Synthesis and Properties of Cross-linked Fluorine and Silicon VAc-VeoVa Polymer Latex Emulsified by Green Mixed Surfactant

LIJUN CHEN, TANTAN SHAO, YILU GONG, XIUMING WANG AND ZHIJUAN SUN

School of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China

ABSTRACT

Cross-linked vinyl acetate and vinyl versatate (VeoVa) polymer latex (VAc-VeoVa10) modified with fluorine and silicon was successfully synthesized via the semi-continuous seeded emulsion polymerization technology. The latex was emulsified by green surfactants of sodium alpha-olefin sulfonate(α-AOS) and cashew phenol polyoxyethylene ethers(BCE-10) and initiated with potassium persulfate(KPS). The chemical structure of the latex was analyzed by fourier transformed infrared (FTIR). The glass transition temperature (T_g) was detected by differential scanning calorimetry(DSC) measurement. The water resistance was determined by the water contact angle (WCA) measurement. The polymerization condition of preparing the latex was optimized. Results showed that the content of surfactant was 2.00Wt% and the mass ratio of α-AOS and BCE-10 was 2:1 and the mass ratio of main monomer was 3:1.The contents of fluorine monomer and the silicon monomer were 8.00 wt% and 1.00wt%, respectively. The amount of the cross-linked monomer was 1.00wt%. In comparison with the conventional latex, the hydrophobic performance of the cross-linked modified VAc-VeoVa copolymer latex was improved.

KEYWORDS: *VAc-VeoVa10, N-methylolacrylamide (NMA), Polymerization condition, Performance*

1. INTRODUCTION

VAc-VeoVa polymer latex has been widely used in cement, composite and waterproof mortar [1-8]. However, its poor water resistance and thermal stability has limited its further development and application. Presently, more and more attention has been paid to the fluoro-silicone latex. The fluoro-silicone latex has been used extensively in many fields such as coatings, glass, and rubber and so on. Fluorine

or silicon polymer latex can be found in many open literatures. Fluorine monomer was also often used as the strategies for chemical structural modification, which led to the improvement of water resistance and thermal stability. Fluorinated copolymers are known to have favorable features, e. g. oil and water repellency, weather resistance, aging and so on as the fluorine atom is low polarizability and strong electronegativity [9-11]. Polyacrylate copolymer containing hexafluorobutyl methacrylate(HFMA) with core-shell structure and narrow particle size distribution was prepared by Xiao et al [12]. Results showed that HFMA was effectively enriched in the emulsion copolymerization. The hydrophobic property and thermal stability of the film were improved in comparison with the conventional latex. Self-crosslinking fluorinated polyacrylate soap-free latices with core-shell structure were synthesized and characterized by Xu et al [13]. Results confirmed that the fluoroalkyl groups of dodecafluoroheptyl methacrylate(DFMA) had the tendency to enrich at the film-air interface. Zhou et al [14] reported that polyacrylate latex containing fluorosilicone was successfully synthesized via emulsifier-free emulsion polymerization, which the polymerizable surfactant was used. The thermal stability of the film was enhanced with the introduction of ethyl silicate (TEOS). Results demonstrated that a layer of fluorosilicone modified polyacrylate film was covered on the finished fabric surface and fluorinated sections had the tendency to be enriched at the film-air interface. Naghash et al[15] prepared triphenyl vinyl silane(TPVS) containing VAc, butyl acrylate(BA) and NMA copolymers by emulsion polymerization. The

obtained copolymers showed that the thermal stability was increased and the water absorption ratio of the latex films was decreased with the increased amount of silicone. Kim et al [16] prepared the self-crosslinking core-shell acrylic copolymer emulsions containing fluorine/silicone in the shell by three-stage seeded emulsion copolymerization. They examined the effect of triethoxy vinyl silane (VTES) on the stable emulsion sample. It was found that the average particle size and viscosity of emulsions increased evidently with increasing VTES content, the contact angle of the latex film increased with increased VTES content upto approximately 6 wt%, and then decreased slightly. Zhang's team [17-19] had prepared successfully fluorine-silicon latex containing acrylate using novel mixed emulsifiers by semi-continuous seeded emulsion polymerization. The investigation of the fluorine-silicon latex containing acrylate indicated that the latex film had good thermal stability and water repellency.

Surfactant plays a vital role in emulsion polymerization which is a common and high efficient method to prepare latex. However, the traditional surfactants such as nonyl phenol polyoxyethylene ether (OP-10) and dodecyl benzene sulfonic acid sodium (SDBS) in emulsion polymerization were difficult to be degraded and easy to be bio-accumulated. Besides, they were originated from fossil fuel and not recycled. Furthermore, the development and production of polymer emulsion is largely limited by the pollution of toxic emulsifier. BCE-10 was green, safe and novel non-ionic surfactant for replacement of OP-10, which was prepared by the natural

cashew nut shell. Furthermore, α-AOS was biodegradable easily, which was used to replace SDBS. Besides, the cross-linked fluorine and silicon VAc-VeoVa polymer latex was emulsified with the mixed surfactants of BCE-10 and α-AOS, which is not reported in the open literature. In this work, we tried to prepare the cross-linked fluorine and silicon VAc-VeoVa polymer latex which was emulsified with BCE-10 and α-AOS.

