coating surface. Figure 2 is an example of IR spectrum of coating surface measured by ATR method using a ZnSe crystal with 45° incident angle. The binder latex content near the coating surface was evaluated as a ratio of absorbance of SB-latex at 700 cm<sup>-1</sup> to that of calcium carbonate at 874 cm<sup>-1</sup>. These wave numbers come from conjugated double bonds of the benzene ring in SB-latex and molecular vibration of calcium carbonate, respectively<sup>4)</sup>.

The distribution of binder latex in coating cross-sections was examined with scanning electron microscope (SEM). The binder latex of coatings was tagged with osmium by exposing the samples to osmium tetroxide (Wako Chemicals, Japan) vaper for 12 hours. Cross sections of the coatings were set on SEM mounts and coated with platinum. Osmium mapping images over cross sections of coatings were obtained using an FE-SEM (S-4000, Hitachi, Japan) with energy dispersive X-ray (EDX) analyzer (EMAX-5770, Horiba, Japan). The conditions for this mapping method were 20 kV accelerating voltage, 30 s scanning time for a scan, 40 accumulation scans, 256 × 256 pixels image size for SEM with 40 × 256 pixels in the center scanned area for osmium mapping.

### **Porosity and light scattering coefficient**

Porosity and light scattering coefficient of the coatings were measured. Porosity was determined by a mercury buoyancy method. This method is to determine the pore volume from coating solid volume and apparent coating bulk obtained by measuring buoyancy of the sample immersed in mercury. The coating samples on film were prepared by drying at 50 °C in advance. Here, the coating solid volume was calculated as a sum of the masses each constituent formulated in the coating colors divided by true density. The light scattering coefficient of the coatings was calculated with the Kubelka-Munk equation from the two kinds of reflectance of the coating over two substrates with different reflectances<sup>5)</sup>.

## **RESULTS AND DISCUSSION**

### **Viscosity**

Table 2 shows viscosities of the coating colors containing several water-soluble polymers. When starch

phosphate, oxidized starch or PVA were included in the coating colors, their viscosities showed much lower values than that of no water-soluble polymer. The viscosity of coating colors containing cellulosic polymers showed relatively high values and increased with increasing the degrees of polymerization or substitution at CMC. These cellulosic polymers may interact with pigment or binder latex and form a network structure. In the case of clay-based coating<sup>6)</sup>, the wet coating structure was expressed with a figurative illustration as a network formed by the shear thinning bridging of adsorbed CMC with solution CMC.

### **Binder migration**

Figure 3 shows the binder latex content near the coating surface obtained by ATR measurements for several kinds of coatings with water-soluble polymers. The surface binder latex contents of the coatings with CMC and cellouronic acid showed low values. SEM photographs with osmium, namely, binder latex distribution of a cross-section of coatings without water-soluble polymer (A) and with CMC (B) were shown in Fig.4. The binder latex in the coating without water-soluble polymer was higher at the coating surface than inside the coating, whereas the binder latex was distributed uniformly across the coating with CMC in the thickness direction. When the values of absorbance ratio obtained by ATR measurement is higher than the value of coating with CMC shown in Fig. 3, the binder latex is rich at the parts close to the coating surface. From these results, it is suggested that CMC or cellouronic acid can prevent binder migration to the coating surface.

Figure 5 shows the surface binder latex content of the coatings with some kinds of CMC. Because the absorbance ratio of SB-latex to calcium carbonate showed almost the same values irrespective of the degrees of polymerization or substitution, the difference of these parameters of CMC commonly used in paper coating did not affect the binder migration. The viscosity of coating color also did not affect binder migration because the viscosity was dependent on the degrees of polymerization or substitution, cf. Table 2. According to general considerations<sup>7)</sup>, greater binder migration is expected with more stably dispersed colors with low viscosities than less stably dispersed colors with high viscosities because more stable colors tend to have more free liquid than less stable systems until they become immobilized. However, binder migration was induced by amylopectin formulated to the coating color with high viscosity as shown in Fig. 3 and Table 2, this contradicts the above theory.

