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Apparent kinetic study of latex interpenetrating polymer networks P(ethyl acrylate)/P(styrene) and P(styrene)/P (ethyl acrylate) by two stage emulsion polymerization

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ABSTRACT

P(ethyl acrylate)/P(styrene) (PEA/PS) latex interpenetrating polymer networks (LIPN) and P(styrene)/P (ethyl acrylate) (PS/PEA) LIPN were synthesized through two-stage emulsion polymerization and the apparent kinetics of polymerization was studied. Conversion versus time for LIPNs polymerization was investigated and rate of polymerization was calculated with the Arrhensius equation. It shows the polymerization of network I obeys the classical kinetic rules of emulsion polymerization showing an increasing-rate stage, a constant-rate stage and a decreasing-rate stage. But the polymerization of network II only appears a constant-rate stage and a decreasing-rate stage. It indicates that network II does not have a nucleus formation stage and the network II is formed on the basis of network I. The apparent activation energies (E_{as}) of LIPNPEA and LIPNPEA/PS in constant-rate period were 45.1 kJ/mol and 80.2 kJ/mol, respectively. However the E_{as} of LIPNPS and LIPNPS/PEA were 42 kJ/mol and 44.3 kJ/mol. It demonstrates that the polymerization E_a value of the network II is related to the properties of its seeded latex (network I).

1. Introduction

Latex interpenetrating polymer networks (LIPNs) constitute a unique type of polymer blend that is prepared by seeded emulsion polymerization (multistage emulsion polymerization). This multiphase polymeric materials exhibit properties that are often superior to those of their component homopolymers due to their morphological structure [1–3]. Since Sperling and Frich [4–6] developed the concept of Millar's IPNs in 1969, latex IPNs (LIPNs), an important type of IPNs, has drawn a great deal of attention from many investigators. In recent years, non-toxic LIPN is more important due to the more stringent environment legislations. LIPN have also received much attention in both scientific and industrial studies because they can often greatly improve the mechanical or other properties of polymers through the unique topological entanglement and interpenetration between networks [7–10]. It is reported some species have been used for industrial production. They have been widely used in plastic modification, rubbers, coatings, adhesives, damping materials, medical materials and so on [10–12].

The latex IPNs are generally synthesized by a two-stage emulsion polymerization technique. The first monomer was emulsion-polymerized and cross-linked to form the seeded latex (polymer I). Monomer II with a cross-linking agent was added into the seeded latex and then polymerized in-situ without forming new particles [13–15]. A variety of complex factors are involved in the synthetic process, the ultimate morphology of the resulting LIPNs and the mechanical properties of the films. These factors involve the method of addition of monomer into the system, the monomer ratio in the two stages and the hydrophilicity of monomers [16–23], the surface tension, the molecular weight of the polymers, the compatibility of the polymers, properties of initiators and degree of cross-linking in either the first or second-stage monomer [24–29]. Studies on LIPNs have mainly focused on the preparation process, morphology and properties. Very little information has been reported on the kinetic feature in particular its apparent kinetics of the polymerization process.

As to the polymerization of LIPN emulsion, its polymerization is carried out with the network I as the seeded emulsion. Consequently, the kinetic feature of polymerization differs from the traditional emulsion polymerization. In this work, two latex IPNs (LIPN PEA/PS and LIPNPS/PEA) were synthesized with cross-linking agent. Preliminary research has been carried out on the apparent kinetics of polymerization process for these latex IPNs. To have a better understanding of the apparent kinetics for different LIPNs, the apparent activation energy of polymerization process of the LIPNs with different seeded latex were calculated and compared.

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Table 1
Typical recipe for the synthesis of LIPN PS/PEA.

Component	Network I (seeded latex)	Network II (LIPN)
EA (g)	20.0	–
S (g)	–	30.0
AA (g)	1.0	1.0
DVB	0.2	0.3
OP-10 (g)	1.5	–
NaHCO3 (g)	0.1	0.15
KPS (g)	0.1	0.15
Deionized water (mL)	150	10

Attempt has been made to investigate the apparent activation energy of different LIPNs and their apparent kinetics regularity. Consequently the rules can be used to predict the morphology of the latex particles, formation of the particles (nucleation) and the particle size distribution. This ability to control particle morphology would significantly enhance the physical properties of these materials and their application.

2. Experimental

2.1. Materials

Styrene (S), ethyl acrylate (EA) and acrylic acid (AA) were purchased from Tianwei Chemical Co. (Tianjin, China) and distilled under vacuum prior to use. Divinyl benzene (DVB) was an industrial product with reduced pressure distillation refinement. Potassium persulfate (KPS, analytically pure), sodium bicarbonate ($NaHCO_3$, analytically pure) and polyoxyethylene (10) octyl phenylether (OP-10) were obtained from Beijing Chemical Plant (Beijing, China).

