Preparing Cationic Surface Sizing Agent By Phase Reversal

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ABSTRACT

This paper relates to paper sizing agent based on terpolymer of styrene(St), dimethylaminoethyl methacrylate(DAM) and butyl acrylate(BA) which have been reacted by solution polymerization and then have been converted into cationic water-soluble polymer by phase reversal. Optimized process parameters for terpolymer preparation were St/BA/DAM equal to 50/25/25(by weight), initiator azobisisobutyronitrile(AIBN) equal to 0.6% and chain transfer agent 2-aminoethyl mercaptan equal to 0.6% by weight of total monomer 70% polymerization concentration. The terpolymer had narrow particle distribution and average particle size of about 100nm. The average molecular weight of terpolymer approached about 50000 and polydispersity index was 1.23. The final copolymer has the desired surface sizing effect for untreated paper, Cobb value 23.2 g/m^2 and fluffing speed 1.76 m/s after surface sizing.

Keywords: *Styrene; Acrylate; Solution polymerization; Phase reversal; Surface sizing agent*

Introduction

Cationic polymer emulsion is homopolymer or copolymer obtained by cationic emulsifier or cationic monomer, whose basic characteristic is the latex particle surface or the polymer itself with positive charge [1,2]. Cationic styrene-acrylate latex is widely used in paper industry and is easy to combine with anionic cellulose. Compared with anionic polymer, its advantages are smaller dosage and better performance without retention aid. It can greatly improve the water-resistance, fold endurance and other strength properties of the sheet. Therefore, preparation of cationic polymer emulsion has generated great interest [3~7]. However, emulsifier with low moleculer weight is easy to bring the adverse effects for the operating environment and polymer performances[8,9], so this study used polymerizable cationic monomer to achieve polymer emulsion without emulsifier. Solution polymerization of butyl acrylate(BA), styrene(St), dimethylaminoethyl methacrylate (DAM) was carried out and then final water-soluble polymer emulsion was obtained by phase reversal process. Quantities ratio of w(St): w(BA) and w(DAM), w(AIBN) and w(2-aminoethyl mercaptan) in the reaction system was investigated on surface sizing performance, final terpolymer was prepared by optimized process and its performance was also evaluated for surface sizing application.

Materials and Methods

Materials

Styrene (St), butyl acrylate (BA), dimethylaminoethyl methacrylate (DAM), benzyl chloride, industrial product; azobisisobutyronitrile (AIBN), 2-aminoethyl mercaptan, acetone, formic acid, isopropanol, deionized water.

Preparation of terpolymer

After mixing all monomers including St, BA, DAM and 2-aminoethyl mercaptan, total isopropanol amounting to 30% by weight of above mixture are introduced into a stirrer-equipped flask with reflux. Then 30% by weight of AIBN initiator is also charged into the flask. The flask is thoroughly purged with nitrogen and heated to 85^0C.

When this temperature is reached, 70% by weight of monomer mixture and the remaining AIBN dissolved in acetone are added with constant speed for 2h, then maintained at this temperature for 2h. 50% by weight of isopropanol is distilled from the reaction mixture after polymerization, formic acid water solution is added into the flask for 30min, meanwhile agitating speed is slow, the reaction mixture has been converted into aqueous emulsion by phase reversal. Benzyl chloride is charged into aqueous emulsion which can completely convert the amino groups into ammonium groups. After stirring for 1h at 80^0C, the reactant mixture was cooled to 40^0C, a homogeneous emulsion of styrene-acrylate copolymer is soon obtained.

Properties analysis of terpolymer

The nonvolatile matter; IR test; viscosity; pH; diameter particle; calcium ion stability; high temperature stability; stability to mechanical shearing; freeze-thawing stability

Preparation and application of surface sizing solution

A solution of 5% by weight of native tapioca starch and

0.015% by weight ammonium persulfate is cooked at 90~96°C for 1h. Then the starch solution is cooled to 60~65°C and maintainedat this temperature, added cationic terpolymer emulsion, 5% by weight of tapioca starch, final starch solution is used as the sizing solution for surface sizing. pH of above blending solution was adjusted to 3~5, poured into the laboratory sizing press which was used for sizing. The newspaper has the base weight of 70g/m^2, wet uptake of paper is 120g/m^2. The surface-sized papers are dried on a drying cylinder over a period of about 1min at a temperature of about 100°C. Before the sizing test, the sheets are conditioned for 24hours at room temperature.

