

Effect of Polymerizable Emulsifiers on the Properties of Polyacrylate Latexes and the Relative Waterborne Inks

Yongming Chen, Xiaoyu Li, and Haiqiao Wang

Beijing Engineering Research Center for the Synthesis and Applications of Waterborne Polymers, Beijing University of Chemical Technology, Beijing 100029, China
E-mail: wanghaiqiao@mail.buct.edu.cn

Abstract. Polyacrylate latexes made from non-polymerizable emulsifiers and their inks typically suffer from poor ethanol resistance stability and low adhesion on biaxially oriented polypropylene (BOPP) and polyethylene (PE) films. In this contribution, a composite emulsifier system containing a polymerizable anionic and a polymerizable non-ionic emulsifier was used to synthesize core-shell polyacrylate latexes. Additionally, a control latex was also prepared using a traditional emulsifier TX-30 to replace the polymerizable non-ionic emulsifier in the above composite emulsifiers. The effect of the polymerizable emulsifier on ethanol resistance, Ca^{2+} resistance stability, and adhesion on PE and BOPP films of the latexes and the inks, and water resistance of the latex films and ink films were studied. The results show that, when compared with the control latex, the one made from double polymerizable compound emulsifier system and its ink demonstrates better ethanol resistance, higher stability of calcium ions and higher adhesion on BOPP and PE. When the ratio of anionic emulsifier to non-ionic emulsifier is 1.5/1 and the total dosage is 2.5 wt%, the latex showed the best comprehensive performance. The calcium ion resistance stability of the latex increased from 5% of the control latex to 25%. Accordingly, the adhesion of yellow ink on BOPP film increased from 92% of the ink based on the control latex to 99% and increased from 99% to 100% on PE film. The adhesion of blue ink on BOPP film increased from 92% to 99%, and from 99% to 100% on PE film. These results indicate that the fully polymerizable emulsifiers can effectively improve the properties of latex. © 2022 Society for Imaging Science and Technology.

[DOI: 10.2352/J.ImagingSci.Technol.2022.66.2.020404]

1. INTRODUCTION

With increasingly stringent environmental regulations in the world, it is a trend to develop water-based environment-friendly products in high pollution industries such as coatings and inks [1–4]. Polyacrylate latex is one of the most widely used film-forming resin (or binder) in water-based products due to its good color and light retention and low cost [5, 6].

Polyacrylate latexes are generally synthesized with traditional non-reactive emulsifiers, and the emulsifiers are extremely important for emulsion polymerization and the properties of the latex [7]. In the latex, the emulsifiers are absorbed on the surface of the latex particles by physical force, and easy to be desorbed from the surface [8–10], resulting in low calcium ion resistance stability of the latex,

thus affecting the stability and other practical performance of coating, inks, and other products. In addition, the emulsifier is easy to migrate to the surface of latex film, resulting in many problems such as slow film-forming speed, poor water resistance, and poor adhesion [11].

An effective strategy to solve these problems is to use polymerizable emulsifier instead of traditional non-reactive emulsifier. The polymerizable emulsifiers are chemically bonded to the molecular chains of the polymers. When the polymer is stored and used, the phenomenon of migration and desorption of emulsifier molecules will not occur [12]. Therefore, polymerizable emulsifiers can significantly improve the physical and chemical properties of latex, such as water- and solvent-resistance. At present, there are many reports about the use of polymerizable emulsifiers to prepare latexes for improving the properties of the latexes. Chen et al. [10] prepared an Ag nano-particles composite coating with good hydrophilicity, wettability, and good antibacterial and fouling resistance via emulsion polymerization by using a polymerizable emulsifier, sodium mono-dodecyl maleate (SMDM). They found that, in a very short time, the nanocomposite coating can approach or even reach the superhydrophilic state. Li et al. [9] prepared two kinds of latexes containing styrene and butyl acrylate using a compound emulsifier system of polymerizable emulsifier, ammonium sulfate allyl nonphenoxy polyethoxy (10) ether (DNS-86), with a non-reactive emulsifier, polyethylene glycol-tert-octyl phenyl ether (Triton X-100). They found that polymerizable emulsifiers can improve the solid content and monomer conversion of the latexes. Gong et al. [13] used DNS-86 to synthesize a silicone-acrylate dispersion with methyl methacrylate (MMA) as the hard monomer and butyl methacrylate (BA) as the soft monomer, and benzyl methacrylate (BZMA) and modified monomer vinyl triethoxysilane (VTEs) as functional monomers. The dispersions demonstrated good thermal and chemical stability, and their relative latex films showed high hydrophobicity. Zhang, et al. [14] compared the properties of pressure-sensitive adhesives (PSA) produced by emulsion polymerization using a conventional and a polymerizable emulsifier, respectively. They found that the latex film with a polymerizable emulsifier showed substantially greater levels of tack, peel, and shear performance because the binding of surfactant to the adhesive polymer backbone inhibits its movement to film surfaces during film formation, which helps maintain

Received June 16, 2021; accepted for publication Sept. 22, 2021; published online Oct. 27, 2021. Associate Editor: Min Xu.

