

Properties of Polyacrylate Soap-Free Hydrosol with Zirconium Chelate

Zhi Hong Huang, Zhi Ming Xie, Zhuo Mei Li

Institute of Polymer Science, Zhongshan University, Guangzhou 510275, People's Republic of China

Received 2 January 2002; accepted 6 May 2002

ABSTRACT: The effect of the amount of triethanolamine zirconium isopropoxide chelate in acrylate terpolymer soap-free hydrosol on the properties of hydrosol and its film was studied. The addition of the chelate increased the hydrosol viscosity to 20 mPas and improved the hydrosol film water resistance; the water uptake was reduced to 0.6%, and

the hydrosol still retained good resolubility. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2858–2860, 2003

Key words: polyacrylate; hydrosol; chelate; crosslinking reaction

INTRODUCTION

Water-based ink has been widely used in paper substrate surface printing for drink and food packaging.¹ The main binder for this use is an alkali soluble emulsion; this means that at high pH, the polymer particles gradually disintegrate until they dissolve completely in the water phase because there are basic neutralized hydrophilic groups, such as carboxyl (COOH) groups, dispersed on the particles.² The alkaline solution behaves very similarly to conventional solvent-borne polymer solutions in *resolubility*, which is the ability of the dry polymer to be redispersed by the same polymer in the wet state. Resolubility is of prime importance because printing at high press speeds would not be possible if the ink dried in the cells of the gravure cylinder meanwhile, cleaning the plate and the rollers is easier when the polymer in the ink is resoluble.^{2,3} However, the hydrophilic polymer backbone in the alkali soluble emulsion deteriorates the water resistance of the ink film. To overcome these drawbacks, new types of polymer combinations have been developed; research has been done in areas including (1) the search for an optimum combination of different hydrophilic and hydrophobic polymers^{3,4} and an increase in particle hydrophobicity in dry film (2) the choice of a crosslinking system that changed the film water resistance.⁵ However, these two methods sometimes seem to neglect particle resolubility. In this study, we developed these methods and used polyacrylate soap-free hydrosol combined with an alkaline crosslinking agent that could improve both hydrosol

hydrophilicity in flow state and water resistance in the fully dried film.

Some of the zirconium chelates and their crosslinked products are light in color and have proven safe when used in ink for food package printing,^{5,6} thus we chose alkaline triethanolamine chelate of zirconium isopropoxide [Zr(TEA)₂(OR)₂; abbreviated as ZrE]. The effect of chelate amount on the properties of the polymer hydrosol and its dried film were studied.

EXPERIMENTAL

Materials

Polyacrylate hydrosol neutralized with ammonia until it reached pH 8 was synthesized in our laboratory; the terpolymer (monomer mass ratio methyl methacrylate : butyl acrylate : acrylic acid (MMA : BA : AA) = 48.77:46.69:4.54) weight content was 30% with 10% as a isopropanol cosolvent (IPA). ZrE was provided by DuPont (Wilmington, DE).

Rheology measurements

Rheology was studied by the measurement of the viscosity [η (mPa s)] against shear rate (s^{-1}). These measurements were performed on a Rheotest 2-50Hz-TYPRV2 meter (Medingen, Sitzfreital, Germany).

Surface tension measurement

A surface tension meter (Experimental Instrument Factory, Chengde, Hubai, China) was used to measure the surface tension of the hydrosol.

Hydrosol stability

Electrolyte stability

Hydrosol electrolyte stability was measured according to ref.⁷ Critical coagulation concentration (ccc) was

Correspondence to: Z. Huang (cheshzh@zsu.edu.cn).

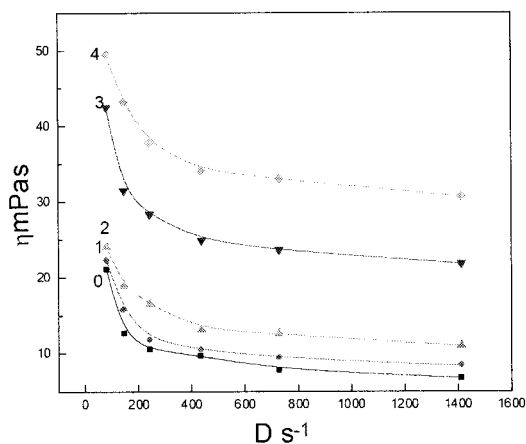


Figure 1 Effect of ZrE amount on the hydrosol rheology.

used to judge hydrosol electrolyte stability; the higher the ccc was the better was the hydrosol electrolyte stability.