2. EXPERIMENTAL

2.1 Materials

Vinyl ester of neodecanoic acid (VeoVa10, 99.0%) was purchased from Foshan Jin Jia New Material Technology Co.Ltd (China). Potassium persulphate (KPS), which was chemically pure, was obtained from Shanghai United Company (China). Vinyl acetate (VAc, 98.0%) was bought from Aladdin Industrial Corporation (China). HFMA was got from Harbin Xeogia Fluorine-silicon Material Co.Ltd (China). VTES was provided by Huarong Chemical Co. Ltd (Qufu, China) Sodium alpha-olefin sulfonate(α-AOS)(35.0 Wt%) was bought from Zanyu Technology Corporation (China). BCE-10 (50.0 Wt %) was obtained from Lvguo New Material Co.Ltd (China). N-methylolacrylamide (NMA)(98.5%) was bought from Aladdin Reagent (China).

2.2 Preparation of polymer latex

Semi-continuous seeded emulsion polymerization was carried out in a 250mL round bottom flask with four mouths, which was equipped with a reflux condenser, stainless-steel mechanical stirrer and two dropping separate funnels. One funnel was the mixed monomers of VAc, VeoVa10, HFMA, VTES and NMA. The other funnel was used to feed initiator. Firstly, 0.40g of anionic surfactant and 0.20g of nonionic surfactant and 40.00g of de-ionized water were charged into the flask which was heated to 75.0 °C by the water bath. During the course of emulsion polymerization, the copolymerization was permitted to proceed with the agitation, which the rotational speed was in the range of 200rmp and 400rpm. Secondly, 10% of KPS solution and 10% of mixed monomers were dropped into the reactor within the range of 10min and 15 min simultaneously. Thus, the blue and white seeded emulsion was obtained. The seeded emulsion was maintained for 20 min to ensure that the monomers were copolymerized adequately in the emulsifier system. Thirdly, rest of KPS and monomers were dropped into the flask within the range of 3h and 4h. The temperature of water bath was increased to 80.0 °C and kept for 1h to increase the conversion of the mixed monomers after the reagent was dropped. Finally, the latex was obtained after it was filtered. The recipe of preparing the latex was presented in Table 1. The pathway of preparing the latex was given in Scheme 1.
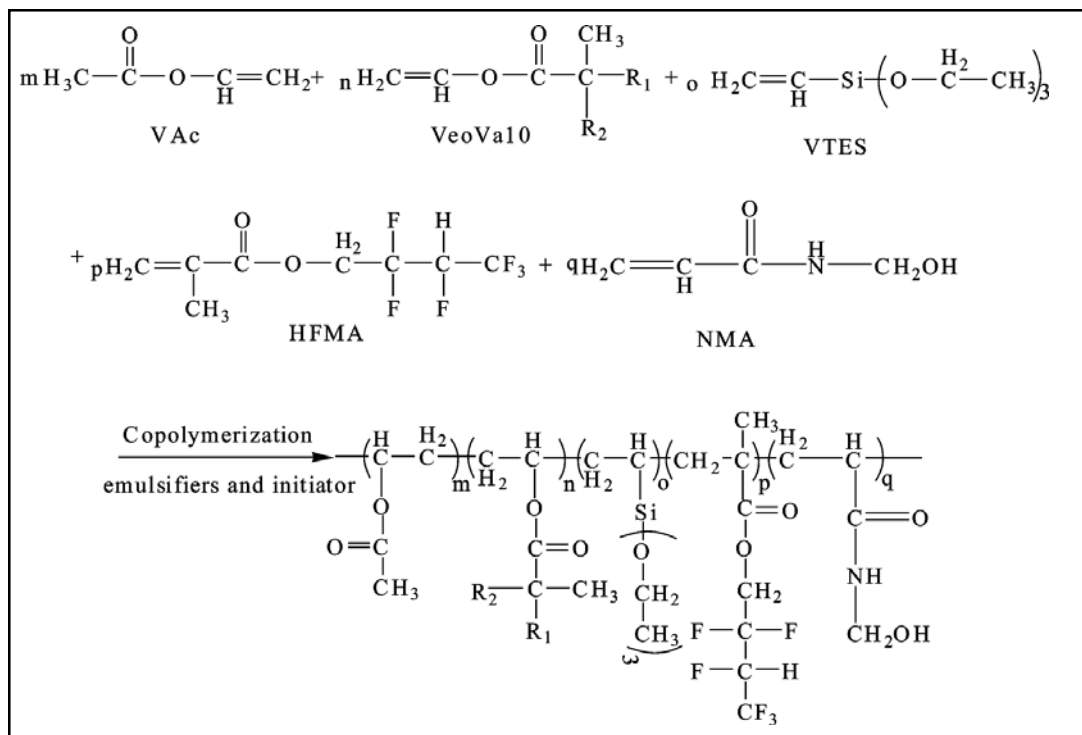
2.3 Characterizations

