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The study of esterifying reaction between epoxy resins and carboxyl acrylic polymers in the presence of tertiary amine

Shaohui Sun *, Peiqin Sun, Dazhuang Liu

Institute of Chemical Engineering, Zhengzhou University, Wen Hua Road 97#, Zhengzhou, Henan Province 450002, China

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Abstract

In this article, the fixed gel/nongel point and critical gel point experiments are designed for formulating the regulation of esterification reaction between epoxy resin and carboxyl acrylic polymer in the presence of tertiary amine in organic solvent. Ternary diagrams are employed to illustrate experimental results. It is disclosed that some factors, such as mole ratio of the ternary reactants, molecular weight of epoxy resin, even the hydrophilic solvent content of system, play important roles in the gelling effect of esterification reaction. In order to explain these experimental results, a suggested reaction process is put forward and, subsequently, a critical gel equation is derived from Carothers gelation theory. The equation provides an explicit connection between the critical gel composition and the relevant parameters of the reaction system such as average carboxyl functionality of acrylic resin, average molecular weight of epoxy resin, the base intensity of tertiary amine, and the solid content of system. The regressive critical gel curve based on the equation is well consistent with the experiment data. It expresses that the suggested reaction process is reasonable. Finally, based on the critical gel equation, the important factors that influence the esterification result are discussed qualitatively. All the achievements are beneficial to understanding the reaction process and avoiding useless gelation in preparing the water-reducible compositions.

Keywords: Epoxy–acrylate; Esterification; Ternary diagram; Gelation

1. Introduction

During the last two decades, legislation in many countries on the reduction of the volatile organic content of paints and coatings has resulted in the development of many new water-reducible coatings. Among these is the water-reducible epoxy–acrylic composition [1–4]. It is suitable for a metal coating, especially for an interior can coating. Several commercially available methods [5,6] have been developed to combine epoxy resin with carboxyl acrylic polymer together. For example, epoxy–acrylate composition is formed from the epoxy resin by the grafting of addition polymer onto aliphatic backbone carbons of the epoxy resin, such grafting being at carbons that have either one or two hydrogens bonded thereto in the ungrafted state [3,7,8]. In another preferred method, self-emulsifiable mixtures are prepared by esterifying epoxy resin with carboxyl acrylic polymer in an organic solvent medium in the presence of tertiary amine [6,9]. Then the adduct react with a base and render it self-dispersible into water

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* Corresponding author. Tel.: +86 371 388 7325; fax: +86 371 388 7329.

E-mail address: shaohui99@zzu.edu.cn (S. Sun).

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in neutralized form. Compared with the free-radical grafting method, the high molecular weight and complexity of the copolymers formed herein lowers the proportion of curing agent needed, and this provides tougher and more impact resistant cured coatings. Indeed, considerable chemical and water resistance is obtained in the absence of curing agent, so it can be omitted. However, from the standpoint of gelation theory, this esterifying practice normally leads to gel because there is more than one equivalent of oxirane functionality in each difunctional epoxide molecule per molecule of carboxyl-functional polymer. Fortunately, the presence of enough amine prevents gelation to occur till the oxirane functionality is entirely consumed.

Although this creative technique involving epoxy resin esterifying with carboxyl acrylic resin in the presence of tertiary amine has many advantages, the extensively industrial utility is limited for the following reasons:

1. The selection and proportion of reactants is only based on the experience and, sometimes, improper recipes lead to the useless gelation of reaction system.
2. The large proportion of amine functions to avoid gelatin in a fashion which is still not fully understood.

Ting [6] thinks that the large amount of amine possibly causes the present of salt formation with the carboxyl groups, which leads to the formation of colloidal particles in the solvent medium as the esterification reaction increases the molecular weight. This withdraws material from solution before it can gel and may provide the reason why systems which theoretically should form a useless gel, do not do so. On the contrary, Spencer [10] believes that the reactions at the 1,2 epoxy groups are competitive between the carboxylate ion of the amine neutralized addition prepolymer and the free tertiary amine. Water as a reaction modifier, can be chosen to favor either the esterification or quaternization reaction. In any event, the respective products formed are the hydroxy ester of the epoxy with the carboxyl-containing addition polymer and a quaternary ammonium group generated from the tertiary amine and the 1,2-epoxy group of the epoxy component. Neither of the assumption can clearly explain our experimental critical gel points.