With the view of investigating the influence of electric charge of water-soluble polymers upon binder migration, anionic cellulosic polymers with carboxyl groups, i.e., CMC and cellouronic acid, and nonionic

cellulosic polymers, i.e., HEC and HPC, were compared. When cellulosic polymer, irrespective of presence of carboxyl groups with it, was included in the coating color, the binder latex did not migrate to the coating surface as shown in Fig. 6. This finding means that electronic charge of cellulosic polymers did not affect binder migration. Ikeda *et al*<sup>2)</sup> investigated about the effect of starch on binder migration and reported that there was no difference in binder migration between anionic starch phosphate and nonionic hydroxyl ethyl starch. Furthermore, TEMPO-oxidized starch with almost all primary alcohol groups at C-6 oxidized selectively to carboxyl groups prepared by TEMPO-NaBr-NaClO systems was compared with commercial oxidized starch and starch phosphate. None of those kinds of starch prevented the binder migration to the coating surface. (Fig. 7) These results suggest that the chemical interactions between carboxyl groups of water-soluble polymers and anionic site of binder latex or pigment were not a main factor to affect the binder migration.

From these results, it became evident that the viscosity of coating colors and the electronic charge of water-soluble polymers formulated in coatings do not effect the binder migration, and linear polysaccharides as cellulosic polymers, irrespective of presence of carboxyl groups with it, have effect in preventing binder migration. This agree with the result obtained by other authors<sup>8)</sup> that addition of polymer, sodium alginate, CMC or PVA, to the paper coatings inhibited binder latex migration, the order of effectiveness in reducing surface latex concentration was alginate > CMC > PVA. Alginate is a linear polysaccharide formed by the  $\beta$ -1,4 linkage which is similar in structure to cellulose. The structural properties of linear polysaccharides were predicted to somehow exert influences on the binder migration mechanisms.

### **Porosity and light scattering coefficient**

Table 3 shows the porosity and light scattering coefficient of coatings. The two parameters of the coatings with CMC or cellouronic acid showed higher values than that of any of the coatings without water-soluble polymers, or with starch or PVA. It is suggested that flocculated structure coming from the interaction between these cellulosic polymers, pigment and/or binder latex contributed to the high porosity of the coatings. A large solid/air interface areas coming from high porosity provides more light scattering. In practice, coatings formulated with CMC or cellouronic acid showed higher light scattering efficiency. Rennel *et al*<sup>9)</sup> reported that a small amount of CMC led to a minor increase in the porosity of coating based on the plastic pigments. For the clay-based coating<sup>10)</sup>, CMC-addition caused a significantly larger increase in the porosity. In that case, it was suggested that pigment flocculation contributed to the higher porosity in addition to a retarded particle reorientation during the consolidation.

Coatings containing CMC or cellouronic acid showed high porosity and high light scattering efficiency. As these cellulosic polymers also have effect in preventing binder migration, water-soluble cellulosic polymers can be expected to work as a coating agent to control the coating properties.

## CONCLUSIONS

In this study, the influence of several water-soluble polymers upon binder migration that occurs during drying and characteristics of the coating were studied. A water-soluble biodegradable polymer from cellulose, i.e., cellouronic acid, was applied as a coating constituent.

High viscosities of coating colors containing cellulosic polymers suggested that the cellulosic polymers might interact with pigments or binder latex and form a network structure. The binder latex content near the coating surface and its distribution over a coating cross-section were examined by ATR measurements and line analysis using FE-SEM/EDX. When anionic cellulosic polymers were included in the coating colors, the binder latex did not migrate to the coating surface and was distributed uniformly across the coating in the thickness direction. These effects were not observed with starch, irrespective of presence of carboxyl groups with it, or polyvinyl alcohol, but observed with nonionic cellulosic polymers. From these results, it became evident that the viscosity of coating colors and the electronic charge of water-soluble polymers formulated in coatings do not effect the binder migration. Linear polysaccharides as cellulosic polymers, irrespective of presence of carboxyl groups with it, have effect in preventing binder migration resulting in binder latex distribution uniformly across the coating in the thickness direction.

Coatings containing CMC or cellouronic acid showed high levels of porosity and light scattering coefficient. The interaction between these cellulosic polymers and pigment and/or binder latex might contribute to the high porosity of the coatings, and large solid/air interface areas coming from high porosity provided more light scattering, which leads to good printability. Therefore, cellulosic polymers are capable of becoming a printability enhancer. Furthermore, development of recyclable-coated paper with good printability can be expected using biodegradable cellulosic polymers.

