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Research Article

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Performance study of SiO2 sol/polyacrylate composite emulsion

Cheng Wu Li

School of Material Science and Engineering, Shenyang Ligong University, China

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ABSTRACT

In this paper，the preparation of nano silica sol was used TEOS hydrolysis. Silica sol was used to compound the SiO2 sol / polyacrylate with acrylate monomer emulsion polymerization, the effect of sol amount and feeding methods of polyacrylate stability and other property of SiO2 / polyacrylate were studied.

Key words: SiO_2, SiO_2 Sol, Polyacrylates, Compound Emulsion and Property

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INTRODUCTION

Nano inorganic/organic polymer composites has become a very important method for the preparation of new materials, will be the future focus direction of the composite material, and related research topics in recent years, research in the field of materials are very active. Nano inorganic/organic polymer composite materials can keep the advantages of organic polymer easy to processing, but also with the nano materials of high strength, high rigidity, and its excellent characteristics of multifunctional characteristics [1].

Acrylic emulsion has the following outstanding properties: wide range of choice monomer, monomer composition can design well. The comprising of lipophilic monomer/hydrophilic selectivity are wide single glass transition temperature range of options and the like. Acrylate monomer generally is less toxic or slightly toxic [2], so the acrylic emulsions is excellent environmental performance. Good film-forming properties of acrylic emulsion, mainly in: film speed, fast dry time and good film gloss, high transparency, uniform emulsion latex particle size distribution, good water resistance film, and low water absorption excellent performance. So more and more acrylic emulsion is used and development.

PREPARATION OF NANO-SILICA SOL / ACRYLATE COPOLYMER EMULSION COMPOUND

THE PREPARATION OF NANO-SILICA SOL

With ethyl orthosilicate, Silone coupling agent KH560 and hydrochloric acid as raw material, use is the hydrolysis of ethyl silicate prepared nano silica slurry. This method is mainly using ethyl orthosilicate hydrolytic reaction, generating nano silicon dioxide [2].The silica nanoparticles dispersion is one of the most important problem. Reunion, hydrolysis reaction generated nanoparticles easily happened cause the growth of the nanoparticles size and dispersed unevenly. Different dispersion solvent dispersion effect of silica nanoparticles have very big difference, then examines the five kinds of dispersion solvent dispersion effect of nano silica [1].

Ethyl orthosilicate in acidic and alkaline conditions are easy to hydrolysis, and product sol under neutral conditions extremely unstable, nanoparticles easily happened together. In alkaline conditions, hydrolytic condensation degree is large, resulting in response of the uncontrolled. At the same time considering the next step for acid emulsion polymerization system, and so is the hydrolysis of ethyl silicate reaction use hydrochloric acid solution as the catalyst [3].

In this article, ethyl silicate hydrolysis reaction is as follows [4]:

(1)SiO4(OC2H5) + 12H2O → Si5O4(OH)12 + 12C2H5OH
(2) Si5O4(OH)12 → 5SiO2 + 6H2O

(1)+(2) SiO4(OC2H5) + 12H2O → 5SiO2 + 12C2H5OH

THE PREPARATION OF NANO-SILICA SOL / POLYACRYLATE COMPOSITE EMULSION
In order to improve the stability of the emulsion polymerization, at the same time improve the emulsion's water resistance, hardness, latex film bibulous rate, such as performance, you must first determine the emulsion system is ethyl silicate and Silone coupling agent A - 174 feeding ratio.

Determine the optimal ratio of silicon compound feeding method is: first set amount of ethyl silicate and A-174 Silone coupling agent is 2% of the total monomers, changing TEOS and silicon coupling agent A-174 was added in the mass ratio of the polymerization system to investigate its effect on the stability of polymerization and the degree of cross-linking the film. Because of the important properties of the water, the water absorption film, latex film, and the film hardness are closely related to the degree of cross-linking, the polymerization stability and by testing the degree of cross-linking of the film in different proportions of the silicon compound can be determined the best emulsion excellent silicon compound feed ratio [5].

Tab. 1 The effects of the content of TEOS and A-174 on the polymerization stability

m_{TEOS}:m_{A-174}	8:1	4:1	2:1	1:1	1:2
Cur/%	0.47	0.54	0.76	1.05	1.58
The cross-linking degree of the film/%	34.2	82.3	84.4	88.9	90.7

The data in table 1 shows that increasing the content of A - 174 is helpful to increase the emulsion film cross-linking degree, but the stability of the emulsion polymerization, at the same time reduce the content of A - 174 increase ethyl orthosilicate TEOS content, although the polymerization stability increased, but the cross-linking degree reduced obviously. So comprehensive consideration, m_{TEOS}: as the best proportion of m_{A-174} = 4:1.