The purpose of this article is to highlight the effects of factors on the gelling of esterification system, such as the average molecular weight of epoxy resin, the solid content of system, the type of amine, the mole ratio of the reactants. Furthermore, based on a suggested reaction process and Carothers' critical gel point theory, the critical gelling equation is determined. The regressive critical gel curve upon this equation agrees with the experimental data. Finally, The discussion upon the equation gives experimental regulation a reasonable explanation. All the achievements help us deeply understand the reaction process and avoid gelling effect in producing the water-reducible compositions. No previous studies of this type have been undertaken on esterifying epoxy resin with carboxyl acrylic polymer.

2. Experimental

2.1. Materials

Butylacrylate (BA), styrene (St) monomers are purchased from Shanghai Chemical Reagent Corporation and distilled under reduced pressure before polymerization. The purified monomers are kept at 4 °C before use. The other materials, such as butyl cellosolve, butanol, Benzoyl peroxide, methacrylic acid (MAA),epoxy resin, Bisphenol A, tributylamine, Dimethylaminoethanol are used without further purification.

The $618^{\#}$, $604^{\#}$ epoxy resins are purchased from Jiangsu Sanmu Chemical Co., Ltd. The average molecular weight (calculated from 1,2-epoxy group content) is 392 and 1667, respectively. The carboxyl acrylic polymer is preformed by ourselves. Molecular weight is in a range from 5000 to 100,000 determined by gel permeation chromatography (GPC).

2.2. Synthesis of polyacrylate

The polyfunctional acrylic polymer is synthesized by charging 126 g of butyl cellosolve and 214 g butanol to a 1 L round bottom flask fitted with a thermometer, nitrogen sparge tube, stirrer and condenser reactor. In a separate vessel, a premix is made of 114 g glacial methacrylic acid, 64 g styrene, 80 g butyl acrylate, and 5.2 g benzoyl peroxide. An inert gas blanket is started and the solvents are heated to 121 °C when ten percent of the premix is added. The heat is increased to obtain reflux and the remainder of the premix is added over two hours. Reflux is maintained for an additional hour. The mixture is then cooled down to room temperature. The acrylic prepolymer solution has a solids content of 42.6% and acid number of 280 mgKOH/g (based on solid content) and a viscosity of 5500 centipoises. The polyacrylate is used as it has been prepared without further purification.

2.3. Preparing epoxy resin solution

2.3.1. Modified epoxy resin

Epoxy resin $618^{\#}$ 100 g and Bisphenol A 44 g, Ethylene glycol monobutyl ether 20 g are charged to a 1 L round bottom flask fitted with a thermometer, nitrogen sparge tube, stirrer and condenser. Under an inert gas blanket, the temperature is raised to 140 °C. 0.3 g tributylamine is added, the heat is turned off and the reaction is allowed to exotherm to 180 °C. The temperature is then reduced to 150 °C, cover the next 30 min, 124 g Ethylene glycol monobutyl ether is then added. Finally, the 1,2-epoxy group content as measured by HBr titration in glacial acetic acid to the crystal violet end point is 0.45 meq/g. The solid content is 50%.

2.3.2. Preparing $618^{\#}$, $604^{\#}$ epoxy resin solution

Epoxy resin $618^{\#}$ 500 g is diluted with a blend solvent comprised of butanol and Ethylene glycol monobutyl ether in a ratio of 33/67 to get 1 L transparent solution. The 1,2-epoxy group content measured by HBr titration in glacial acetic acid to the crystal violet end point is 2.55 meq/ml. The solid content is 0.5 g/ml.

Epoxy resin $604^{\#}$ 500 g is also diluted with a blend solvent comprised of butanol and Ethylene glycol monobutyl ether in a ratio of 23/77 to get a 1 L transparent solution. Heat is supplied if necessary. The 1,2-epoxy group content as measured by HBr titration in glacial acetic acid to the crystal violet end point is 0.6 meq/ml. The solid content is 0.5 g/ml.

2.4. Experimental design

In order to learn the correlation between the reactants mole ratio and gelling, two types of esterifying reaction are designed to investigate the effect of reactants proportion on the gelling of system.