1062-3701/2022/66(2)/020404/7/\$25.00

the performance of the adhesive film. Bi et al. [15] prepared high hydrophobic films using latexes synthesized with polymerizable emulsifiers. The films showed excellent antibacterial and anti-adhesion properties, the antibacterial rate and inhibition adhesion efficiency were more than 99.9%. Clearly, it is an effective strategy to improve the performance of the polyacrylate latex and its corresponding products by using polymerizable emulsifiers instead of traditional non-reactive emulsifiers.

Recently, polyacrylate latex has been used more and more widely as a binder in the field of water-based ink. As a core component of waterborne ink, polyacrylate latex binder plays a decisive role in the performance of waterborne ink. To meet the demand of water-based ink performance in practical application, the polyacrylate latex should have good calcium ion stability, high adhesion on BOPP or PE and other plastic substrates, good water-resistance of the film. However, the polyacrylate latex prepared with traditional emulsifiers generally has poor calcium ion stability, and its adhesion on BOPP or PE is also low, and its corresponding latex film has poor water resistance. In addition, in the practice application, it is often necessary to add a certain amount of ethanol into the ink to improve the drying speed of the ink, which requires the polyacrylate latex to have a very good ethanol resistant stability. However, because ethanol can dissolve the emulsifier around the latex particles and destroy the protective layer of the emulsifier, polyacrylate latexes generally have poor tolerance to ethanol. In view of the advantage of polymerizable emulsifiers, it is reasonable to believe that it is helpful to solve these problems using polymerizable emulsifiers instead of traditional non-reactive small molecular emulsifiers. To the best of our knowledge, there is no report about the effect of polymerizable emulsifiers on the properties of latex binders and their waterborne inks. Especially, there is no study on ethanol resistance of polyacrylate latex and its ink. In addition, the study about the polymerizable emulsifiers in the above-mentioned literature is almost based on a sole anionic polymerizable emulsifier or a composite emulsifier system composed of a polymerizable anionic emulsifier and a non-reactive non-ionic emulsifier, but there are few reports on the combination of polymerizable anionic emulsifier and polymerizable non-ionic emulsifier.

In this contribution, a “soft core and hard shell” latex was synthesized with MMA/BA/EHA as the main monomer via emulsion polymerization by using composite emulsifiers composed of a polymerizable anionic emulsifier SR-10 and a polymerizable nonionic emulsifier. At the same time, a control latex was also synthesized via using a non-reactive non-ionic emulsifier TX-30 to replace the polymerizable nonionic emulsifier in the above composite emulsifier. The effect of the emulsifier on the properties of the latex and its waterborne ink was studied in detail.

Table I. Formulation used to synthesize the latex.

	MMA/g	BA/g	EHA/g	TPGDA/g	DAAM/g	AA/g
Seed	8.5	11.5	7.7	0.2	1.68	0
Core layer	74.5	100.5	81.3	2.5	15.12	0
Shell layer	198.0	19.5	49.5	0	0	5.5

2. EXPERIMENTAL

2.1 Materials

Methyl methacrylate (MMA), Butyl acrylate (BA), Shanghai Jiamei Fine Chemical Co., Ltd.; 2-Ethylhexyl acrylate (EHA), Jiangsu Itrade Chemical Co., Ltd.; Dodecanethiol, Maclean; Allyloxy fatty alcohol oxyethylene ether ammonium sulfate (SR-10), CADEKA Corporation; alkyl phenol polyoxyethylene ether (TX-30), Jiangxi Hongrun Chemical Co. Ltd; methylallyl alcohol polyoxyethylene ether (608), Jiangsu DYNAMIC CHEMICAL Co., Ltd.

2.2 Synthesis of Water-Based Polyacrylate Latexes

Polyacrylate Latexes were synthesized by semi-continuous seed emulsion polymerization. The detailed preparation procedure is the same as described in literature [16]. A typical monomer formulation used to synthesize the latex is listed in Table I.

2.3 Preparation of Water-Based Ink

The water-based ink was prepared by adding a water-based blue paste or water-based yellow paste into polyacrylate latex according to the mass ratio of 3:7, then stirring at a certain speed for 30 min.

2.4 Preparation of Latex Film

The as-prepared polyacrylate latex (10g) was first poured into a Teflon disk (8 mm × 6 mm) and dried at room temperature for 3 days, then the latex film (1mm thickness) was dried in a vacuum oven at 60°C for 12 h to remove the residual water. Finally, the obtained transparent latex film was placed in a desiccator and stored at room temperature.