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## REFERENCES

- 1 Kline, J. E., 1993 Advanced Coating Fundamentals Symposium proc., Tappi Press, Atlanta, USA, 93 (1993)
- 2 Ikeda, A., Enomae, T. and Onabe, F., Japan Tappi, 55 (2) 82 (2001)
- 3 Isogai, A. and Kato, Y., Cellulose 5 (3) 153 (1998)
- 4 Tachibana, T., Fujihira, S., Shigetomi, K. and Nagai, K., Japan Tappi, 46 (11) 96 (1992)
- 5 Hamada, H., Enomae, T., Onabe, F. and Saito, Y., Japan Tappi, 55 (11) 79 (2001)
- 6 Whalen-Shaw, M., Gautan, N., 1990 Coating Conference proc., Tappi Press, Boston, USA, 371 (1990)
- 7 Whalen-Shaw, M. *et al*, Binder Migration in Paper and Paperboard Coatings, Tappi Press, chapter 2 (1993)
- 8 Steven, G., 1991 Coating Conference proc., Tappi Press, Atlanta, USA, 221 (1991)
- 9 Rennel, C., Eriksson, U. and Rigdahl, M., Nordic Pulp and Paper Research J., no. 4, 254 (1994)
- 10 Eriksson, U. and Rigdehl, M., 1993 TAPPI Advanced Coating Fundamentals Symposium proc., 19 (1993)

Table 1 CMC samples used in this study

NO.	Degree of substitution	Degree of polymerization	Brookfield viscosity (mPa·s), 25 °C
1	0.8	110	10 (2%)
2	0.8	360	30 (2%)
3	0.8	480	300 (2%)
4	0.45~0.55	460~500	15 (1%)
5	0.7~0.8	460~500	750 (2%)
6	0.85~0.95	460~500	200 (2%)

Manufactures: 1~3; Noviant, 4~6; Dai-ichi kogyo seiyaku

Table 2 Viscosity of coating colors

Water-soluble polymer	Brookfield viscosity (mPa·s), 25 wt% solids
None	17
CMC 1	22
CMC 2	25
CMC 3	28
CMC 4	30
CMC 5	38
CMC 6	32
HEC	24
HPC	24
Cellouronic acid	15
Starch phosphate	3
Oxidized starch	4
Amylopectin	36
PVA	4

Table 3 Properties of coatings

Water-soluble polymer	Porosity (%)	Specific scattering coefficient (m <sup>2</sup> /kg)
None	46	173
CMC 2	50	182
Cellouronic acid	49	202
Starch phosphate	47	141
PVA	46	173