2.4.1. Fixed point experiment

A series of epoxy acrylic polymer mixtures are prepared in different reactants proportion by charging acrylic prepolymer and epoxy resin solution in a round bottom flask fitted with a stirrer, thermometer and condenser and heated to about 95 °C. Dimethylaminoethanol is then added upon the recipe and the reaction temperature is maintained at 95 °C over 1 h. During that time, some recipes lead to gel in the reactive process, which are defined as gel points. Others yield a stable transparent solution, which are defined as nongel points. All the results are displayed in ternary diagram.

2.4.2. Critical gel point experiment

The critical gel point is obtained by fixing the amount of acrylic prepolymer and amine used in the reactor. When the reactor temperature is elevated to 95 °C, add the epoxy resin in the amount of surely nongel. One hour later, when the epoxy groups are entirely consumed, add epoxy resin every hour in minimum amount gradually until the reactive mixture just gel.

2.5. Determination of dissociation constants of amine and carboxyl acrylic polymer

In order to learn the carboxyl or amine existing state in the complex organic solvent which is important factor to the esterification reaction, nonaqueous potentiometric titration method is employed to determine the acidic dissociation constant of the carboxyl groups in acrylic polymer or base dissociation constant of tertiary amine in the same blend organic solvent as the medium of esterifying reaction.

3. Results and discussion

3.1. The gel regulation described by ternary diagram

The experimental results of fixed points of epoxy resin $618^{\#}$ or $604^{\#}$ are illustrated in Fig. 1 or Fig. 2

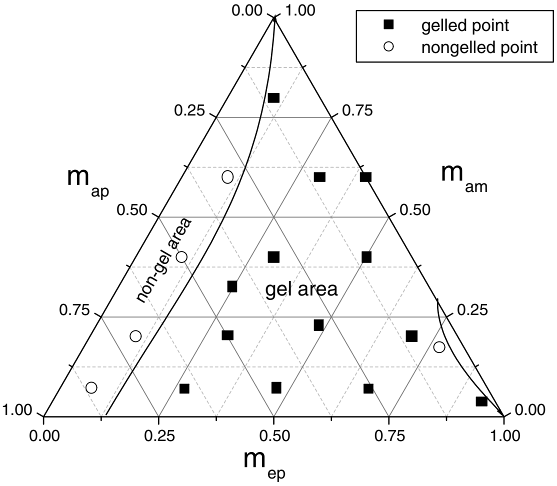

Fig. 1. The fixed points experiment of $Ep618^{\#}$/amine/acrylate ternary reaction system in organic solvent.

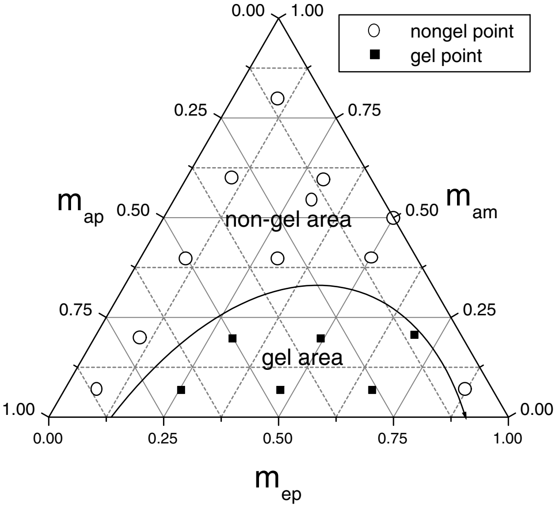

Fig. 2. The fixed points experiment of $Ep604^{\#}$/amine/acrylate ternary reaction system in organic solvent.

respectively. The lines express the rough boundary of gel and nongel area. It is clear that the gel area of Ep618$^{\#}$ is larger than Ep604$^{\#}$, especially when the mol-ratio of epoxy group and amine exceeds the carboxyl functional group. It means the low molecular weight epoxy resin is more activity than the high molecular weight epoxy resin in the same reactant mole ratio.