2.5 Preparation of Ink Spline

The prepared ink was scraped on the plastic substrate with 4#wire rod, then the obtained spline was put into a desiccator to dry at 50°C for 10min, and then was blown for 1–2 min with a hot air blower.

2.6 Characterization

The glass transition temperature (T_g) of the polyacrylate latexes were measured by Differential Scanning Calorimeter (DSC, Mettler Toledo Differential Scanning Calorimeter, TA Instruments Co., Ltd). The Z average particle size was measured by dynamic light scattering (DLS, Malvern Zeta-sizer, Nano-ZS, UK). The contact angle of water on polyacrylate latex films was tested using contact angle meter (Data physics-OCA 20, Germany). The morphology of latex particles was analyzed by transmission electron microscope (TEM, Hitachi HT7700, Hitachi High-Tech Co., Ltd).

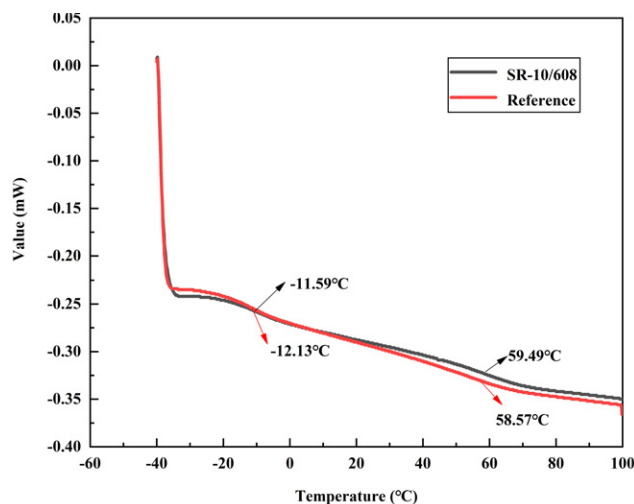


Figure 1. DSC curves of the latex and the control latex.

Measurement of adhesion of the latex was carried out in accordance with the test standard ISO 2409-2006. A 3M tape is covered on the ink samples, then is quickly peeled off from the plastic surface at 90 degrees. The remaining ink film on the spline accounts for the percentage of the total ink film is recorded as the adhesion ratio.

Characterization of the stability against ethanol of the latex is conducted as follows: Ethanol with a mass fraction of 20% is added to latexes, and then the mixture is put into an oven at 50°C for different times. The changes in particle size and viscosity of the latexes with time are recorded.

Measurement of water absorption of latex film: The latex film with a mass of about 0.5g was completely immersed in 50 mL of deionized water for 24, 48, and 72 h, respectively, and then the water on the surface was wiped off and weighed one by one. Water absorption (S) of the latex film (S) is calculated according to formula Eq. (1):

$$S = \frac{m_1 - m_2}{m_1} \quad (1)$$

Where m_1 (g) is the mass of the latex before immersion, m_2 (g) is the mass of the latex after immersion.

3. RESULTS AND DISCUSSION

3.1 Latex Tg and Morphology Analysis

Tgs of a typical polyacrylate latex film and the control latex were measured by DSC, and the results are shown in Figure 1. It can be seen that both latexes have two glass transition temperatures, proving that the prepared latexes possess a core-shell composite structure. The Tgs of the latex film are -11.6°C and 59.5°C, which are higher than that of the control latex of -12.1°C and 58.6°C. This may be because that the double bond of the emulsifier 608 was broken off, and the emulsifier was grafted onto the polymer molecules [17], resulting in an increase of side-chain volume of the polymer chain, which leads to the increase of Tg, because Tg of the polymer increases with the increase of side-chain volume.

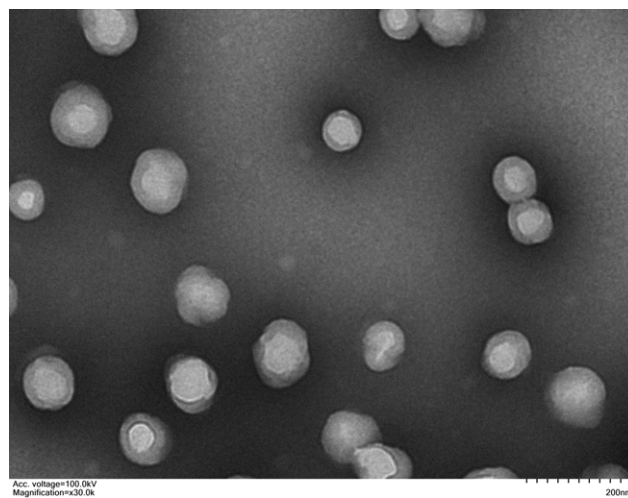


Figure 2. TEM diagram of the latex.