The conversion rate of mixed monomers was calculated with the following formula: conversion rate $(100\%) = \frac{Mr \times Ms\% - M1}{M2} \times 100\%$; where Mr stands for the mass of reactant; Ms% is the solid content; M_1 is the mass of not volatile material; M_2 is the mass of volatile material. The coagulation rate of polymer emulsion was calculated with the following formula: coagulation rate

TABLE 1. Recipe of preparing latex

Components	Weight/g	Components	Weight/g
VAc	20.25	KPS	0.18
VeoVa10	6.75	α-AOS	0.40
HFMA	2.40	BCE-10	0.20
VTES	0.30	De-ionized water	70.00
NMA	0.30		

Scheme 1. Pathway of preparing latex

$(100\%) = \frac{Mc}{Mt} \times 100\%$; where M_c is the mass of coagulation solid; M_t is the mass of total monomer. The chemical structure of the latex film was characterized by Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet infrared AVATAR370, USA) and FTIR spectra were recorded in a range from 4000cm^{-1} to 400 cm^{-1}. The glass transition temperature (T_g) of latex film was determined by differential scanning calorimetry (DSC, Q100, USA) measurement at a heating rate of 10 °C /min under nitrogen atmosphere and the temperature scale is ranged from -60 to 60 °C. The mechanical stability of the latex was tested by the centrifugal machine with the rotational speed of 4000 rpm for 30 min. Calcium ion stability test was verified through adding 2 ml CaCl$_2$ aqueous solutions (0.50 wt%) into 8 ml latex in a test tube and it was left standing for certain time at room temperature to weight the gel content. The water resistance of the latex film was measured water contact angle (WC, Germany) with

the pendant drop method at room temperature. Water uptake percentage is calculated by the equation: $Wu(100\%) = \frac{w - d}{d} \times 100\%$, where w is the weight of latex film absorbed into de-ionized water; d is the weight of latex film dried in an oven at 70.0 °C.

3. RESULT AND DISCUSSION

3.1 FTIR and DSC analysis of latex film

FTIR spectrum of the latex film was given in Figure 1. The absorption peak of 3433.6cm^{-1} was attributed to the group of –OH, which was the hydroxyl groups(-OH) of Si-OH because of the part of hydrolysis of VTES functional monomer. The characteristic absorption peaks that occurred at 2961.6 and 2874.1cm^{-1} were the stretching vibration of –CH$_3$ and –CH$_2$. The

strong peak spectrum band of bending vibration absorption peak of C=O at 1732.8 cm^{-1} indicated that the esters existed in the copolymer. The absorption peak of 1675 cm^{-1} was the group of N-H. The bending vibration absorption peak of 1434.1 cm^{-1} was the characteristic group of CH$_3$-CO-O-. 1370.6 cm^{-1} was the bending and stretching vibration of C-C. The strong bending vibration absorption of 1228.8 cm^{-1} may be the characteristic peaks of -OCH- or -CF$_2$. The band of 1104.3cm^{-1} was the bending vibration of C-H in plane. The band
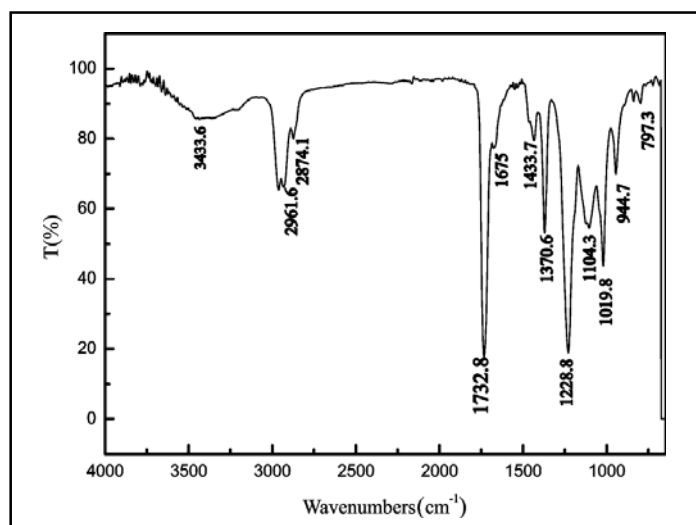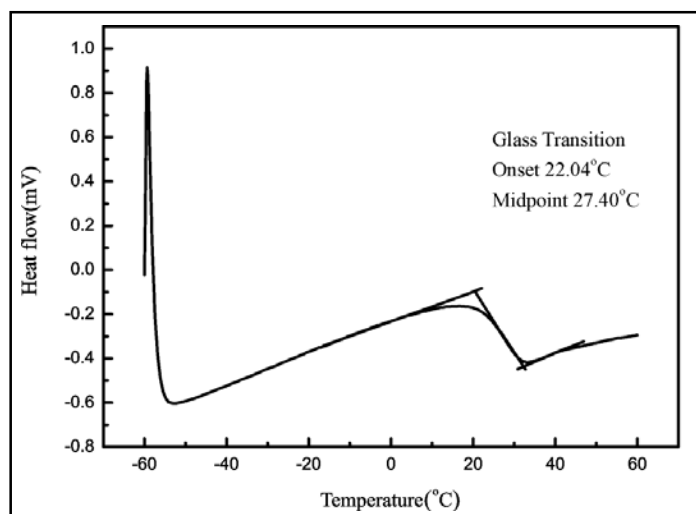