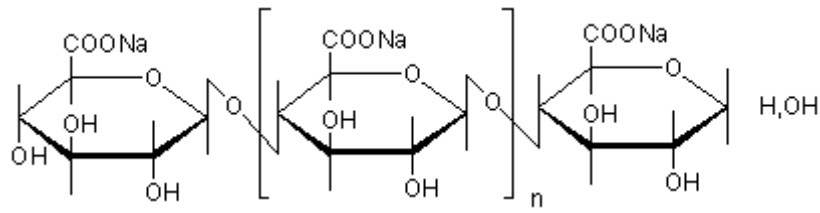


Fig. 1 Cellouronic acid

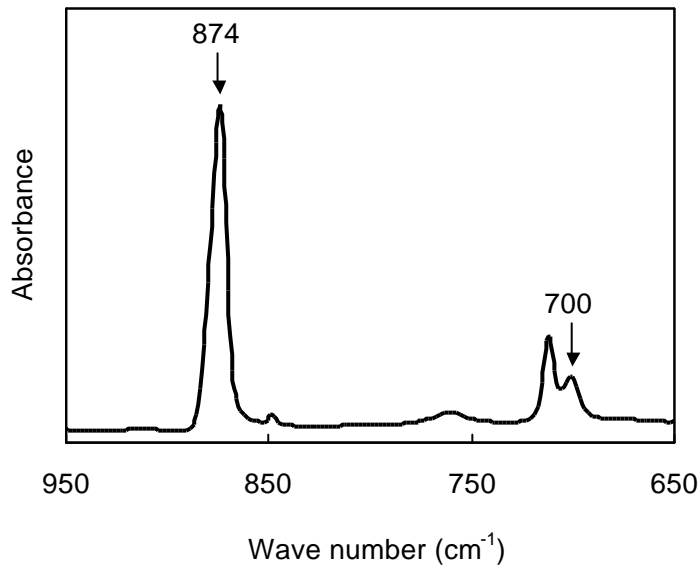


Fig. 2 IR spectrum of coating surface measured by ATR method

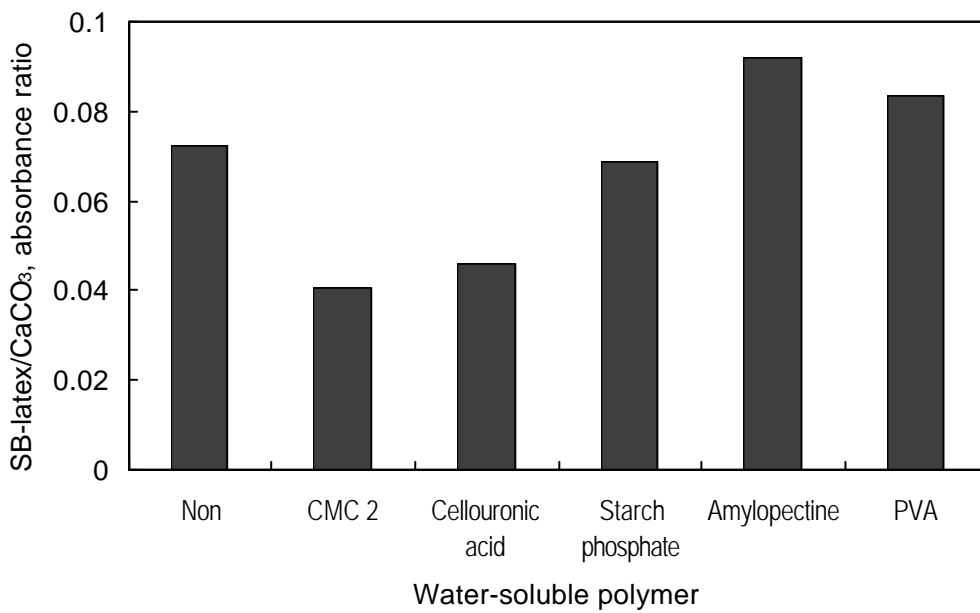


Fig. 3 Surface binder latex content of the coatings with several kinds of water-soluble polymers

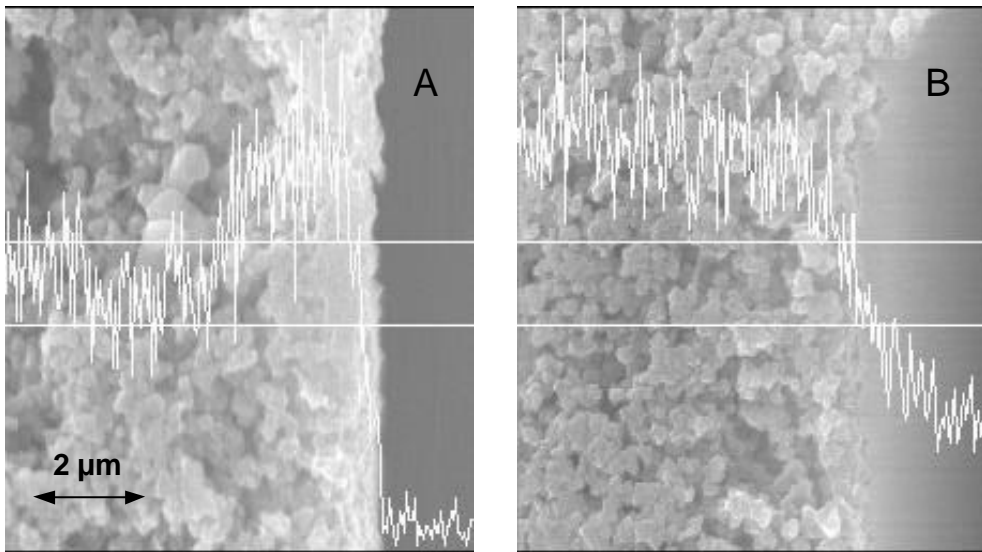


Fig. 4 SEM photographs with latex distribution of a cross-section of coatings. A: no water-soluble polymer, B: CMC formulated