Freeze–thaw stability

Hydrosol freeze–thaw stability was judged according to η increment when the samples thawed; the freeze–thaw stability was good when the samples kept their η after freezing. We put the hydrosol in the refrigerator at (-17°C) for 48 h and then thawed it at room temperature for a certain time. A Zahn cup (4#) was used to measure hydrosol η .

Film water resistance

The hydrosol film water resistance was judged by the water uptake (U_w) after the tested samples were soaked in water. We sprayed the hydrosol films on a polytetrafluoroethylene (PTFE) plate, dried them at different temperatures for 30 min [a sample was dried at room temperature (RT) for 7 days]; weighed them as m_1 , soaked them in water for 24 h, cleaned the film surface water with paper tissue, weighted them again as m_2 , and calculated the weight increment percentage, or U_w , as follows:

$$U_w = \frac{m_2 - m_1}{m_1} \%$$

RESULTS AND DISCUSSION

Rheology of polyacrylate hydrosol with ZrE

The viscosities of hydrosols before and after the addition of ZrE are shown in Figure 1. The number listed on the curve represents the chelate weight (grams) in 100 mL of hydrosol.

The addition of ZrE in hydrosol increased the hydrosol η (Fig. 1). Alkaline ZrE with triethanolamine

could convert $-\text{COOH}$ to $-\text{COO}^-$ in the polymer. The negative ions in the polymer chain attracted a thick layer of water, and triethanolamine in ZrE could also closely link the polymer and water by H bonding. All of these increased the hydrosol η . However, when the ZrE amount was less than 2%, the hydrosol η was not changed so much, and the hydrosol still retained good flowability, which is needed for practical use.

Surface tension of polyacrylate hydrosol with ZrE

ZrE decreased the hydrosol surface tension (Fig. 2). Alkaline ZrE increased the polymer hydrophilicity, and the hydrophilic parts of the particles acted as surfactants more efficiently; meanwhile, as the polymers were more in a stretch configuration, more cosolvent was released from the originally buried hydrophobic particle core, and the cosolvent was helpful for the decrement of surface tension.⁸

Polyacrylate hydrosol stability

The stabilities of the hydrosol are listed in Table I.

The hydrosol electrolyte stability was slightly improved by the increment of ZrE. As mentioned previously, ZrE increased the polymer ionization and increased the hydrosol electrolyte stability.

ZrE had no notable effect on hydrosol freeze–thaw stability because ZrE provided two opposite effects on the stability. First, in the hydrosol, ZrE could link the polymer and water by H bonding as its component had enough OH groups, leading to gel formation when the hydrosol was frozen. This was unfavorable for hydrosol freeze–thaw stability. Second, however, ZrE linked on the polymer showed steric stability. The ring structure could separate the polymers and decrease the chance of polymers being linked each other, which was helpful for the hydrosol stability. These

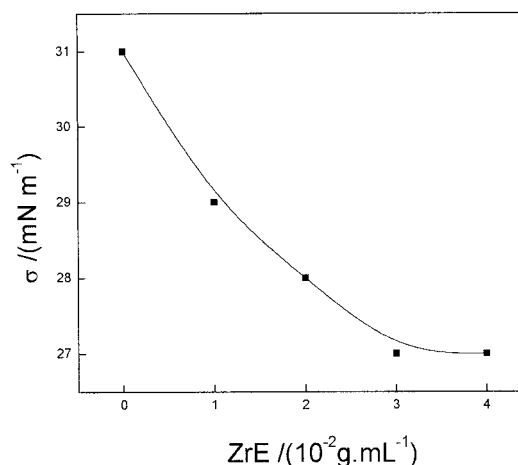


Figure 2 Effect of ZrE amount on the hydrosol surface tension.