Fig. 1. FTIR of latex film

Fig. 2 DSC of latex film

at 1019.8 cm^{-1} was also observed, which may be the C-O-C stretching vibration in ester group. The characteristic absorption peaks of C-F appeared in the band of 944.7cm^{-1}. It can be confirmed that all the monomers took part in the polymerization and the latex had been prepared successfully.

The DSC curve of the latex film is presented in Figure 2. It is found that T_g of the latext film is 27.40 °C, which is different from that of p(VeoVa10) homopolymer (-5-0°C) and p(VAc) homopolymer (39°C). The DSC curve showed that only single glass transition existed, which also confirming the formation of the random copolymer.

3.2 Influence of amount of emulsifier on conversion rate and coagulation rate

Influence of amount of emulsifier on the conversion rate and coagulation rate of latex was shown in Figure 3. It was obvious that the conversion rate of the monomer was increased with the increased amount of emulsifier when the amount of the emulsifier was less than 2.00%. It may be the reason that the VAc and VeoVa10 monomer entered the inside of the micelle formed by the α-AOS and BCE-10 emulsifiers when the mixed emulsifiers reached the value of CMC(critical micelle concentration). Besides, the conversion rate of monomer was the highest when the amount of the mixed emulsifiers was 2.00%. However, the conversion rate of monomer was decreased when the amount of emulsifiers was more than 2.00%. This may be caused by the fact that the excessive amount of emulsifiers led to the increase of the micelles and the degree of saturation. However, the influence of the increased amount of the coagulation rate was on the contrary. In fact, when the amounts of α-AOS and BCE-10 emulsifiers was 1.00wt%, the conversion rate of mixed monomers was
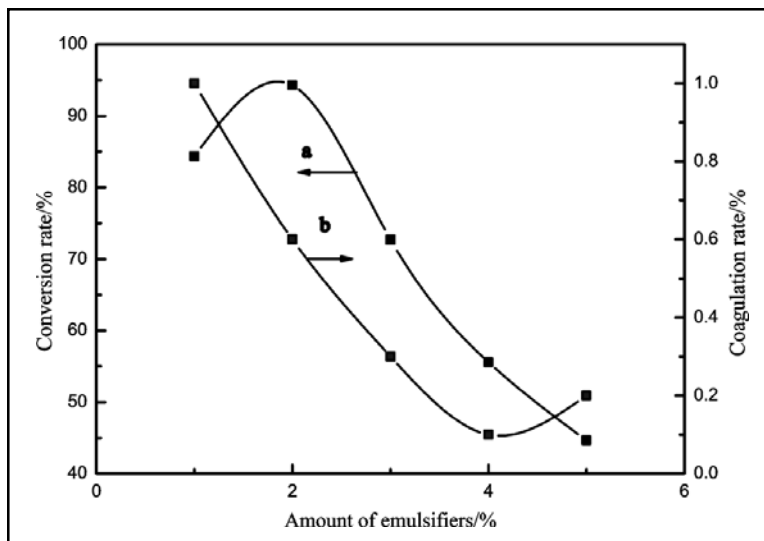

Fig. 3 Effects of amount of emulsifier on conversion rate and coagulation rate
(a: Conversion rate; b: Coagulation rate)

so low that the odor of the latex smelled terrible and the latex was delaminated partly. This can be explained by the fact that the molecular structure of BCE-10 contained the polymerizable double bonds (Seen in Scheme 2) had a growing trend to self-polymerization at a certain amount. The polymerization process could not be performed completely before the BCE-10 amount reached saturation on the surface of the thick water layers [20]. Furthermore, the conversion ratio of the mixed

monomers was decreased with the increased amount of the emulsifier when it was more than 2.00%. The latex particles were completely covered by emulsifiers and it was too hard for the free radical of initiator to enter inside the reaction of latex particles when the concentration of the emulsifiers was excessively high. As the result, the reaction did not proceed completely and the conversion was decreased. Thus, the amount of mixed emulsifiers was 2.00 wt%.
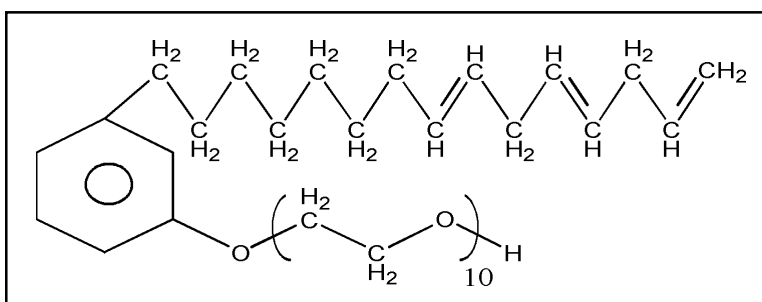
Scheme 2. Molecular structure of BCE-10