Results and Discussion

Impact of synthesis process on polymer performance

Impact of quantitive ratio of St/BA on polymer performance

Glass transition temperature (Tg) of styrene-acrylate polymer as surface sizing agent has a great affect on its sizing performance[11]. Mass ratio of styrene as hard monomer and butyl acrylate as soft monomer will change Tg of polymer. Meanwhile 25% DAM by weight of total monomers is assumed for obtaining stable polymer emulsion in the lab, mass change of styrene and butyl acrylate was explored to impact on polymer performance. The impacts of quantitive ratio of St/BA on polymer performance were tested and the properties were listed in Table 1.

Tg below 20°C is easy to cause dry polymer to become sticky at room temperature and bring application issues after surface sizing of paper when mass ratio of St/BA is too low.

TABLE 1
St/BA monomer ratio influence on the performance of the product

St:BA	60s Cobb(g/m^2)	IGT(m/s)
65:10	25.7	1.55
60:15	25.1	1.63
55:20	24.6	1.74
50:25	23.5	1.75
45:30	22.7	1.75
40:35	22.5	1.76

Process parameters of solution polymerization: total monomers 60% solvent 40% initiator 0.4% by weight of total monomers train transfer agent 0.2% by weight of total monomer total reaction time is 4h.
Process parameters of phase reversal: preferred molar ratio of formic acid and amino groups is equal to1.0, reaction time is 2h, solid content of polymer solution is about 30%.

Butyl acrylate is a soft monomer with high price whose high dosage will make the film forming temperature of terpolymer too low. Low Tg is good for film spreading of polymer as surface sizing agent when drying temperature is fixed at spot. More spreading area of film brings better sizing effect on surface of sheet and higher fluffing speed because of closer combination of surface sizing agent and base sheets. But big steric effects between styrene and butyl acrylate make polymerization difficult and bring more residual monomer, meanwhile reactivity ratio difference can't improve the performance and increase the cost of raw materials.

Mass ratio of styrene and butyl acrylate is confirmed as 50:25 after considering water resistance and fluffing speed of sheet after surface sizing.

Impact of DAM dosage on polymer performance

Surface charge density of colloidal particle is the most important factor to affect the stability of emulsion and the performance[11]. Based on DLVO theory(classical colloid stability theory), higher surface charge density brings more powerful mutual repelling force among colloidal particles which can reduce the trends of settling and agglomerating, the final polymer will have the preferred stability. DAM is cationic soft monomer whose dosage is related to the charge density of polymer particles and affects the hydrophilicity and cohesive force of polymer. DAM dosage is very important to the performance of polymer and must be explored when keeping the fixed mass ratio 2:1 of styrene/butyl acrylate. As can be seen, all of the dosages gave the acceptable results. The impact of DAM quantity on polymer performance was tested and the properties were listed in Table 2.

DAM dosage is vital for solubility property of polymer, sediment is easy to generate from emulsion if DAM dosage is not enough, but the least DAM dosage is used for achieving polymer as surface sizing agent and the preferred water-resistance of paper. Suitable DAM dosage is 25% by weight of total monomer for the stability and surface sizing effect of polymer. Theoretical glass transition temperature of polymer is about 26.6°C when keeping the mass ratio of St/BA/DAM 50/25/25.

TABLE 2
DAM monomer ratio influence on the performance of the product

St+BA:DAM	60s Cobb (g/m^2)	IGT (m/s)
65:35	27.5	1.65
70:30	25.9	1.73
75:25	23.5	1.75
80:20	23.2	1.79
85:15	-	-

Process parameters of solution polymerization: total monomers 60%, solvent 40%, initiator 0.4% by weight of total monomers, train transfer agent 0.2% by weight of total monomer, total reaction time is 4h.
Process parameters of phase reversal: preferred molar ratio of formic acid and amino groups is equal to1.0, reaction time is 2h, solid content of polymer solution is about 30%.

Above table 2 showed that DAM dosage was very critical to maintain the stability of polymer emulsion when DAM dosage was 20% by weight of total monomers, sediment appeared at the polymer emulsion after a few days.

Impact of solution polymerization concentration on polymer performance

The impact of solution polymerization concentration on polymer performance was tested and the properties were listed in table 3.

Isopropanol is used as solvent for solution polymerization.

TABLE 3
Polymerization concentration influence on the performance of the product

Monomer(%)	60s Cobb (g/m^2)	IGT (m/s)
80	-	-
75	24.9	1.67
70	23.6	1.75
65	23.3	1.77
60	23.5	1.75

Process parameters of solution polymerization: initiator 0.4% by weight of total monomers, train transfer agent 0.2% by weight of total monomer, total reaction time is 4h.
Process parameters of phase reversal: preferred molar ratio of formic acid and amino groups is equal to1.0, reaction time is 2h, solid content of polymer solution is about 30%.

