Study on Kinetics of Polymerization and Moisture-Proof Property of Acrylate Copolymer Latexes Used to Coating Corrugated Paperboard

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Abstract:
Corrugated paperboard for transport package have been affected by damp easily in the condition of being carried out from the refrigerator, or being shipped to oversea, or preserved in damp conditions or humid climates. The strength of the corrugated paperboard will drop down to 50% when environmental relative humidity comes up to 85%. Acrylate copolymer latexes, which was prepared with Methyl Methacrylate /Butylmethacrylate/Styrene as main monomers and by semi continuous emulsion polymerization technique, was used to coat Corrugated paperboard to improve its moisture-proof properties. The water absorbing capacity of coated paper was merely 19.7% after being dipped in water for 15min, and ring resistance-compensating intensity of coated paper having been dipped in water for 4min remain 0.26% higher than of uncoated paper.

The influence of particle size and molecular weight of Acrylate copolymer latexes on moistureproof properties was investigated. Moisture-proof property and Kinetics of Polymerization of Acrylate copolymer latexes was investigated. The result showed that the larger molecular weight of Acrylate copolymer latexes is and smaller latex diameter is, the more outstanding its moistureproof is. The kinetics equation of emulsion polymerization of Acrylate copolymer latexes with Methyl Methacrylate(MA) /Butylmethacrylate(BA) /Styrene(St)as main monomers was $R_p = k_1 [E]^{0.72} [I]^{0.68} [A]^{-1.21}$ and apparent activation energy $E_a = 151.6$ kJ/mol in stage of nucleation, $R_p = k_2 [E]^{-1.12} [I]^{0.59} [A]^{2.3}$ ([E] $> 9.957 \times 10^{-2}$ mol/L), $R_p = k_2 [E]^{1.12} [I]^{-0.59} [A]^{2.3}$ ([E] $> 9.957 \times 10^{-2}$ mol/L) and apparent activation energy $E_a = 131.13$ kJ/mol in stage of chain growth.

Keyword: Acrylate copolymer latexes; coating for Corrugated paperboard; Kinetics of Polymerization

1. Preface
With the development of food industry, packaging industry has developed rapidly. In the modern packaging, corrugated carton has already become the most widely used package vessel, especially in transport package, because of its excellent performance and environment friendly course of production.

However, corrugated paperboard for transport package has been affected by damp easily in the condition of being carried out from the refrigerator, or being shipped to oversea, or preserved in damp conditions[1,2]. The resistance of the corrugated paperboard will drop 50% when its relative humidity comes up to 85%[3], thus the inner product will be damaged owing to the paperboard broken. Thus it can not meet the requirements of packaging of Seafood, fruit etc which must be stored at low temperature. Therefore, it will make sense to improve the moisture-proof function of the corrugated paperboard.

It will be good method that coating is used to coat Corrugated paperboard to improve its moisture-proof properties.

2. Experiment
2.1. Regents and solutions
All reagents were of analytical grade. mixture of OP-10 and Dodecyl sulfonate is used as emulsifier, Ammonium persulfate as initiator.

2.2. Procedure
1) Process of polymerization
Acrylate copolymer latexes was prepared with Methyl Methacrylate(MA) /Butylmethacrylate(BA) /Styrene(St) as main monomers and by semi continuous emulsion polymerization technique, ratio of monomer MAA/BA/St is 1: 1: 0.47, flow chart is shown Fig. 1.

2) Calculation of conversion of monomer and polymerization rate
a) conversion of monomer in stage of nucleation (0-40min):
$$E = \frac{x_c - x}{x_c} \times 100\%$$ (1)
b) conversion of monomer in stage of chain growth (50-135min):
\[
E = \frac{m_a + R_{a} \cdot t - (m_w + R_{w} \cdot t) \cdot t \cdot 0.01}{m_a + R_{a} \cdot t} \times 100\% \tag{2}
\]