RESULTS AND DISCUSSION

EMULSION POLYMERIZATION RATE AND CONVERSION RATE
Emulsion polymerization of polymerization rate is one of the important indicators to measure polymerization controllability; polymerization rate too fast or too slow can cause polymerization controllability. Conversion rate is a measure of degree of polymerization of important indicators. So the study of polymerization rate and conversion rate is very necessary. Table 2 is the influence of dosage of silicon compounds on conversion, figure 1 is the effects of dosage of silicon compounds on polymerization rate results.

Tab. 2 The effects of the content of silicon compounds on the converion

The amount of silicon compounds/%	Theoretical solid content/%	Theoretical solid content/%	Theoretical solid content/%
0	50.3	50.2	99.9
1	49.6	49.5	99.7
2	49.5	49.4	99.5
3	49.2	49.7	99.4
4	48.4	49.1	99.7
5	48.7	48.2	99.9

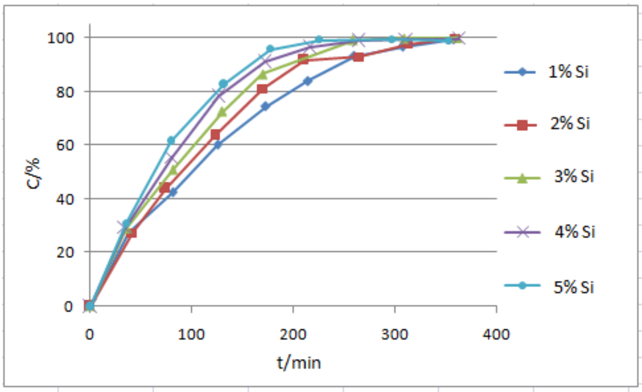

Fig. 1 Effects of the content of silicon compounds on rate of polymerization

Figure 1 shows that the result of the dosage of silicon compounds on the polymerization monomer conversion are effect is very small, can close to 100%, and when the dosage of silicon compounds in the range of 1% to 3%, the polymerization rate increased with the increase of silicon content is accelerated, the bigger the dosage of silicon compounds, the higher the monomer conversion rate under the same reaction time; But when the dosage of silicon compounds increased to 4% when begin to decline. This is because as you progress through the polymerization reaction [5], A - 174 in the event of A free radical copolymerization of siloxane group generated by hydrolysis of silicon hydroxyl at the same time, the hydrolysis of TEOS also happen to generate hydroxyl silicon, silicon hydroxyl and condensation reaction between the hydroxyl silicon.

THE STABILITY OF EMULSION POLYMERIZATION

Emulsion polymerization is the emulsion stability must first research various performance indicators. If the emulsion polymerization stability of the emulsion polymerization process is not stable, repeatable operability is poor, cannot be used in production. Table 3 is a silicon compound dosage effect on the stability of the polymerization [7].

Tab. 3 The effects of the content of silicon compounds on the polymerization stable

The amount of silicon compounds/%	Theoretical solid content/%	Theoretical solid content/%	Polymer stability/%
0	50.3	50.2	0.20
1	49.6	49.5	0.31
2	49.5	49.4	0.45
3	49.2	49.7	1.56
4	48.4	49.1	6.00
5	48.7	48.2	3.78

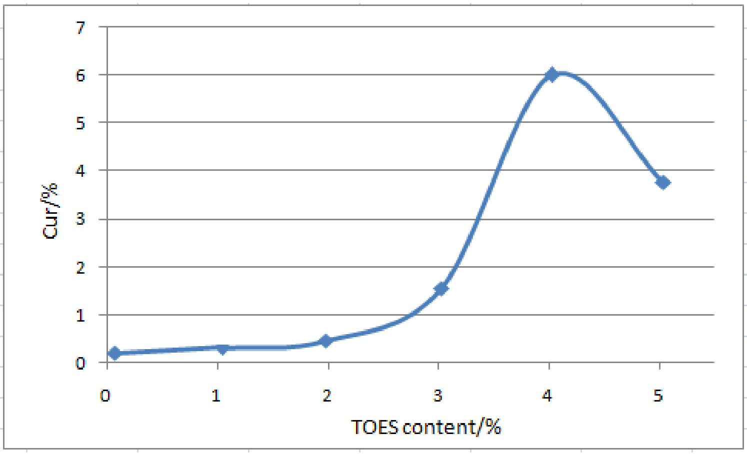

Fig.2 Effects of the content of silicon compounds on the polymerization stable

The figure 2 shows that with the increase of dosage of silicon compounds in system, polymerization stability, floc formation rate increases, polymerization stability decreased, and the dosage of silicon compounds increased to 4%, the floc formation rate is maximum, but when the dosage of more than 4% silicon compounds, aggregate stability and reduced.