More isopropanol has stronger solvency for monomers and polymer and is good to control heat from polymerization process. But more isopropanol causes higher cost and has stronger train transfer ability for reactant, thus final polymer has low molecular weight. Less solvent will bring high polymerization concentration which easily cause polymer to become gel and adverse reaction among monomers. Above samples showed that polymer became gel when monomer concentration was 80% by weight. In order to introduce as little solvent as possible into the final polymer, it is suitable to carry out solution polymerization with 70% concentration by weight based on the final polymer.

Impact of initiator concentration on polymer performance

AIBN is the suitable initiator in solution polymerization when keeping the mass ratio of St/BA/DAM 50/25/25. The impact of initiator concentration on polymer performance was tested and the properties were listed in table 4.

More AIBN usage will generate the more active points among monomers which can enhance full reaction of monomers, final polymer emulsion has lower odor. But more AIBN usage also causes residue and AIBN was toxic substance, so optimum usage is very important.

TABLE 4
Initiator concentration influence on the performance of the product

Initiator(%)	60s Cobb(g/m^2)	IGT (m/s)
0.2	24.6	1.69
0.4	23.6	1.75
0.6	23.2	1.76
0.8	23.3	1.75
1.0	23.5	1.77

Results indicate that there is some improvement in water-resistance and fluffing speed of paper after surface sizing. When AIBN dosage is more than 0.6% by weight of total monomers, there is only a little performance improvement but it will raise the cost. 0.6% AIBN dosage by weight is optimum for the stability of polymer emulsion and residual monomer amounts.

Impact of chain transfer agent concentration on polymer performance

Chain transfer agent usage will strongly impact the viscosity of polymerization system and reaction among monomers, but more usage can't improve the conversion ratio of monomers and the performance of final polymer, on the contrary it will raise the cost of raw materials.

2-aminoethyl mercaptan is used as chain transfer agent. Other synthesis parameters are the same as above examples. The impact of chain transfer agent on polymer performance was tested and the properties were listed in table 5.

TABLE 5
Chain transfer agent concentration influence on the performance of the product

Chain transfer agent(%)	Initiator (%)	Conversion rate(styrene%)
0.1	0.6	85.6
0.2	0.6	90.7
0.3	0.6	93.8
0.4	0.6	94.2
0.5	0.6	94.5

Styrene is the main monomer and its conversion rate is representative. Tab.5 results indicate that styrene has the suitable conversion rate when chain transfer agent dosage is 0.3% by weight of total monomers regarding its high price.

Physical properties analysis of final polymer

Based on the above explored examples, raw materials for cationic emulsion are: 50g styrene, 25g DAM, 25g BA, 0.6g AIBN, 0.3g 2-aminoethyl mercaptan, 43g isopropanol, 7.32g formic acid. Cationic surface sizing agent is obtained by solution polymerization and phase reversal on the acidic condition.

Physical properties of final polymer

In order to get stable final polymer with good quality, the physical properties must be tested under different conditions for confirming internal quality for good suitability at spot. Results were listed in Table 6.

TABLE 6
Physical properties of styrene-acrylate emulsion

Property	Observation/Value
Appearance	light yellow clear liquid
Solid content/%	30±1%
pH	3.0 5.0
Viscosity(mPa·s)	< 50
Ca^{2+} stability	qualified
High temperature stability	qualified
Mechanical stability	qualified
Freezing-thawing stability	qualified
Water solubility	easy soluble

IR spectrum analysis

IR spectrum of final polymer is given in Figure 1.