The morphology of the latex particles was characterized by TEM. The latex particles were negatively stained by phosphotungstic acid (PTA). PTA is widely used as an electron stain when TEM is used to characterize the core-shell structure of latexes. In the TEM diagram, the inner core pattern is generally bright because it is not stained or light-stained, while the outer shell is dark because it is deposited with PTA. As can be observed from Figure 2 that, the latex particles as-synthesized demonstrated a clear shell-core double-layer structure, and the shell pattern is dark, while the core layer is relatively bright.

3.2 Contact Angle Analysis

The non-reactive emulsifier exists around the latex particles in the form of physical adsorption. With the evaporate of water, the emulsifier would migrate to the surface of the film with low surface tension. Because of the effect of hydrophilic groups in the emulsifier, the surface of the latex film becomes more hydrophilic, which increases the surface roughness of the latex film and decreases the contact angle between the surface of the latex film and water. Here, the water contact angles of the latex films with different mass ratios of the polymerizable anionic emulsifier to the polymerizable non-ionic emulsifier, and that of the control latex film were measured, and the results are shown in Figure 3.

The water contact angle of the control latex film is 62°. When the emulsifier TX-30 in the control latex was replaced by the polymerizable emulsifier 608, the contact angle of the latex film increased significantly, indicating that the emulsifier 608 weakens the hydrophilicity of the film surface. This result also proves that the use of the polymerizable emulsifier can effectively solve the problem of non-reactive emulsifier easily migrating to the surface of the film, which leads to enhancement of the hydrophilicity of the film surface. In addition, the mass ratios of SR-10 to 608 also have an effect on the hydrophilicity of the film surface. That is, with the increase of 608 content in the compound emulsifier system, the contact angle of the latex film decreases. Because the emulsifier SR-10 contains ionic

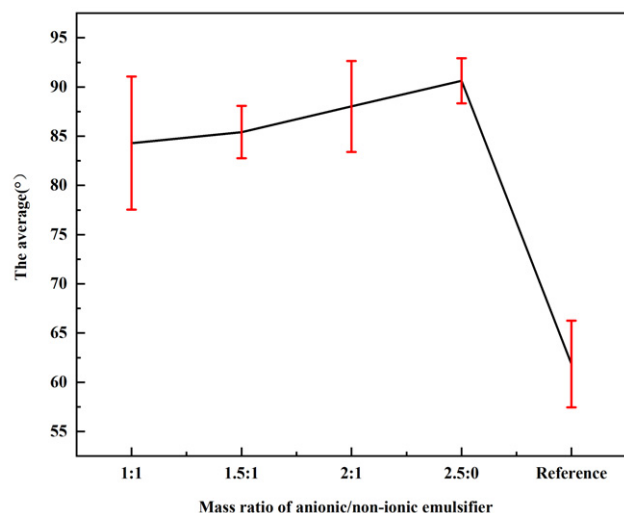


Figure 3. The water contact angle of the latex films.

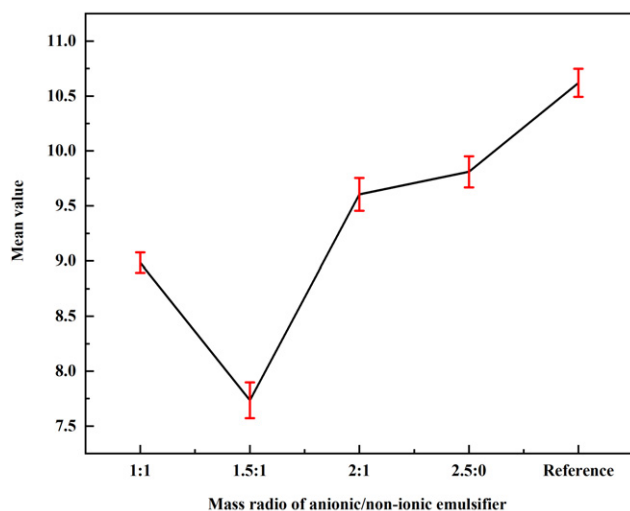


Figure 4. Water absorption of the latex films.

groups with stronger hydrophilicity, with the increase of the SR-10 and the decrease of 608 in content, the hydrophilicity of the surface of the latex films becomes stronger and stronger, resulting in a gradual increase in contact angle.

3.3 Water Absorption of Latex Film Analysis

Previous studies have found that the use of the polymerizable emulsifier 608 can make the latex film more hydrophobic because it avoided migration of non-reactive emulsifier. Therefore, these latex films would have better water resistance, that is, smaller water absorption rate. Here, the effect of emulsifier on the water absorption rate of the latex films was studied, and results are shown in Figure 4.