LATEX FILM HARDNESS

Tab. 4 The effects of the content of silicon compounds on the cross linking index

The amount of silicon compounds/%	Cross-linked content/%	Cross-linked content（Include sketone and hydrazine system）/%
0	16.8	84.5
1	65.5	92.3
2	81.9	98.3
3	86.2	99.7
4	91.3	Solidified after half an hour
5	95.6	Solidified immediately

Indicate: In the table 4, including sketone and hydrazide system is mean to add diacetone acrylamide and the adipic dihydrazide in the emulsion, and the additives accounted for 2% of the total units.

High hardness of emulsion latex film made after coating, can improve the scrub resistance of coatings [7], made from wood coatings can improve the resistance of paint surface wear resistance.

Data in table 4 shows that with the increase of dosage of silicon compounds in milk poly system, emulsion film hardness increased obviously. When the dosage of 1%, film hardness is up to 2 h and when the dosage increased to 4% film hardness of 4 h. This can explain, TEOS was carried out in situ hydrolysis in the process of emulsion polymerization, the generated hydroxyl silicon nanoparticles on the silicon hydroxyl and carboxyl of cross-linking acrylate polymer structure, the formation of Si - O - Si evenly dispersed in the polymer, inorganic network formed at the same time Si - O - Si inorganic network with polyacrylate molecular chain between each other with united. The cross-linking structure of the space network is greatly improving the film hardness.

THE EMULSION PARTICLE SIZE AND DISTRIBUTION

Emulsion particle size and size distribution directly affects the performance of polymer emulsions. Emulsion color is closely related to the particle size and distribution, general small particle size of emulsion pan blue light.The smaller the emulsion particle size, coating with better gloss and transparency is higher. Table 5 and 3, respectively are silicon compound dosage on the average particle size and its distribution influence results.

Tab. 5 the effects of the content of silicon compounds on the particle

The amount of silicon compounds/%	The average particle size/mm	The average particle size/±nm	Polydispersity Index
0	154	3.5	0.005
1	154	2.6	0.009
2	158	5.4	0.005
3	171	1.8	0.056
4	193	4	0.097
5	201	14	0.215

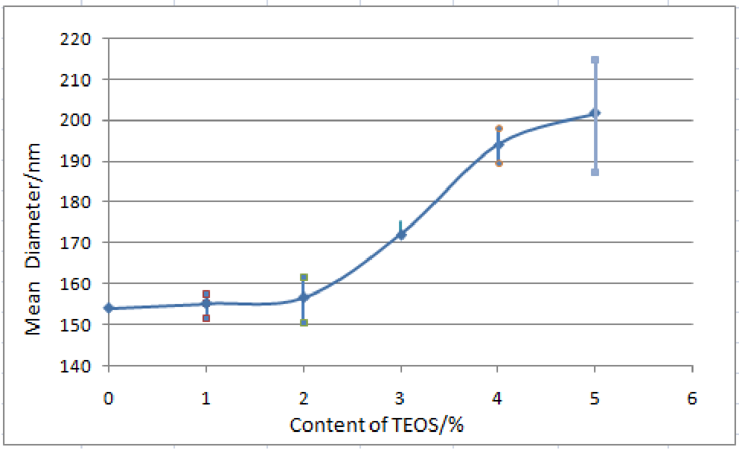

Fig. 3 The effects of dosage of silicon compounds on the Mean Diameter of particles

Table 5 and figure 3 show that with the increase of dosage of silicon compounds in emulsion polymerization system, increasing average particle size of latex particle, the particle size of dispersion index increase again to reduce the trend, and the dosage of silicon compounds was 2% more dispersion index to obtain the minimum value. Nanometer Si02 generated this is because, in the latex [4], it contains a large number of silicon hydroxyl, the dosage, the emulsification effect, but the dosage of silicon compounds increased to a certain amount, the increase in the number of silicon hydroxyl generated, latex particles on the surface of the hydration layer thickness increases, appear coalescence phenomenon, make particles easier to reunite in the surface of the latex particles, which resulted in increased size, at the same time, with the increase of dosage of silicon compounds, increased risk of latex particle aggregation, increase floc, is also another reason of emulsion particle size increases [9].