2.2. Polymerization procedure

2.2.1. Polymer network I (the seeded latex) polymerization

Polymerization was conducted in a 500 ml round bottomed, four-neck flask fitted with a mechanical stirrer, nitrogen inlet, condenser, and pipette inlet. The reactor was immersed in a thermostated water bath to maintain constant temperature. The typical recipe for LIPN PEA/PS is given in Table 1. The recipe of LIPNPS/PEA is the same as that of LIPN PEA/PS, only different monomers are used in network I or network II. Deionized water and emulsifier were stirred and gently warmed in a bottle. Monomer I mixture, which contained cross linker and acrylic acid, were added under stirring at a constant speed at the specified temperature. Then initiator was added to the reaction system. At the meantime, the time to carry out the polymerization of network I was noted.

2.2.2. Polymer network II (LIPN) polymerization

After the preceding polymerization has been performed, a mixture of monomer II, acrylic acid and cross linker was added to the seed latex (network I). Then the initiator was added and the time noted simultaneously. The polymerization reaction was carried out under constant temperature. The process of polymerization is the same as that of the seeded latex but no added emulsifier.

2.3. Characterization

2.3.1. The calculation of polymerization conversion, the rate of polymerization and the apparent activation energy of polymerization process

The monomer conversion was determined by a conventional gravimetric method.

The curve of conversion versus time was obtained at the different temperatures. The rate of polymerization could be evaluated by the differential calculation of the curve of conversion versus time (C%–t). Then the curve of polymerization rate to conversion (R_{p}– C%) could be described. As with the classical emulsion polymerization, the process included an increasing-rate interval, a constant-rate interval and a decreasing-rate interval. The majority of the monomer had reacted to the polymer in the constant-rate interval as the zero index reaction. The apparent activation energy in the constant-rate interval was calculated according to the Arrhenius equation [30,31].

$$R_{\mathrm{p}} = A\mathrm{e}^{-E_{\mathrm{a}}/RT} \tag{1}$$

$$\ln R_{\mathrm{p}} = \frac{-E_{\mathrm{a}}}{RT} + \ln A \tag{2}$$

A line was obtained from the relationship of $\ln R_{\mathrm{p}}$ to $1/T$. E_{a} was calculated from the slope K of the line.

$$E_{\mathrm{a}} = -KR \tag{3}$$

where R_{p} is the rate of polymerization; A, constant index; R, gas constant; T, polymerization temperature; E_{a}, the apparent activation energy; K, the gradient of the line.

The particle size and size distribution of latexes were determined by dynamic light scattering (DLS) using a 90 Plus particle size analyzer (Brookhaven Instrument Corporation, USA). The samples of latexes were diluted with distilled water to adjust the solid content to around 0.05 wt% and were placed directly in the cell. All measurements were carried out at 25 °C at a fixed angle of 90°, and the measurement time was 3 min.

3. Results and discussion

3.1. Polymerization kinetics of LIPN network I (seeded latex PEA) at different temperatures

The seeded latex PEA (network I) was synthesized by the above polymerization technique and the polymerization conversion was measured with the gravimetric method. Fig. 1 shows the evolution of instantaneous and overall conversion versus time for emulsion polymerization of network I (PEA), carried out at different polymerization temperatures, respectively. It can be seen that there is an initial period of very low instantaneous conversion. This slow start to polymerization is due to the low nucleation rate. Under these initial conditions monomers and radicals resulting from the decomposition of initiator need to diffuse into the micelle to form primary

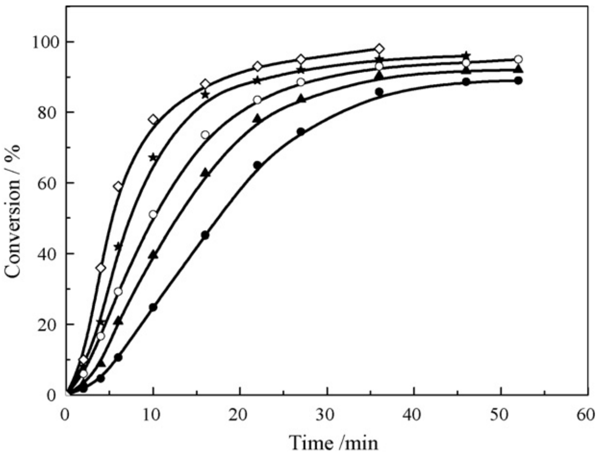

Fig. 1. The curves of conversion versus time for PEA emulsion polymerization of network I (seed latex) at different temperatures: (●) 65 °C, (▲) 70 °C, (○) 75 °C, (★) 80 °C, (◊) 85 °C.