It can be seen from Fig. 4 that the emulsifier has a significant effect on the water absorption rate of the latex films. Not surprisingly, the water absorption rate of the film based on the latex synthesized with polymerizable non-ionic emulsifier was significantly lower than that with a traditional non-ionic emulsifier. In addition, one can find that the mass

Table II. Surface roughness of the latex films.

SR-10/608 mass ratio	1:1	1.5:1	2:1	2.5:0	Reference
Roughness (nm)	10.4	7.03	4.22	6.44	11.8

ratio of the anionic to non-ionic emulsifier also has an effect on the water absorption of the latex films. This can also be explained by the fact that SR-10 contains ionic groups with stronger hydrophilicity than 608. So as the ratio of anions to non-ions increases, the water absorption of the films increases accordingly. As for that the film with a high water absorption when the ratio of anions to non-ions is 1:1, it may be caused by the poor performance of the latex obtained under this emulsifier formula, which leads to poor film quality. As a result, when the mass ratio of SR-10 to 608 was 1.5:1, the relative latex film possessed the lowest water absorption rate.

3.4 Surface Morphology Analysis

The surface morphology of the films was characterized by AFM for studying the effect of emulsifiers. The AFM images are shown in Figure 5, and the surface roughness of the latex films measured by AFM is summarized in Table II.

The surface roughness of the film based on the latex synthesized with a traditional non-ionic emulsifier is 11.8 nm. Clearly, it is larger than that based on the film with a polymerizable non-ionic emulsifier, therefore the film surface of the latter is smoother. This result can be explained by the enrichment of the non-polymerizable non-ionic emulsifier at the film-air interface caused by the flux of water carrying the emulsifier towards the surface during film drying [18], which leads to the film surface becoming rough.

In addition, the mass ratio of the SR-10 to 608 also has an effect on the surface roughness, and the surface roughness decreases with the decrease of the amount of emulsifier 608. When the ratio of SR-10 to 608 is 2:1, the surface roughness of the latex film is only 4.22 nm. However, when SR-10 was used as the sole emulsifier, the roughness of the obtained latex film rose to 6.44 nm.

3.5 Latex Stability Against Ethanol Analysis

Stability of latex against ethanol is an extremely important property for the application in the ink printing field. In the practical application of the waterborne ink, a certain amount of ethanol was generally added into the ink to improve the drying speed of the ink and the printing speed. However, the protective layer of the emulsifiers around the latex particles will be thinned or destroyed after adding ethanol due to the dissolving effect of ethanol on emulsifiers, resulting in a change of latex in particle size and viscosity. Generally, the large the particle size and viscosity of the latex change with time, the worse its stability. Here, stability against ethanol of the latexes was characterized for evaluating the effect of the polymerizable emulsifier. The results are listed in Table III and Table IV.

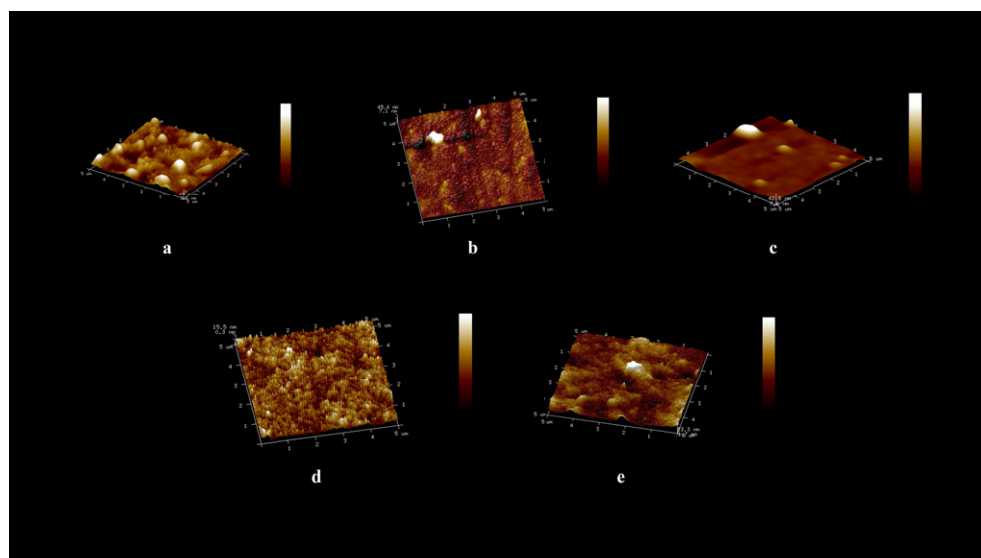


Figure 5. AFM images of the latex films. (a) control sample; (b) SR-10/608 is 1:1; (c) SR-10/608 is 1.5:1; (d) SR-10/608 is 2:1; (e) SR-10/608 is 2.5:0.