where \(E(\%)\) is conversion of monomer at times \(t\), \(x_{0}(\%)\) and \(x(\%)\) is concentration of monomer in the emulsion at initial, at times \(t\), \(m_a\) and \(m_w\) is amounts of Monomer and total amounts of Monomer, emulsifier and initiator added in the stage of nucleation \(g\) \(R_a\) and \(R_{w}\) is additional amount of Monomer and additional amount of Monomer ,emulsifier and initiator per minute \(g\cdot min^{-1}\) in the stage of chain growth respectively. \(t\) is time of addition, min; polymerization rate \(R_p\) \(mol\cdot min^{-1}\) may be calculated by equation:

\[
\left\{\begin{array}{ll}
\frac{d[R]}{dt} = k_{p}([M]_0 - [M]) \\
\end{array}\right.
\]

where \([M]_0\) is total concentration of mixed monomer added

3) Molecular weight of Acrylate copolymer latexes was determined by viscosity method[4], particle diameter was measured by spectrophotometer[5].

3. Results and discussion

3.1. Effect of stirring speed on polymerization rate and characteristics of Acrylate copolymer latexes

When polymerization temperature is 83°C, Dosage of emulsifier 5.9%, Dosage of initiator1.5%, the Relationship between conversion of monomer and polymerization time at different stirring rate and Relationship between polymerization rate(Rp) and Stirring speed(A) was shown in Fig. 2 and Fig.3, respectively.

\[R_p = \frac{[M]_0}{dt}\]

\[\ln R_p \propto -A^{1.21}\]

\[\ln A \propto R_p^{2.3}\]

Fig. 2 illustrates relationship between conversion of monomer (ε) and polymerization time(t) at different stirring speed, when polymerization time is in 0~40min and 50~135min, plot of E versus t lies on a straight. Result in Fig.3 show that plot of lnRp versus lnA lies on a straight line with a slope of -1.21 in stage of nucleation and 2.3 in stage of chain growth In the 200-400 rpm range, i.e., \(R_p \propto [A]^{1.21}\) in stage of nucleation, \(R_p \propto [A]^{2.3}\) in
stage of chain growth.

Research show that plot of water adsorption (y%) of paper coated with Acrylate copolymer latexes versus soaking time (x) may be described as $y = ax^{0.5}$, where “a” was defined as water adsorption coefficient. Fig. 4 illustrates plot of stirring speed versus water adsorption coefficient (a). Fig. 5 illustrates plot of stirring speed versus particle diameter and molecular weight.

3.2. Effect of emulsifier on polymerization rate and characteristics of Acrylate copolymer latexes

When polymerization temperature is 83$^\circ$C, stirring speed 350(rpm), Dosage of initiator 1.5%, the Relationship between conversion of monomer and polymerization time at different dosage of emulsifier and Relationship between polymerization rate (Rp) and dosage of emulsifier was shown in Fig. 6 and Fig. 7, respectively.

Fig. 6 illustrates relationship between conversion of monomer ($\varepsilon$) versus polymerization time (t) at different dosage of emulsifier, the effect of emulsifier on conversion of monomer was more complex, result in Fig. 7 show that plot of lnRp versus ln[E] lies on a straight line with a slope of 0.72 in stage of nucleation and with a slope of 1.1 (when [E] ≤ 9.957 $\times$ 10$^{-2}$ mol/L) and -1.12 (when [E] > 9.957 $\times$ 10$^{-2}$ mol/L) in stage of chain growth, therefore Rp$_{1}$ $\propto$ [E]$^{0.72}$ in stage of nucleation, Rp$_{2}$ $\propto$ [E]$^{1.1}$ (when [E] ≤ 9.957 $\times$ 10$^{-2}$ mol/L) and Rp$_{2}'$ $\propto$ [E]$^{-1.12}$ (when [E] > 9.957 $\times$ 10$^{-2}$ mol/L) in stage of chain growth.

Fig. 8 illustrates plot of dosage of emulsifier versus water adsorption coefficient (a). Fig. 9 illustrates plot of dosages of emulsifier versus particle diameter and molecular weight. Fig. 8 and Fig. 9 show that with the increase in dosage of emulsifier, water adsorption coefficient (a) increase, i.e., water resistance of coated paper become poor, molecular weight and particle diameter decrease, i.e. the larger molecular weight and...
particle diameter are, the less water adsorption coefficient of coated paper is, the better water resistance of coated paper is. That is not in agreement with result in Fig6 and Fig7, it is possible that emulsifier which is hydrophilic result in poor in water resistance of coated paper.