In this article USES the soap-free emulsion polymerization of emulsion was prepared by the emulsion particle size around 150~200 nm, conform to the architectural latex and the application range of the antirust emulsion.

In figure 4, we can see that with the increase of dosage of silicon compounds, film cross-linking content increase, namely the increase of cross-linking degree. Even in ketene. Hydrazine cross-linking formulation, with the increase of dosage of silicon compounds, emulsion cross linking material content in the membrane is also increased obviously. We suggest that the addition of TOES, coupling agent A- 174, under the synergy of hydrolysis was generated with silicon hydroxyl silicon nanometer Si02 or hydroxyl groups grafted in acrylate copolymer side chain formed on the junction [6].

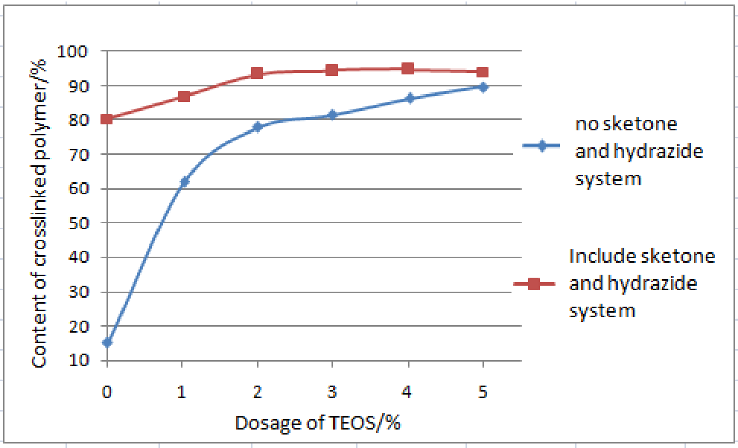

Fig. 4 Effects of the dosage of silicon compounds on the content of cross-lined polymer

THE EMULSION MINIMUM FILM-FORMING TEMPERATURE

Table 6 data shows that the minimum film-forming temperature of the emulsion basic has nothing to do with how much dosage of silicon compounds, and the generated hydroxyl silicon, in the water before volatile or in front of the coating is dry, cross linking basic did not occur. Investigation of six kinds of the minimum film-forming temperature of emulsion dosage of silicon compounds containing silicon emulsion test results are the same 14.18 ℃, and the blank sample emulsion of the minimum film-forming temperature of 20 ℃.The influence factors of the minimum film-forming temperature are: glass transition temperature, emulsion particle size, film forming agent, dry conditions and storage time, etc [8]. Due to the five kinds of emulsion in addition to the content have obvious different silicon compounds, the influence factors of other conditions are consistent, this is due to silicon hydroxyl and siloxane condensation reaction occurred at the same time, also generates small molecular substances such as ethanol and methanol.

Tab. 6 The effects of the dosage of silicon compounds on the MFT

The amount of silicon compounds/%	Minimum film forming temperature MFT/℃
0	20
1	14-18
2	14-18
3	14-18
4	14-18
5	14-18

VISCOSITY OF THE EMULSION POWER

Table 7 is the dosage of silicon compounds in the emulsion viscosity and its viscosity changes affect the outcome.

Tab. 7 Effects of the dosage of silicon compounds on the viscosity of latex

The amount of silicon compounds/%		0	1	2	3	4	5
Emulsion viscosity/mPa.s	0d	33.7	31.2	26.5	25.5	29.3	36.6
	15d	33.9	31.5	27.0	25.8	31.1	38.3
	30d	34.5	32	27.3	26.2	33.5	40.4
	45d	36.4	32.4	27.6	26.5	37.5	42.0
	70d	37.3	33.3	27.8	27.1	39.6	45.3

It can be seen from table 7 and figure 5, the composite emulsion viscosity increased after 70 days, but the increase was small, present the target store emulsion is stable, and the dosage of silicon compounds have little impact on stability [8]. And silicon compound dosage increased, the viscosity increased slightly. The silicon compound emulsion viscosity average of the dosage of 3% minimum, dosage of silicon compound emulsion viscosity change with 2% minimum, dosage of silicon compounds for 5% of the average viscosity of emulsion, the largest and the largest viscosity change with storage time is 5% and 4%.

THE WATER ABSORPTION OF FILM

Table 8 is silicon compound dosage O %, respectively, 1%, 2%, 3%, 4%, 5% of latex film bibulous rate determination results.