Table III. Change of the latexes containing 20wt% ethanol in particle size with time.

Mass ratio of anionic /non-ionic emulsifier	Latex particle size(nm)	Particle size of the Latexes containing 20 wt% ethanol (nm)		
		0d	1d	2d
1:1	140	193	217	311
1.5:1	127	162	163	157
2:1	122	163	188	309
2.5:0	109	154	140	182
Reference	122	152	205	208

Table IV. Change of the latexes containing 20 wt% ethanol in viscosity with time.

Mass ratio of anionic/non-ionic emulsifier	Latex viscosity (mPa.s)	Viscosity of the Latexes containing 20wt% ethanol (mPa.s)		
		0d	1d	2d
1:1	63	230	346	354
1.5:1	57	94	124	107
2:1	61	202	368	346
2.5:0	55	91	97	97
Reference	104	148	141	144

It can be found from Table III that the particle size of all the latexes increased significantly after adding ethanol. Although the increment of the control latex in particle size was the smallest, only 30 nm, the change of the size after 2 days in the oven at 50°C was very large, increased by 86 nm, which indicates that its ethanol resistance stability is poor. In contrast, the particle size change of the latex with SR-10/608 mass ratio of 1.5:1 was slightly larger than that of the

control latex after adding ethanol, but the size change was smaller after 2 days in the oven, only increased by about 30 nm, suggesting that this latex possesses better ethanol resistance stability than the control latex. As for the other latexes, because the emulsifiers used in the synthesis are not the best formula, the stability of the as-synthesized latexes is not good enough, resulting in their poor ethanol resistance stability.

It can be seen from the variation of viscosity in Table IV that, after adding ethanol, the viscosity of the latexes all increased. Among these latexes, after being placed in the oven at 50°C for 2 days, the viscosity of the control latex changed the least and even became smaller. Besides, the two latexes with SR-10/608 mass ratio of 1.5:1 or 2.5:0 also shown small viscosity variation. Because viscosity of the latex is affected by its particle size, and decreases with an increase in the particle size, the slight change of viscosity does not necessarily suggest the good ethanol resistance stability of the latex. Only when the particle size and viscosity of latex change very small simultaneously, it shows that the latex has good ethanol resistance stability. Thus, it can be concluded that the latex synthesized with SR-10/608 mass ratio of 1.5:1 has the best ethanol resistance stability among these latexes. Obviously, better stability against ethanol of this latex than the control latex can be attributed to the application of polymerizable emulsifier 608, because it overcomes the problem of the non-reactive emulsifier TX-30 easy to desorb from the latex particle surface.

3.6 Ca²⁺ Resistance Stability Analysis

Water-based ink is mainly composed of binder, color paste and some additives, such as coalescent aids, wetting agent, etc. Color paste generally has high content of electrolyte. Traditional non-ionic emulsifiers exist around latex particles by physical adsorption, and are easy to desorb in high concentration electrolyte environment, leading to

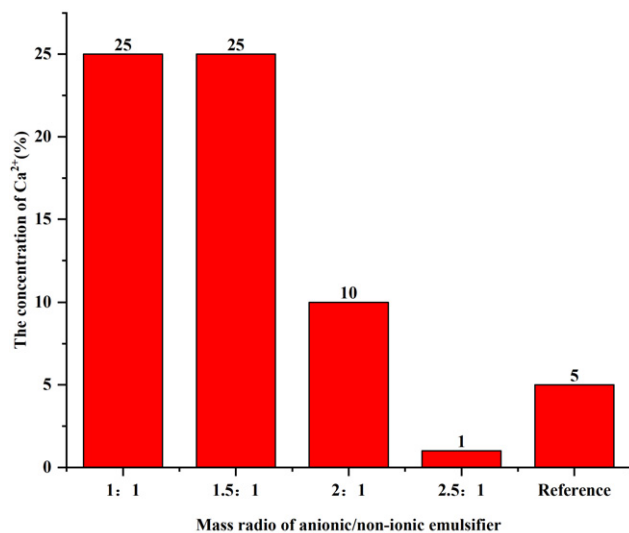
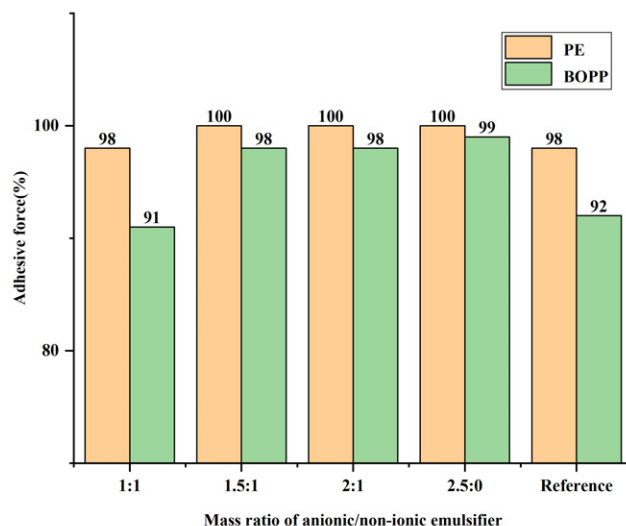
Figure 6. Ca^{2+} resistance stability of the latexes.