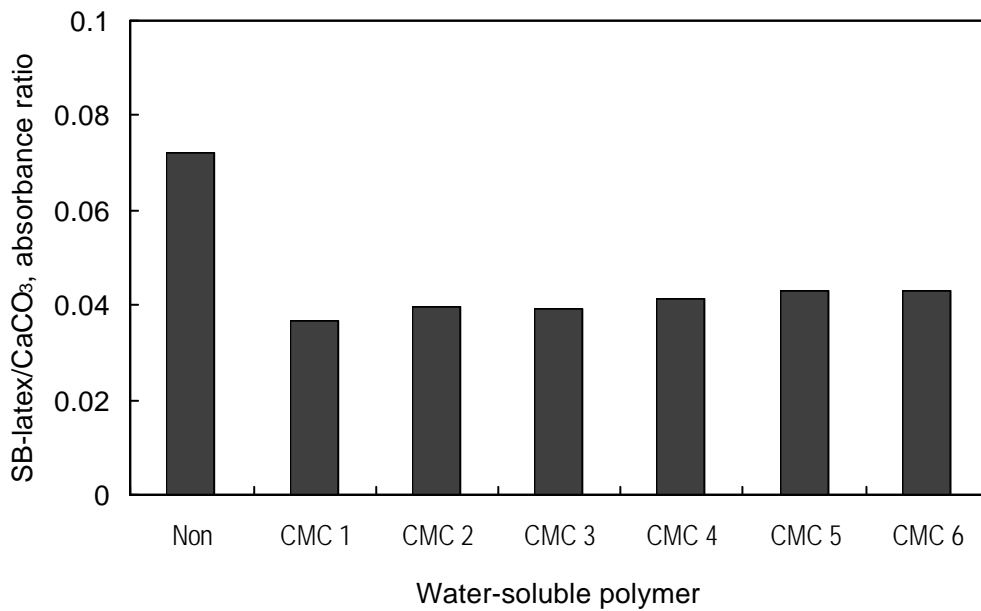


Fig. 5 Surface binder latex content of the coatings with some kinds of CMC

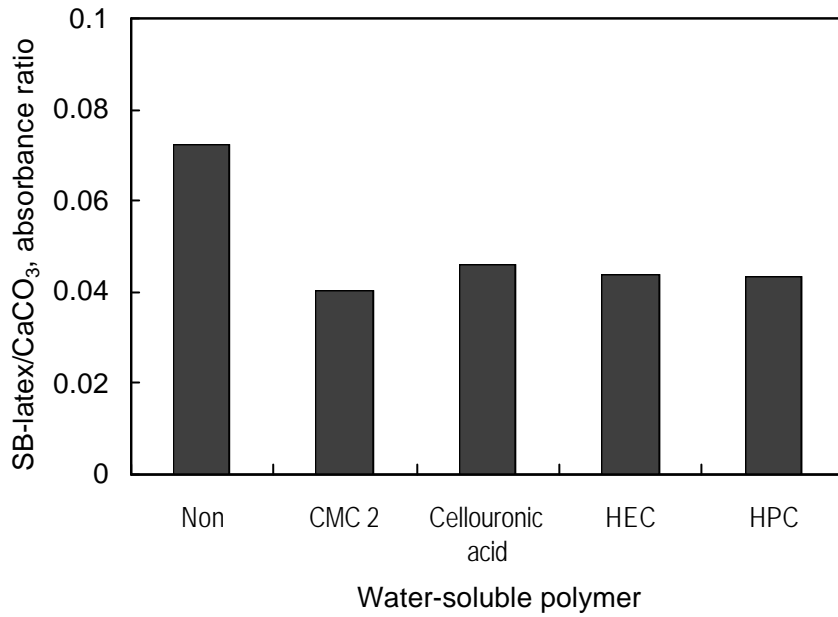


Fig. 6 Surface binder latex content of the coatings with cellulosic polymers

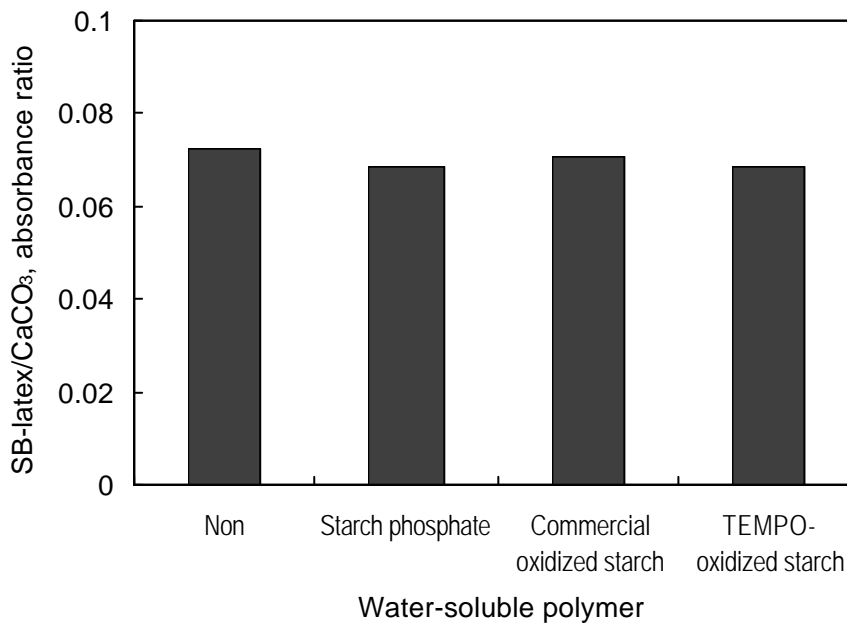


Fig. 7 Surface binder latex content of the coatings with some kinds of starch