From the point of preparing aqueous composite coatings, the amount of carboxyl functional group must exceed the amount of epoxy group. The sufficient carboxyl groups can render composition self-dispersible in water in neutralized form. Our following research is focus on the left corner of ternary diagram where carboxyl ratio is more than 0.5, epoxy and amine ratio is less than 0.5. In this area, the critical gel points are measured elaborately. The result is shown in Fig. 3. It can be seen firstly the amount of epoxy resin allowed to be used in the system increases along with the increasing of amine's amount, but the relation is not a linear function. Secondly, in accordance with Figs. 1 and 2, the smaller the epoxy resin molecular weight is, the more possible the reaction tends to gel when other reaction conditions are the same. Thirdly, the solid content of system is also an important factor to influence the esterification process. The less solvent, the greater the danger of gelation is. That is exposed when we reduce the quantity of solvent to the extent that solid content increase from 50% to 65% (wt%) accordingly, the previous critical gel point turns to gel point rapidly during the esterification process. In addition, the temperature of esterification reaction is always fixed at 95 °C for the benefit of comparing the experimental data. In this temperature, the esterification reaction can be finished within 1.5 h at which time the 1,2 epoxy content falls to 0 meq/g.

3.2. The possible esterification process

The scheme of esterification reaction between acrylic polymer and epoxy resin is shown in Fig. 4. There is few theoretic study on esterification mechanism despite the industrial importance. In the reference of the previous knowledge of epoxy resin [11] in the curing process, the possible reaction details between acrylic carboxyl polymer and epoxy resin in organic solvent medium in the present of sufficient tertiary amine are represented schematically in Fig. 5. Except the main well known reactions (R1, R2, R5), we take the self-polymerization of epoxy resin (R4, R7) into account, which is always ignored before.

R1 is an acid–base neutralizing balanced reaction between carboxyl group of acrylic polymer and free tertiary amine, as we have known.

R2 expresses the esterification reaction that epoxy group reacts with the carboxyl ionic group to form addition polymeric hydroxy ester, a reaction which would normally lead to gel. However, in order to make high-performance coatings, we expect more oxirane functions combined with carboxyl functions in R2 to the point of almost gel.

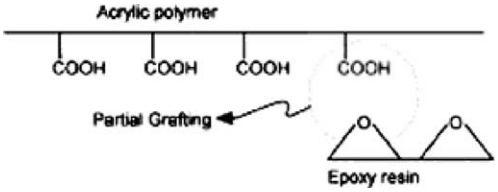

Fig. 4. The scheme of esterification reaction between acrylic polymer and epoxy resin.

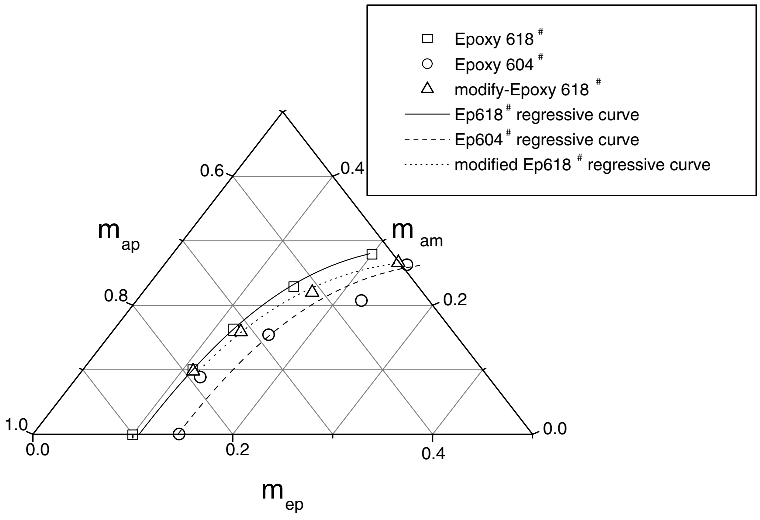

Fig. 3. The experimental critical gel points of three different epoxy resin in esterification reaction and the regressive critical gel curves of them based on Eq. (9).