3.3 Effect of mass ratio of mixed emulsifiers on properties of latex

Usually, the mixture of nonionic and anionic emulsifier was often adopted in practice. The use of the mixture of nonionic and anionic surfactant can improve the cloud point of nonionic surfactant greatly and make the surfactant molecules be alternately absorbed onto the surface of latex particles, which reduced static repulsion among the ions on the same latex particle and charge density on the surface of latex particles. In addition, anionic surfactants are absorbed onto the surface of latex particles which form surface electronegative layer. The influence of different mass ratios of mixed emulsifier on properties

of latex was given in Table 2. In Table 2, it can be found that the conversion rate of the mixed monomers was the highest and Ca^{2+} stability, mechanical and storage stability of the latex were good when the mass ratio of mixed emulsifier of α-AOS to BCE-10 was 2 to 1. Furthermore, the coagulation rate varied slightly. Thus, the mass ratio of ±-AOS to BCE-10 was chosen to be 2:1 in this work.

3.4 Determination of amount of initiator

The influence of amount of conversion rate and coagulation rate was given in Figure 4. The conversion rate of monomers is gradually increased with the increased amount of initiator. However, the amount of coagulum was

TABLE 2. Influence of different mass ratios of mixed emulsifier on properties of latex

Mass ratio of α-AOS to BCE-10	2:1	1:1	1:2	1:3
Conversion rate/%	90.34	83.97	83.40	81.43
Coagulation rate/%	0.50	0.60	0.30	0.40
Appearance of emulsion	◎	◎	◎	◎
Mechanical stability	●	●	●	●
Storage stability	●	●	●	●
Ca²⁺ stability	●	●	●	●

Notes: ◎ means that the appearance of the emulsion is translucent with white and blue light.
        ● stands for the good stability of emulsion.+ means that there is a little flocculation.
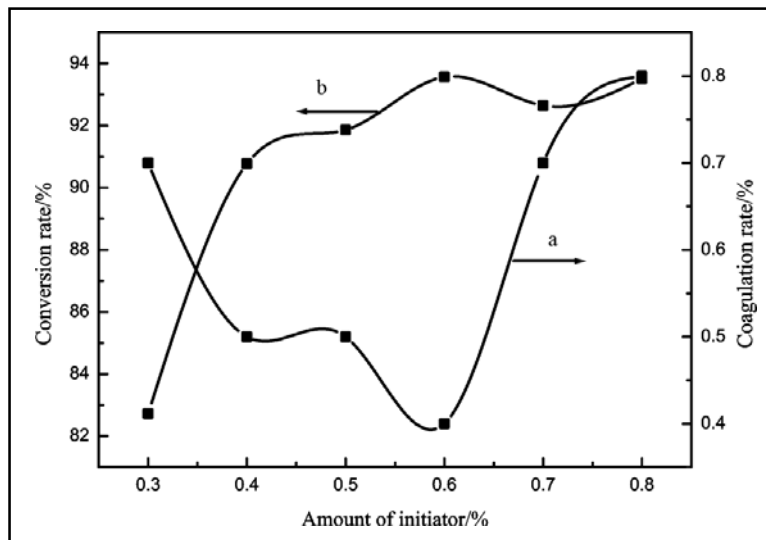

Fig. 4. Influence of amount of initiator on conversion rate and coagulation rate
(a: Coagulation rate; b: Conversion rate)

decreased firstly, and then was increased with the increased amount of initiator. According to kinetic equation of polymerization reaction, when the amount of initiator was small, the probability that the latex particles obtained free radicals was fewer. Therefore, the number of effective latex particles, which took part in the polymerization reaction, was fewer, and the polymerization rate was fewer. The ultimate conversion rate was lower after the specific reaction time. When the amount of initiator was increased, the probability that the particles of the polymer obtained free radicals was increased. Thus the reaction rate was quickened, and the ultimate conversion rate was raised. In addition, KPS belonged to the

electrolyte. Part of KPS acted as the electrolyte if the amount of KPS was excessively large. The concentration of the electrolyte in the system was increased. However, the increase of concentration of K^+ had a negative effect on the stability of the emulsion polymerization. The amount of coagulum was increased. Thus, the stability of the emulsion polymerization was decreased. Therefore, initiator was continuously dripped into the reaction system and the dripping rate was strictly controlled to keep the polymerization rate constant besides that the overall amount of initiator was strictly controlled. In this work, the amount of the initiator was 0.60%.