When polymerization temperature is $83^\circ C$, stirring speed 350rpm, Dosage of emulsifier 4.9%, the Relationship between conversion of monomer and polymerization time at different dosage of initiator and Relationship between polymerization rate(Rp) and dosage of initiator was shown in Fig.10 and Fig.11 respectively.

Fig. 11 show that plot of $\ln R_p$ versus $\ln [I]$ lies on a straight line with a slope of $-0.68$ in stage of nucleation and with a slope of $0.59$ in stage of chain growth, i.e., $R_p \propto [I]^{-0.68}$ in stage of nucleation, $R_p' \propto [I]^{0.59}$ in stage of chain growth.

Fig. 12 illustrates plot of dosage of initiator versus water adsorption coefficient(a). Fig. 13 illustrates plot of dosage of initiator versus particle diameter and molecular weight.

3.3. Effect of initiator on polymerization rate and characteristics of Acrylate copolymer latexes

When polymerization temperature is $83^\circ C$, stirring speed
3.4 Effect of polymerization temperature on polymerization rate

When stirring speed is 350(rpm), Dosage of emulsifier 5.9%, Dosage of initiator 1.5%, the Relationship between conversion of monomer and polymerization time at different polymerization temperature and Relationship between polymerization rate(Rp) and polymerization temperature(T) was shown in Fig. 14 and Fig. 15, respectively.

Fig. 14 illustrates relationship between conversion of monomer(E) versus polymerization time(t) at different polymerization temperatures.

Fig. 15 illustrates relationship between lnRp versus 1/T lies on a straight line with a slope of -18242 in stage of nucleation and 15772. The apparent activation energy(Ea) of polymerization can be calculated by equation of Arrhenius[6]:

stage of nucleation : \( E_a = 151.6 \) (kJ/mol)
stage of chain growth : \( E_a = -131.1 \) (kJ/mol).

Fig. 16 illustrates plot of polymerization temperature versus water adsorption coefficient(a). Fig. 17 illustrates plot of polymerization temperature versus particle diameter and molecular weight.

To sum up the above, molecular weight have a greater effect than particle diameter on water resistance of coated paper, the dosage of emulsifier also have a great effect on water resistance of coated paper, the less molecular weight and particle diameter of Acrylate copolymer latexes are, the less water adsorption coefficient(a) is, the better water resistance of coated paper with Acrylate copolymer latexes is poor.

4. Conclusion

stirring speed, polymerization, dosage of emulsifier, dosage of initiator have great effect on polymerization...
rate, molecular weight, particle diameter and water resistance of coated paper with Acrylate copolymer latexes. The kinetics equation of emulsion polymerization of Acrylate copolymer latexes with Methyl Methacrylate/Butylmethacrylate/Styrene as main monomers is \[ R_{p1} = k_1 [E]^{0.72} [I]^{-0.68} [A]^{-1.21}, \] \[ E_{a1} = -151.6 \text{ kJ/mol in stage of nucleation}, \] \[ R_{p2} = k_2 [E]^{1.1} [I]^{0.59} [A]^{2.3} ( [E] \leq 9.957 \times 10^{-2} \text{ mol/L}), \] \[ R'_{p2} = k_2 [E]^{-1.12} [I]^{0.59} [A]^{2.3} ( [E] > 9.957 \times 10^{-2} \text{ mol/L}) \] and apparent activation energy \[ E_{a2} = -131.13 \text{ kJ/mol in stage of chain growth}. \]

Molecular weight have a greater effect than particle diameter on water resistance of coated paper, the dosage of emulsifier also have a great effect on water resistance of coated paper, the less molecular weight and particle diameter of Acrylate copolymer latexes are, the less dosage of emulsifier is, the less water adsorption coefficient (a) is, the better water resistance of coated paper with Acrylate copolymer latexes is.

Reference