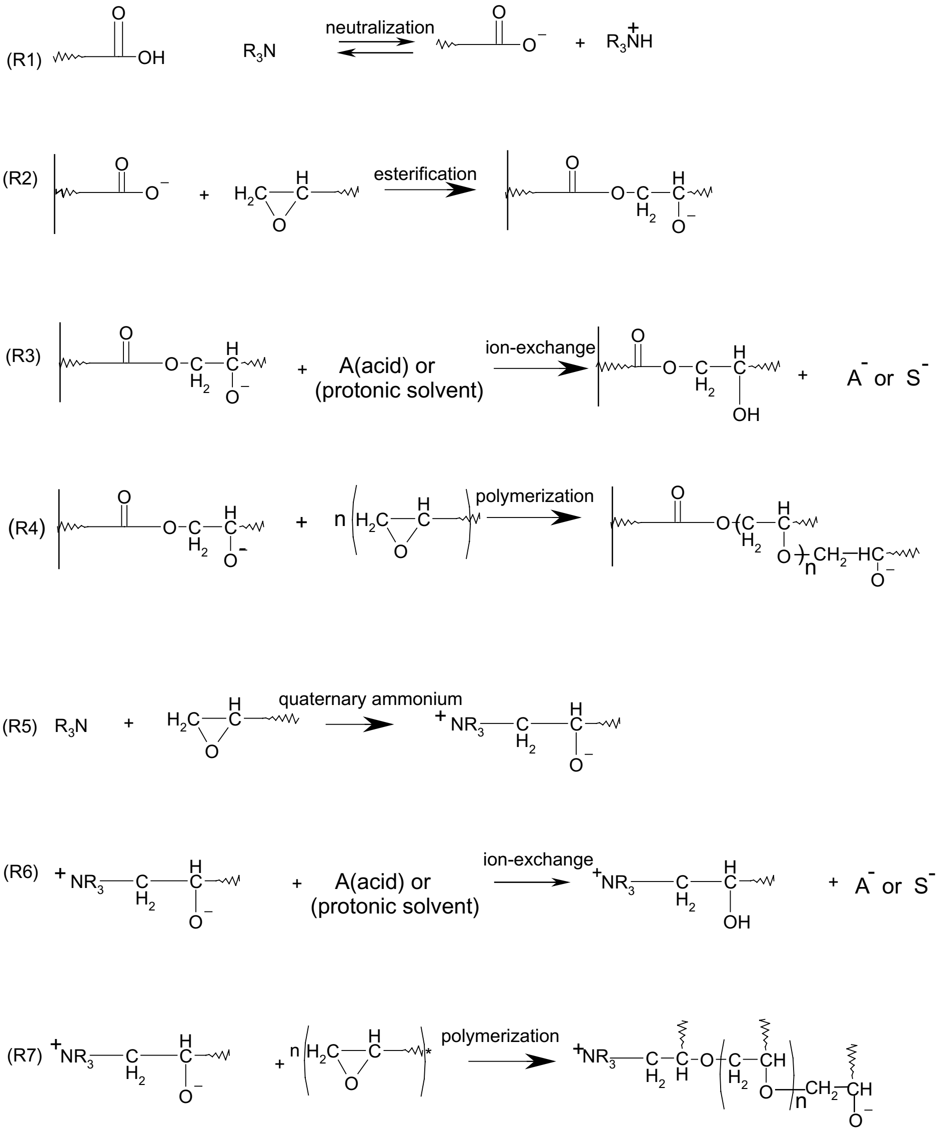

Fig. 5. The possible reactions in the complex epoxy/amine/acrylate ternary system in organic solvent.

R3 and R6 express the ion-exchange reactions between oligomeric alkyloxy-ion and small molecules, such as butanol, water. These protogenic molecules can give proton and terminate the polymerization.

R4 and R7 express the alkyloxy-ion initiating self-polymerization of epoxy resin, which is popular in epoxy resin curing process in the presence of amine catalyst. In general, reaction rate of R7 is faster than R4, and herein they are treated as a whole without identifying for the benefit of discussion. We suggest this kind of reactions may take place in some extent in the esterification system because the yellow gelation appears when the concentration of oxirane and amine are high enough in the reaction process. That is the characteristic of epoxy resin curing process. Furthermore, taking R4 and R7 into account can explain experiment perfectly.

R5 expresses the reaction that free tertiary amines as a mono-functional material react with materials containing oxirane functions to yield adducts containing quaternary ammonium groups. From the standpoint of gel, R1 and R5 is not gel, but the reactions R2, R4 and R7 may form three-dimensional structure and result in gelatin in the end. The gelling effect of epoxy resin is expected in conventional curing procedure. On the contrary, it must be avoided in the process of preparing the epoxy–acrylic water-reducible composition coating. Based on these reaction formulations and the experimental data, we will conclude the critical gel equation by Carothers gel theory.