3.5 Effect of mass ratio of VAc to VeoVa on properties of latex

The effect of different mass ratios of monomers on properties of the latex was presented in Table 3. It was obvious that different monomer mass ratios had no obvious influence on the appearance of latex, storage stability, chemical stability and mechanical stability is better. Furthermore, the effect of different mass ratios of monomers on the appearance of the latex

film was given in Figure 5. The appearance of the latex was moderate when the mass ratio of VAc to VeoVa10 was 3:1. The appearance of the latex film was sticky when the mass ratio of VAc to VeoVa10 was less than 3:1. However, the appearance of the latex film was fragile when the mass ratio of VAc to VeoVa10 was more than 3:1. In the latex, VeoVa10 was a soft monomer, which brought the film with a certain degree of flexibility and improved the stability of the latex moderately. On the contrary, VAc was a hard monomer, which offered the film with high operating temperature, a certain luster and brought the latex film with scratch resistance. Thus, the mass ratio of VAc to VeoVa10 was 3:1 in this study. Besides, the influence of different mass ratios of VAc to VeoVa on the water contact angle of the latex film was shown in Figure 6. The contact angle was decreased with the decreased amount of VeoVa. This result was in agreement with the previous findings [21-23]. The branched structure and steric effect of the VeoVa10 protected VAc units against hydrolysis. The effect of the different mass ratios of VAc to VeoVa10 on the water uptake percentage of the latex film was presented in Figure 7. The change water uptake percentage

TABLE 3. Effect of different mass ratios of VAc to VeoVa on properties of latex

Mass ratio of VAc to VeoVa10	Chemical stability	Appearance of latex	Storage stability	Mechanical stability
21.00:9.00	Good	●	®	®
22.50:7.50	Good	●	®	®
24.00:6.00	Good	●	®	®
25.50:4.50	Good	●	®	®
27.00:3.00	Good	●	®	®

Notes: ◎ means that the appearance of the emulsion is translucent with white and blue light.
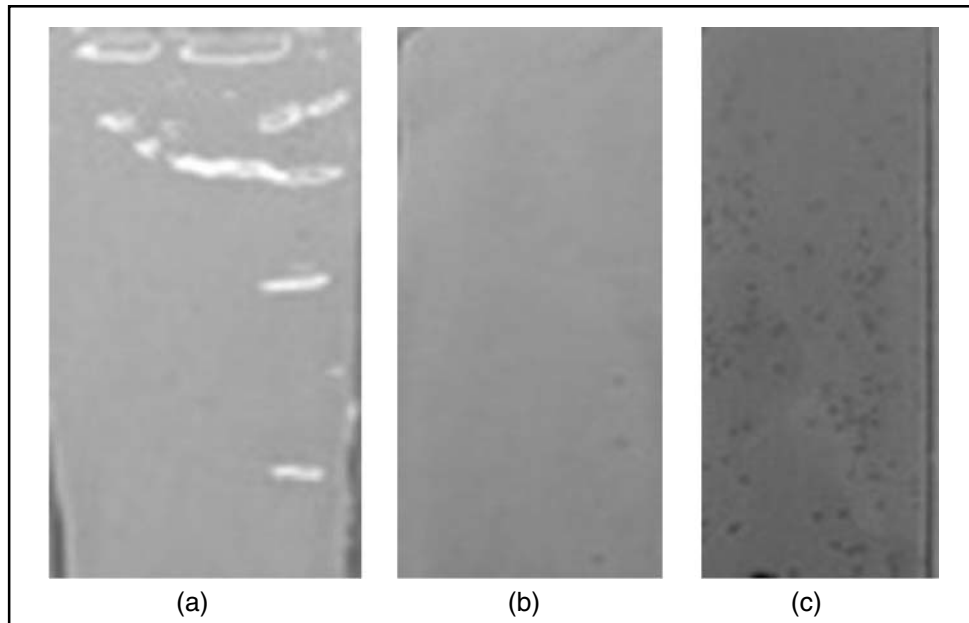● stands for the good stability of emulsion.

Fig. 5. Influence of different mass ratio of VAc to VeoVa10 on
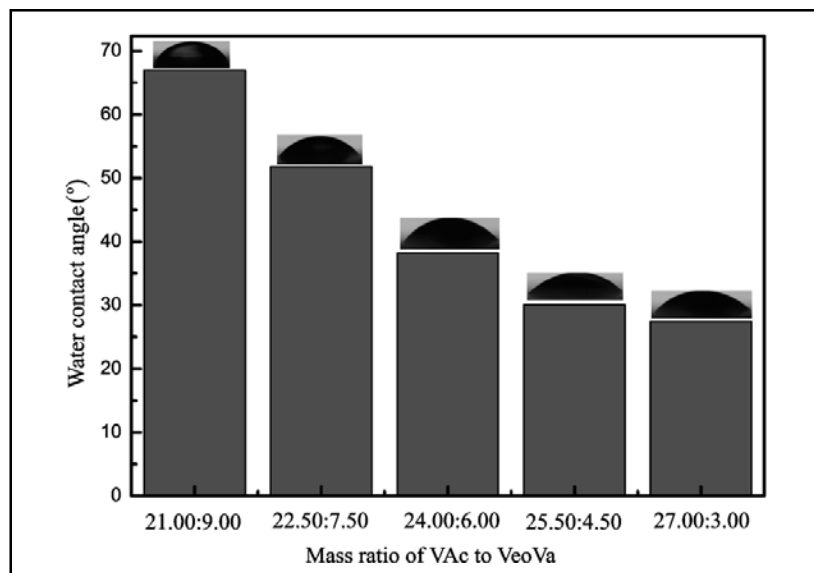appearance of latex film (a: 7:3; b: 3:1; c: 9:1)