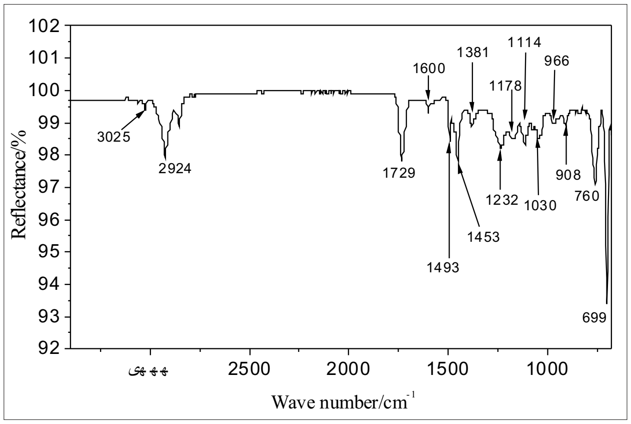

Figure 1 IR spectrum of polymer

In the FT-IR spectrum, 3025cm^{-1} is CH stretching vibration absorption peak of benzene ring , 1600cm^{-1} and 1493cm^{-1} are skeleton vibration peaks of the benzene ring, 1114 cm^{-1} and 966cm^{-1} are =CH in plane bending vibration peaks of the benzene ring, 699cm^{-1} and 760cm^{-1} C-H bending vibration of the single-substituted benzene ring; 2924cm^{-1} is symmetric stretching vibration absorption peak of methylene; 1729cm^{-1} is vibration peak of ester carbonyl, 1453cm^{-1} is the antisymmetric C-H bending vibration of the methyl ($-CH_3$), 1381cm^{-1} is symmetric bending vibration of methyl ($-CH_3$) of the C-H; 1232cm^{-1}, 1178cm^{-1} are the antisymmetric and symmetric stretching vibration of C-O-C; 1030cm^{-1} is stretching vibration peak of C-N. IR spectra of the polymer confirmed the monomers styrene, butyl acrylate and dimethylaminoethyl methacrylate.

Particle distribution of polymer

Styrene and butyl acrylate and dimethylaminoethyl methacrylate are copolymerized with 0.6% AIBN by weight, particle distribution of polymer is shown in figure 2. The average particle diameter is 99.1nm.

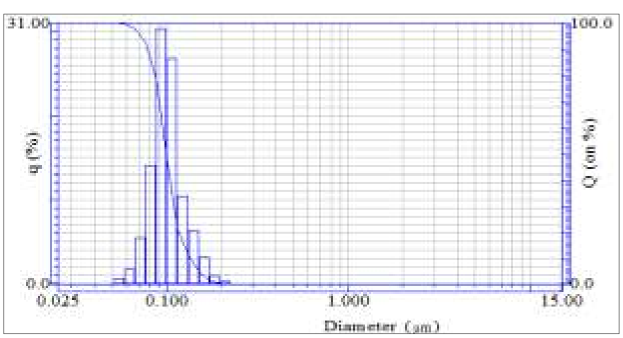

Figure 2 Particle distribution of polymer

Molecular weight determination of polymer

Molecular weight distribution of final polymer is shown in Figure 3.

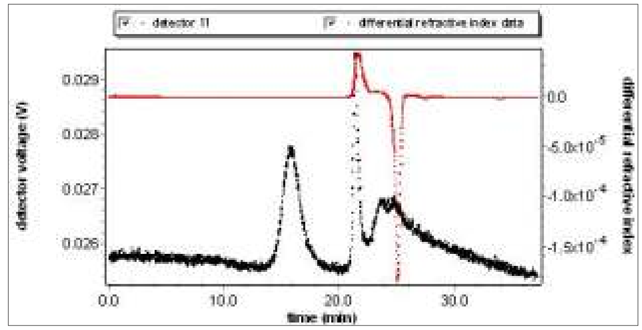

Figure 3 Molecular weight distribution of polymer

Polymer is diluted in ultrapure water and methanol whose volume ratio is 1:1, molecular weight of polymer is analyzed by hydrophilic Chromatography column of Shimadzo company. Test results are showed at Figure 3. X-axis represents eluting time of polymer, Y-axis represents response signal of detector. When polymer solution is eluted by chromatographic column, polymer with higher molecular weight is first detected because of exclusion effect of chromatography column. Eluting time of polymer is 21.1-25.1min. By calibrating with standard polyethylene glycol samples, number average molecular weight of polymer is 50118, weight average molecular weight is 61660, polydispersity index is equal to 1.23.

Conclusions

This paper relates to the solution polymerization of styrene, butyl acrylate and dimethylaminoethyl methacrylate which have been converted into cationic water-soluble surface sizing agent by phase reversal. These factors which are monomer composite, initiator dosage, polymerization concentration, chain transfer agent dosage are explored for polymer performance. Optimized process parameters are: St/BA/DAM equal to 50/25/25(by weight), initiator AIBN equal to 0.6% and chain transfer agent 2-aminoethyl mercaptan equal to 0.6% by weight of total monomer 70% polymerization concentration. The final polymer has good mechanical stability and solubility. It is analyzed by IR spectroscopy and particle distribution and molecular weight were also determined. The terpolymer has narrow particle distribution, whose average particle diameter is 99.1nm, Mn is 50118, Mw is 61660, polydispersity index is 1.23. The final copolymer has the desired surface sizing effect for untreated paper, Cobb value 23.2 g/m^2 and fluffing speed 1.76 m/s after surface sizing.

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