3.3. Critical gel equation concluded by Carothers theory

It is difficult to calculate the above reactions rate or extent because the accurate kinetics data related to the polymeric reactions are absent. So we try to describe the characterization of this complex esterification by Carothers gel theory.

3.3.1. Simulate Ep604# gel/nongel boundary

According to Carothers gel theory, the polymeric reaction between two functions is completed without gelling must fulfill the condition that the average functionality of reaction system is no more than $2(\bar{f} \leqslant 2)$, as well as the critical gel condition is $\bar{f} = 2$. In the epoxy/amine/acrylate ternary solution system, functional equivalent ratio of three reactants has the following relationship of $m_{EP} + m_{AP} + m_{AM} = 1$, m is the equivalent ratio of one reactant, the subscript AP, AM or EP represents acrylic polymer, tertiary amine or epoxy resin correspondingly. In order to evaluate the applicability of Carothers gel theory in the complex esterifying system, we first take into account the main reactions of R2, R5 and put all the other possible reactions aside. When acrylic polymer and amine are in large proportion in the reaction system, ① $m_{AP} + m_{AM} > m_{EP}$, Otherwise, when epoxy resin is in large proportion, ② $m_{AP} + m_{AM} < m_{EP}$, the average functionality $(\bar{f})$ can be expressed respectively as the following Eq. (1) or (2).

$$\bar{f} = \frac{2 \times N_{EP} f_{EP}}{N_{EP} + N_{AP} + N_{AM}} \tag{1}$$

$$\bar{f} = \frac{2 \times (N_{AP} f_{AP} + N_{AM})}{N_{EP} + N_{AP} + N_{AM}} \tag{2}$$

In the above equations, the symbol N denotes the number of molecule, f is the functionality of one reactant, the subscript AP, AM, EP has the same meaning like the above. It is known that $N_{EP} = \frac{m_{EP}}{2} \times N_A$, $N_{AP} = \frac{m_{AP}}{f_{AP}} \times N_A$, N_A is Avogadro's number. If we assume that $\bar{f} = 2$, $f_{AP} = 25$, $f_{EP} = 2$, $N_{AM} = m_{AM}$, Eqs. (1) and (2) can be rewritten as

$$1.08 m_{AP} + 3 m_{AM} = 1 \tag{3}$$

and

$$m_{AP} = \frac{m_{EP}}{2} \tag{4}$$

From Eqs. (3) and (4), the simulated cursorily gel/nongel boundary of Ep604# is illustrated in Fig. 6. Although we ignore many details, such as tertiary amine acid–base neutralizing reaction with acrylic carboxyl polymer (R1), which reduces the great amount of tertiary amine, the shape of simulated curve is still similar to experimental curve. It makes clear that Carothers gel theory is applicable to describe the gel regulation in the complex esterification system.

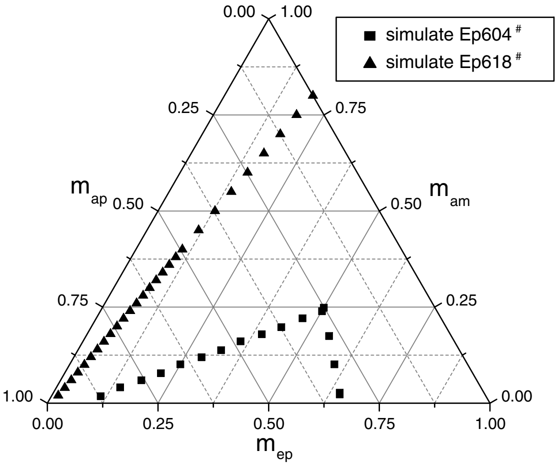

Fig. 6. Simulate the critical gel curve cursorily by Carothers gel theory.