Fig. 6. Effect of different mass ratios of VAc to VeoVa on water contact angle of latex film
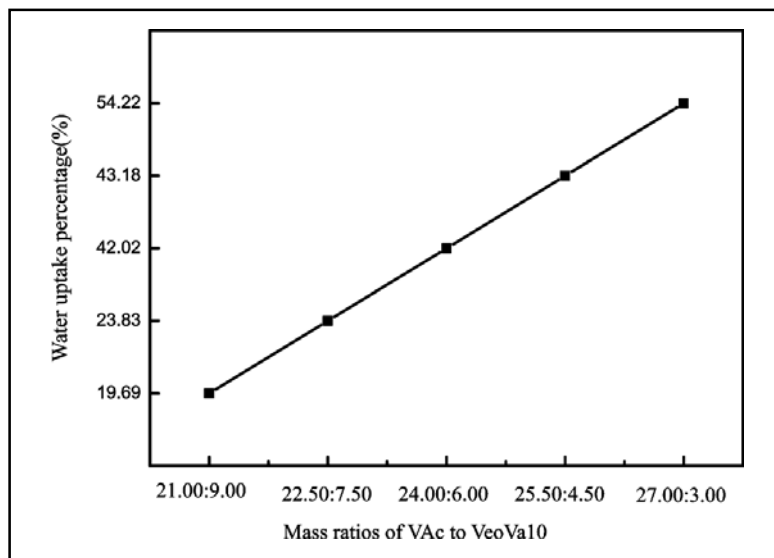
Fig. 7. Influence of different mass ratios of VAc to VeoVa10 on water uptake percentage of latex film

of the polymer film was in accordance with the water contact angle of the latex film.

3.6 Influence of amount of functional monomers on water resistance of latex film

The influence of the amount of VTES and NMA monomers on the water resistance of the latex film was presented in Figure 8. The contact angle of the latex film was decreased and then increased with the increased amount of VTES and NMA monomers. It may be caused by the fact that the organic silicon was difficult to be emulsified and enter into the micelle due to its low surface energy and the long chain of macromolecular structure. Furthermore, it cannot be polymerized richly when the amount of silicon was more than 5.00wt%. However, the contact angle of the latex film was increased with the increased amount of NMA. NMA is copolymerized with vinyl monomer to form thermoplastic polymer since there existed two reactive functional groups in the molecular structure of cross-linking monomer, i.e. vinyl group and methylol group, which can run addition reaction and condensation reaction, respectively. The cross-linking reaction made the polymer turn from linear structure to network molecule. The bonding among molecular chains of the polymer was close so that small molecules were hard to penetrate into them. Therefore, the contact angle of the latex film was increased with the increased amount of NMA. Besides, the contact angle of the latex can be further improved after the introduction of HFMA monomer (Seen Figure 9). The obvious increment of the contact angle was caused by the fact that more fluorine atom was introduced into a single polymer, and more fluorine atom tended to locate on the film surface during the film formation to minimize
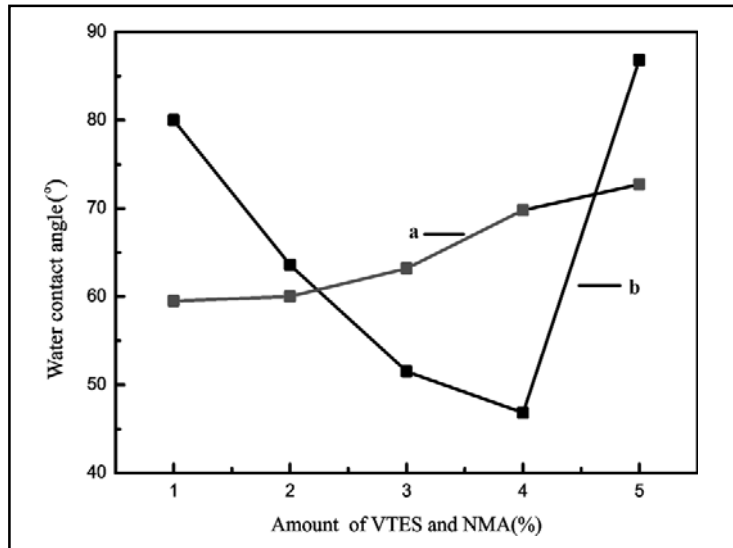
Fig. 8. Influence of amount of VTES and NMA on contact angle of latex film (a:VAc-VeoVa copolymer modified by NMA; b: VAc-VeoVa copolymer modified by VTES)
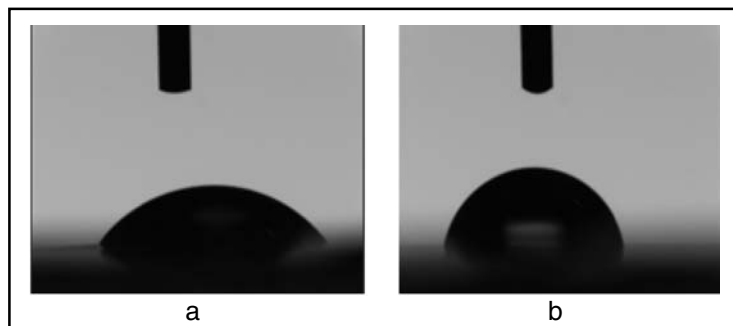