TABLE I
Effect of ZrE Amount on Hydrosol Stability

ZrE amount (g/100 mL of hydrosol)	0	1	2	3	4
Electrolyte stability: ccc (M)	0.75	0.76	0.76	0.78	0.78
Freeze-thaw stability					
Viscosity of hydrosol before freezing (s)	7.4	10.0	13.5	15.5	21.5
Viscosity of the hydrosol after thawing (s)	7.4	11.0	14.0	15.5	21.5

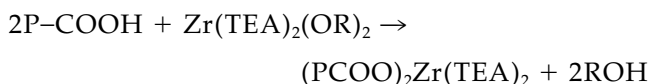
opposite effects resulted in a hydrosol freeze-thaw stability.

Film U_w

The hydrosol film U_w is shown in Figure 3.

The test film was dried at RT for 7 days or dried at 80, 100, 120°C for 30 min.

The water resistance of the hydrosol film with ZrE dried for 7 days at RT was improved notably. Similar experiment results were observed by Ricardo when he used a Zr compound in a polyacrylate emulsion;⁵ he described this as a chemical crosslinking reaction in a polymer film under this condition. The chelate could react with polymer like this:⁶



Here, P-COOH represents polymer with carboxyl groups. One of the reaction products is IPA thus, we think at RT, the existence of IPA in the hydrosol could oppress the hydrolysis of isopropyl oxide in ZrE. When the hydrosol was dried, IPA evaporated, the oppression was released, part of ZrE gradually began to crosslink with the polymer, and the film water

resistance increased. At higher temperatures, IPA in the hydrosol could easily evaporate, and the crosslinking reaction sped up; the film water resistance was improved more rapidly and notably. When dried at 120°C for 30 min, the hydrosol film U_w was reduced to only 0.6%. The mechanism of the crosslinking reaction will be discussed in our next article.

From the previous measurements, we obtained a satisfied complex system that could retain good flowability and film water resistance, and this met the requirements of what we began to study.

With regard to another key property for ink use, resolubility, we tested the film resolubility of the polyacrylate soap-free hydrosol with 2% ZrE according to ref. 3. The test film was dried at RT for 1 h. The sample solved in the same hydrosol within 30 s, showing good resolubility.

CONCLUSION

The effect of ZrE amount on the properties of the polyacrylate hydrosol showed that (1) the hydrosol retained good flowability with 2% ZrE, and (2) ZrE decreased the hydrosol surface tension, increased the hydrosol electrolyte stability, and had no effect on the freeze-thaw stability. The addition of ZrE in the hydrosol improved the hydrosol film water resistance, when the film was dried at 120°C for 30 min, the film U_w dropped down to 0.6%, which overcame the drawback of alkali soluble emulsions in water-based inks. Meanwhile, the hydrosol with ZrE still retained reversibility as an alkali soluble emulsion.

References

- Hutchinson, G. H. *Surf Coat Intern* 1999, 5, 233.
- Padget, J. C. *J Coat Technol* 1994, 66, 839, 89.
- Peters, A.; Honen, P.; Overbeek, A.; Griffioen, S.; Annable, T. *Surf Coat Int B* 2001, 84, 169.
- Smith, G. A.; Boucher, S. P.; Grinstein, R. H.; Henkel Corp.; U.S. Pat 5,373,045; 1994.
- Nagila, M. P. S. *Polym Engin Sci* 1999, 39, 543.
- Shakir, Y. *Handbook of Crosslinkers*; Chemical Industrial Press: Beijing, 1990; Chapter 4.
- Ono, H.; Saeki, H. *Colloid Polym Sci* 1975, 253, 744.
- Zhu, J.; Bierwagen, G. P. *Prog Org Coat* 1995, 26, 87.

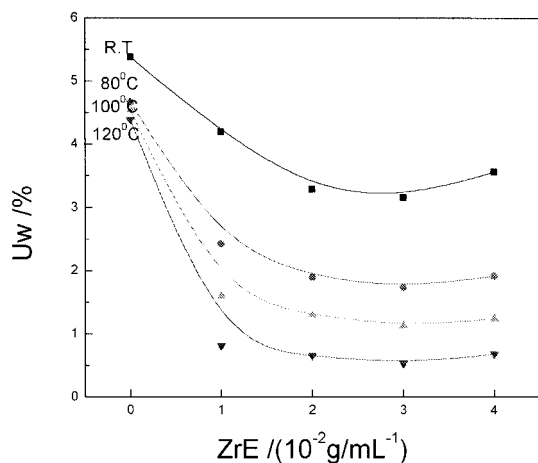


Figure 3 Effect of ZrE amount on film U_w .