3.3.2. Simulate Ep618# gel/nongel boundary

Different from the epoxy resin 604# where the average molecular weight is 1666, Ep618# has a smaller average molecular weight about 392. The small molecular size of Ep618# makes its oxirane functions more active than Ep604#. This can be seen in Fig. 1 that Ep618# has more chance to gel than Ep604#. Excepting the esterification (R2), we conclude that more Ep618# take part in the self-polymerizations of R4, R7 which can increase the molecule weight and even lead to gel in another reaction mechanism different from R2. The gelation existing in the upper or right part of the tertiary diagram in Fig. 1 supports this opinion and demonstrates that gelation still generates in the manners of R4, R7 despite there is few carboxyl functions in the reaction system. Therefore, how to introduce the reactions extent of R4, R7 properly into the simple Carothers gel equation is an important problem which influences the simulation effect of critical gel curve.

It is known that the self-polymerization reactions R4, R7 would consume epoxy groups and even lead to gel. In this process, epoxy molecule acts like a multi-functional substance which can react with more than 2 others to form reticulation gradually. So, if the reaction R4 or R7 occurs in the epoxy/amine/acrylate ternary solution system, the actual functionality of epoxy resin would exceed $2(f_{EP} < 2)$. To verify the above suggestion, we take the values ($f_{AP} = 25, f_{EP} = 9, f_{AM} = 1$) into Eq. (1), then get the following result:

$$1.01 m_{AP} + 1.25 m_{AM} = 1 \tag{5}$$

The simulated curve of Eq. (5) is also illustrated in Fig. 6. The shape of the simulated curve agrees with the experimental result of Ep618# in principle. This successful simulation indicates that different reactions (R2, R4, R7) in the esterification process can be unified in the critical gel equation by the corrected value of epoxy functionality parameter (f_{EP}). When the regressive value of f_{EP} is more than 2, it expresses that the self-polymerization (R4, R7) among epoxy groups in the presence of amine catalyst has occurred indeed. The higher value the f_{EP}, the more reaction extent of R4, R7.

3.3.3. Simulate critical gel curve by modified Carothers theory

In addition to the self-polymerization, there are at least two factors we should think over to describe the gel regulation accurately. One is the acid–base neutralization (R1), which consumes a great deal of tertiary amine in the solution. Because of it, the real concentration of amine participating in R5 is actually less than the original concentration. Therefore the number of N_{AM} in Eq. (1) must be recalculated. The other factor is the effect of solid content of reaction system. The hydrophilic solvent can afford proton to terminate ionized macro-molecular groups by ion-exchanging reaction, is known in Fig. 5 (R3, R6). This kind of reaction reduces the molecular weight of production. It means that protonic solvent molecule as one of reactants is helpful to decrease the average functionality of epoxy resin as well as the danger of gelation, which is consistent with the experimental result. So we have to introduce a new parameter S into Eq. (1) to represent the virtual effect of solvent molecule reacting with ionized group. It is clear that the value of S is depended on the solid content of the reaction system. The higher the solid content is, the smaller the S value is. As we have mentioned, the following study is limited in the condition that the proportion of carboxyl group is much more than the proportion of epoxy group or amine, just in the left corner of tertiary diagram. The excessive carboxyl functions in epoxy–acrylate composition can neutralize with a base and disperse itself into water to form a stable emulsion.

When $m_{\mathrm{AP}} > m_{\mathrm{EP}}$, $m_{\mathrm{AP}} > m_{\mathrm{AM}}$, Eq. (1) can be modified to get the following equation (6). Based on the acid–base balance theory, the amount of N_{AM} among Eq. (6) can be expressed with Eq. (7), where K_{b} is the dissociation constant of tertiary amine in the reaction solution, and N_{A} is Avogadro's number. Because the carboxyl group is excessive ($m_{\mathrm{AP}} > m_{\mathrm{AM}}$), the whole reaction system is a buffer solution comprised of excessive carboxyl group and ionized carboxyl group. The amount of ionized carboxyl group is almost equal to the total amount of amine because of the acidic environment of the system. Therefore the balance concentration of hydroxyl is given by Eq. (8). Where K_{S} is self-dissociation constant of the blend solvent, and K_{a} is dissociation constant of the carboxyl groups of acrylic polymer in the same blend organic solvent.