Fig. 9. Contact angles of latex film
(a: 51.8°, VAc-VeoVa10 copolymer film; b.:77.0°, VAc-VeoVa copolymer modified by HFMA,VTES and NMA)

the interfacial energy, which can increase the hydrophobic property of polymer.

4. CONCLUSIONS

VAc-VeoVa10 latex modified by VTES, HFMA and NMA was prepared successfully via semi-continuous seeded emulsion polymerization. The conditions of preparing the resultant latex were optimized. The optimum conditions of preparing the resultant latex were the flowing: the amount of the emulsifier was 2.00wt% and their mass ratio was 2:1; the amount of the initiator was 0.60wt%; the mass ratio of main monomer was 3:1; the amounts of functional monomer(HFMA, VTES, NMA) was 8.00wt%, 1.00wt%, 1.00wt%, respectively. The resultant

latex was confirmed by FTIR, DSC and WC measurements. In comparison with the conventional latex, the hydrophobic performance of the cross-linked modified VAc-VeoVa copolymer latex was improved.

Acknowledgements

REFERENCES

1. M. Afridi, Z.U. Chaudhary, Y. Ohama, K. Demura, M.Z. Iqbal. *Cement and Concrete Research* **24**(1994)1199.

2. M Afridi, Y. Ohama, Z. Iqbal, K. Demura, *Cement and Concrete Composites* **17**(1995)17.

3. Z.H. Xiang, *Chemical Building Materials* **5**(2005)7.

4. X.W. Zhang, Study on Preparation of Redispersible Polymer Powders. Northwest Normal University, 2008.

5. X.Y. Ji, X.M. Pan, Y.P. Lv., *China Adhesives* **20** (2011)470.

6. R. Wang, P.M. Wang, *Construction and Building Materials* **25**(2011)4210.

7. R Wang, P.M. Wang, L.J. Yao, *Construction and Building Materials* **27**(2012)259.

8. Y.V. Ustinova, T.P. Nikiforova, *Procedia Engineering* **111**(2015)807.

9. B. Ameduri, R. Bongiovanni, G. Malucelli, A. Pollicino, A. Priola, *Journal of Polymer Science part A-Polymer Chemistry* **37**(1999)77.

10. W.H. Ming, R.L. Van, G.R. Vande, G.W. Van, M. Krupers, *Polymer Bulletin* **47**(2001)321.

11. R.L. Van, W. Ming, G.R. Vande, L.R. Vander, G. De, T. Loontjens, P.C. Thune, J.W. Niemantsverdriet, *Macromolecules* **37**(2004)408.

12. X.Y. Xiao, J.F. Liu, *Chinese Journal of Chemical Engineering* **16**(2008)626.

13. W. Xu, Q.F. An, L.F. Hao, D. Zhang, M. Zhang, *Applied Surface Science*, **268**(2013)373.

14. J.H. Zhou, X. Chen, H. Duan, J.Z. Ma, *Fibers and Polymers* **18**(2017) 625.

15. H.J. Naghash, *Polymer*(Korea) **34**(2010)306.

16. D.H. Kim, Y.H. Lee, C.C. Park, H.D. Kim, *Colloid and Polymer Science* **292**(2014)173.

17. C.F. Zhang, T.T. Xu, Z.B. Bao, Z.R. Fu, L.J. Chen, *Journal of Adhesion Science and Technology* **31**(2017)1658.

18. C.F. Zhang, T.T. Xu, Z.B. Bao, L.J. Chen, *Designed Monomers and Polymers*, 20(2017)118.

19. W. Li, T.T. Xu, C.F. Zhang, Z.B. Bao, L.J. Chen, *Journal of Macromolecular Science part a-Pure and Applied Chemistry* **53**(2016)104.

20. G.L. Xu, L.L. Deng, X.F. Wen, P.H. Pi, D.F. Zheng, J. Cheng, Z.R. Yang, *Journal of Coatings Technology and Research* **8**(2011)401.

21. O.W. Smith, M.J. Collins, P.S. Martin, D.R. Bassett, *Progress in Organic Coatings* **22**(1993)19.

22. G.A. Vandezande, O.W. Smith, D.R. Bassett, Vinyl acetate polymerization,in:P.A.Lovell,M.S.El-Aasser(Eds.), Emulsion Polymerization and Emulsion Polymers. Wiley, John & Sons, England, 1997,563.

23. A.C. Aznar, J. I. Amalvy, *Latin American Applied Research* **36**(2006)149.