Figure 8. Adhesion of the blue inks on BOPP and PE thin films.

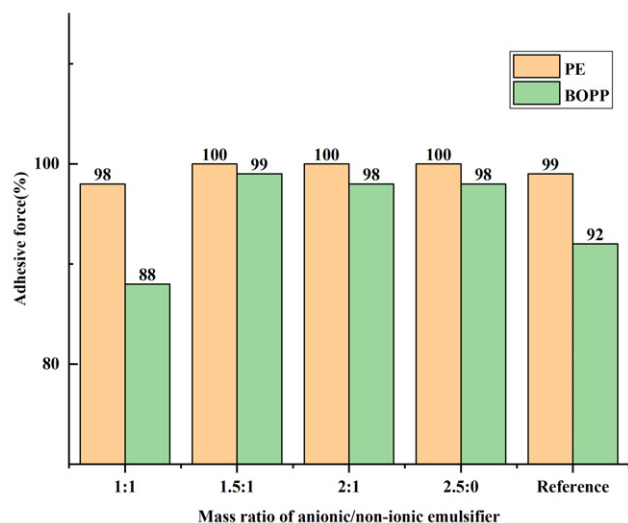


Figure 7. Adhesion of the yellow inks on BOPP and PE thin films.

ink instability. Reactive emulsifiers are chemical bonded in the latex particles, providing stable steric hindrance, making it difficult for electrolyte ions to penetrate into the double electric layer, so they can effectively improve the stability of Ca^{2+} . Improvement of calcium ion stability of latex binder is very important for the practical application. In the experiment, the calcium ion stability of the latexes was measured for studying the effect of the polymerizable emulsifier 608. The results are shown in Figure 6.

The Ca^{2+} resistance stability of the latex prepared by the traditional non-ionic emulsifier is 5%. When the non-ionic emulsifier TX-30 was replaced by the polymerizable 608, the as-synthesized latexes all showed higher Ca^{2+} stability than the control latex. Especially, the Ca^{2+} resistance stability of the two latexes synthesized with SR-10/608 mass ratio of 1:1 and 1.5:1 reached an astonishing 25%. Also, it can be found that when SR-10 was used as sole emulsifier, the Ca^{2+} resistance stability of the latex only reached 1%,

even lower than that of the control latex, which highlights the importance of non-ionic emulsifier to the improvement of Ca^{2+} resistance stability of latex. These results indicate that using polymerizable non-ionic emulsifier instead of non-reactive non-ionic one is an effective strategy to improve the calcium ion stability of latexes.

3.7 Adhesion Analysis

In the experiment, yellow and blue ink were prepared, respectively, by mixed color paste with latex without adding any other additives, to evaluate the effect of the polymerizable emulsifier 608 on the adhesion of ink on the BOPP and PE films. The results are shown in Figure 7 and Figure 8.

It can be found that, in comparison with ink based on control latex, all inks based on the latexes synthesized with fully polymerizable emulsifiers demonstrated higher adhesion, whether on BOPP film or PE film. The adhesion on BOPP film of the yellow ink was increased from 92% of the control sample to 99%, and from 99% of the control sample to 100% on PE film. For blue inks, the adhesion on BOPP film was increased from 92% of the control sample to 99%, and on PE film was increased from 98% of the control sample to 100%. Kientz, et al. found that [18], emulsifiers can migrate towards the interfaces of the film, film-air or film-support during the drying period of latex. Obviously, when the emulsifier accumulates on the interface between the film and substrate, it will harm the adhesion of the ink on the substrate. Thus, the improvement of the adhesion on the BOPP and PE film of the inks relative to the control ink should be attributed to the role of the polymerizable emulsifier 608.