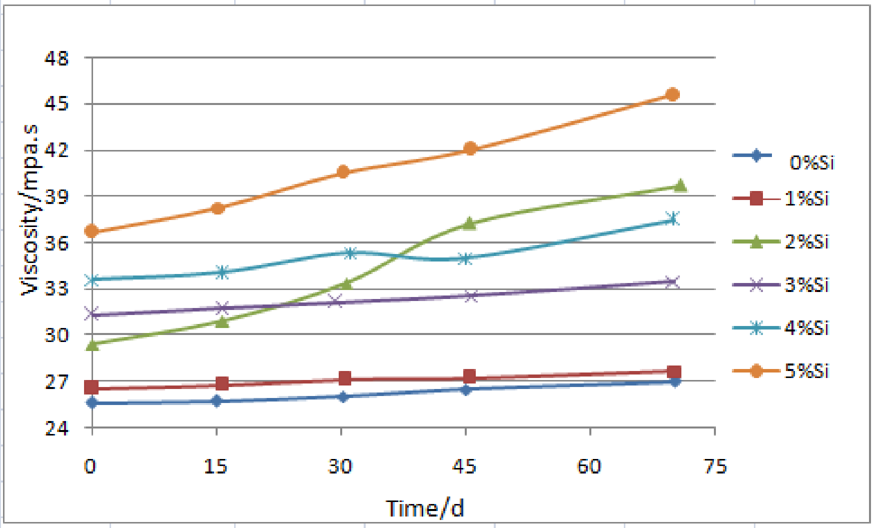

Fig. 5 The effects of the dosage of silicon compounds on the viscosity of latex

Tab. 8 Effects of the dosage of silicon compounds on the water absorption of film

The amount of silicon compounds/%	0	1	2	3	4	5
Water absorption/%	22.3	19.1	17.5	17.1	15.0	11.2

The data of table 8 shows that with the increase of dosage of silicon compounds, film bibulous rate is lower, that with the increase of dosage of silicon compounds, film cross linking degree increase, water resistance increased

THE EMULSION CALCIUM ION STABILITY

Calcium ion is used to evaluate the emulsion stability to resist the ability of the because of soluble salt in the packing material, also known as chemical stability. Emulsion stalling 48 h of CaCl2 solution, if not a gel, without stratified phenomenon, the stability of calcium ions. Table 9 shows the emulsion stability of calcium determination results.

Tab. 9 The stability of Ca^{2+}

The amount of silicon compounds/%	The stability of Ca^{2+}
0	Uniform and stable
1	Uniform, stable
2	Uniform and stable
3	Uniform and stable
4	Uniform and stable
5	Uniform and stable

DILUTE EMULSION STABILITY

PH value represents the system of hydrogen ion concentration, the lower the pH value, the greater the hydrogen ion concentration. Hydrogen ions and other captions, plays a lower negatively charged the stability of the latex particles of polymer emulsion. Table 10 is acid alkali on the determination results of composite emulsion stability.

Tab. 10 The stability of dilution

Sample	Shake and observe	Still observed after 24 hours
Take emulsion 5ML and neutralized to PH = 1	Stable and non-hierarchical	Homogeneous and no precipitation
Take emulsion 5ML and neutralized to PH =12	Stable and non-hierarchical	Homogeneous and no precipitation

CONCLUSION

This paper, by means of soap-free emulsion polymerization, the preparation of nano silica/acrylic ester compound emulsion, the study of the performance the following conclusions

1) In the presence of reactive emulsifier, directly to the oxygen ethyl orthosilicate, methyl acryloyl propyl silane three oxygen radicals (A - 174) soap-free emulsion polymerization with acrylic ester monomer, can be prepared by in situ hydrolysis method of the stability of the nano Si02 sol-gel/polyacrylate composite emulsion. When the

dosage of silicon compounds is less than 5%, the stability can be obtained from nano Si02 /polyacrylate composite emulsion, and the introduction of acrylate polymer silica particles side chains to form potential junction can be coordinated to improve water resistance and hardness of the acrylate copolymer. When added to the polymerization system is ethyl silicate and the proportion of the coupling agent A - 174 for m_{TEOS}: m_{A-174} = 4:1, the stability of the emulsion polymerization is best.

2) Compound content is higher, the polyacrylate/nano silicon dioxide composite latex film of the greater the degree of cross-linking, bibulous rate is lower, the greater the hardness. When the dosage of silicon compounds in 2% ~ 3%, the dosage of coupling agent A - 174 for TEOS usage of 20%, the hardness of the composite can reach more than 2 h, and water resistance performance and so on, the polymerization stability and storage stability can achieve ideal result.

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