4. CONCLUSION

In this contribution, a compound emulsifier system composed of a polymerizable anionic emulsifier SR-10 and a polymerizable non-ionic emulsifier 608 was used to prepare core-shell polyacrylate latexes. At the same time, a control

latex was also synthesized by using a non-reactive emulsifier TX-30 to replace 608 for comparative studying the role of the emulsifier 608. The studies showed that the use of emulsifier 608 can avoid the migration of TX-30 to the surface of the film or the interface between the film and substrate during the drying period of latex. As a result, the ethanol resistance stability and Ca^{2+} resistance stability of the latexes were significant enhanced relative to the control latex. Moreover, the surface roughness of the corresponding latex films was lower. In addition, the adhesion on the BOPP and PE film of the corresponding inks was also greatly improved. Ca^{2+} resistance stability was increased from 5% of the control latex to 25%. The adhesion of the yellow inks on BOPP film and PE film was increased from 92% to 99%, and from 99% to 100%, respectively. The adhesion of the blue inks on BOPP film and PE film was increased from 92% to 99%, 98% to 100%, respectively. The results will widen avenues for the application of polyacrylate-based waterborne inks in BOPP and PE thin films.

REFERENCES

- Y. Su, Y. D. Shen, and L. Wang, "Surface properties and application of fluorinated emulsifier-free emulsion surface sizing agent," *Appl. Mech. Mater.* **316-317**, 923–926 (2013).
- G. W. Fu, D. K. Wang, R. Q. Chen, and C. P. Wang, "Effect of polymerizable emulsifier on emulsion polymerization of acrylate," *China Adhes.* **30**, 18 (2021).
- Y. L. Sun, W. H. Qiao, L. Hong, and H. Z. Liu, "Polymerizable emulsifier of maleic acid and its application in emulsion polymerization," *Macromolecule Bull.* **01**, 16–23 (2003).
- K. Landfester, "Polymer dispersions and their industrial applications," *Macromol. Chem. Phys.* **204**, 542–542 (2003).
- Y. Du, *Synthesis and Properties of Polyacrylate Emulsion for Gravure Printing Ink* (Beijing University of Chemical Technology, Beijing, 2019).
- X. L. Wei and H. Q. Fu, "Research progress of modified waterborne acrylate pressure sensitive adhesive," *Chem. Eng. Prog.* **31**, 176–184 (2007).
- T. Y. Cao, Q. L. Liu, and J. S. Hu., *Synthesis and Application of Polymer Emulsion* (Chemical Industry Press, Beijing, 2007).
- E. Aramendia, J. Mallego, and C. Jeynes, "Distribution of surfactants near acrylic latex film surfaces: A comparison of conventional and polymerizable surfactants," *Langmuir* **19**, 3212–3221 (2003).
- P. Li, Z. P. Zhou, W. W. Ma, and T. F. Hao, "Core-shell emulsion polymerization of styrene and butyl acrylate in the presence of polymerizable emulsifier," *J. Appl. Polym. Sci.* **133**, 43091–43094 (2015).
- Y. Chen, Y. Ding, and J. P. Zheng, "A polymer nanocomposite coating with enhanced hydrophilicity, antibacterial and antibiofouling properties: Role of polymerizable emulsifier/anionic ligand," *Chem. Eng. J.* **379**, 122268 (2019).
- D. R. Zhao, *Polymer synthesis technology* (Chemical Industry Press, Beijing, 1997).
- E. Aramendia, M. J. Barandiaran, J. C. De la Cal, and J. Grade, "Improving latex performance by using polymerizable surfactants," *ACS Symp.* **801**, 168–179 (2002).
- Y. Gong, T. Shao, X. Chen, S. Cao, and L. Chen, "Silicone acrylate dispersion based on semi-continuous seed emulsion polymerization using polymerizable emulsifiers," *Chem. Pap.* **74**, 2875–2882 (2020).
- J. Zhang, Y. Zhao, M. R. Dubay, S. J. Severtson, L. E. Gwin, and C. J. Houtman, "Surface enrichment by conventional and polymerizable sulfated nonylphenol ethoxylate emulsifiers in water-based pressure-sensitive adhesive," *Ind. Eng. Chem. Res.* **52**, 8616–8621 (2013).
- Y. Bi, Z. Wang, L. Lu, X. Niu, Y. Gu, and L. Wang, "A facile route to engineer highly superhydrophobic antibacterial film through polymerizable emulsifier," *Prog. Org. Coat.* **133**, 387–394 (2017).
- C. Yin, X. Li, and H. Wang, "Study of factors on ethanol resistance stability of water-based acrylic resin emulsion," *China Academic Conference on Printing & Packaging and Media Technology*, March 2017 Lecture Notes in Electrical Engineering (Springer, Singapore, 2017), Vol. 417, pp. 857–863.
- J. Lv, "Applied Research of Polymerizable Emulsifiers in Acrylate Emulsion Polymerization," Master's thesis (Anhui University, Anhui, P. R. China, 2011).
- E. Kientz and Y. Holl, "Distribution of surfactants in latex films," *Colloids Surf. A* **78**, 255–270 (1993).