$$\bar{f} = \frac{2 \times N_{\mathrm{EP}} f_{\mathrm{EP}}}{N_{\mathrm{EP}} + N_{\mathrm{AP}} + N_{\mathrm{AM}} + S} \tag{6}$$

$$N_{\mathrm{AM}} = m_{\mathrm{AM}} \cdot N_{\mathrm{A}} \times \frac{[\mathrm{OH}^-]}{[\mathrm{OH}^-] + K_{\mathrm{b}}} \tag{7}$$

$$[\mathrm{OH}^-] = \frac{K_{\mathrm{S}}}{K_{\mathrm{a}}} \cdot \frac{[\mathrm{COO}^-]}{[\mathrm{COOH}]},$$

$$[\mathrm{OH}^-] = \frac{K_{\mathrm{S}}}{K_{\mathrm{a}}} \cdot \frac{m_{\mathrm{AM}}}{m_{\mathrm{AP}} - m_{\mathrm{AM}}} \tag{8}$$

When we put Eqs. (6)–(8) together and order $\bar{f} = 2$, the following equation (9) would be concluded. S^* express the term concerned with the parameter S.

$$m_{\mathrm{AP}} + \frac{2m_{\mathrm{AP}}}{f_{\mathrm{AP}}(f_{\mathrm{EP}} - 1)} + m_{\mathrm{AM}} + \frac{2 \cdot K_{\mathrm{S}}}{(f_{\mathrm{EP}} - 1) \cdot (K_{\mathrm{a}} \cdot K_{\mathrm{b}})} \cdot \frac{m_{\mathrm{AM}}^2}{(m_{\mathrm{AP}} - m_{\mathrm{AM}})} + S^* = 1 \tag{9}$$

The acid dissociation constant of carboxyl group of acrylic prepolymer in the blend butyl cellosolve and butanol organic solvent was determined as $pK_{\mathrm{a}} = 7 \pm 1$ by nonaqueous potentiometric titration method. In the same blend solvent, the value of base dissociation constant of dimethylaminoethanol is $p(K_s/K_{\mathrm{b}}) = 7.0$. So, the value of $\frac{K_{\mathrm{S}}}{K_{\mathrm{a}} \cdot K_{\mathrm{b}}} = 1$ can be introduced into Eq. (9). The value of f_{AP} expresses the average molecular weight of preformed carboxyl acrylic polymer, which has been determined by GPC method. We take it as an unknown parameter deliberately in order to validate the following simulated effect. Except that, there are still two parameters f_{EP}, and S^* in Eq. (9). As we known, the value of f_{EP} expresses the extent of reactions (R4, R7 in Fig. 5), the value of S^* expresses the extent of reactions (R3, R6 in Fig. 5) of solvent participating in. They are difficult to determine. However, when the experimental data of m_{AP} and m_{AM} are taken into Eq. (9), the two parameters as well as f_{EP} can be confirmed by nonlinear curve fitting method. The regressive parameters are listed in Table 1 and Fig. 3 shows the corresponding regressive curves.

The molecular weight of acrylate prepolymer is in the range from 5000 to 100,000 determined by the gel permeation chromatography (GPC). From the regressive value of $f_{\mathrm{AP}} = 65$, we can estimate the acrylic polymer weight is 13,000. It is in agreement with the result of GPC. The fact of regressive values of f_{EP} all exceed 2 shows that a considerable proportion of oxirane functions react with each other by self-polymerization. Moreover, in this process, the less molecular weight is, the higher reaction extent of self-polymerization is. As for the modified Ep618$^{\#}$, it has been defunctionalized to reduce the functionality less than 2 in the modified process. So, despite the modified Ep618$^{\#}$ molecular weight is close to Ep604$^{\#}$, the value of f_{EP} is smallest. Another interesting result is the regressive value of S^*, which contributes the significant (about 10%) proportion in Eq. (9). This fact demonstrates the important role of solvent in the reaction system. The protogenic solvent is preferred to reduce the possibility of gel, that is the

Table 1
Values of parameters in Eq. (9) confirmed by NLCF method

Indentification code	Regressive result			
	Value of f_{AP}	Value of f_{EP}	Value of S^*	R^2
Ep618#	66.5	7.99	0.10	0.999
Ep604#	65.6	6.5	0.14	0.969
Modified Ep618#	64.6	5.86	0.11	0.997

reason why proper water is added to the esterification system in Spencer' patent [10].

3.4. The effects of some factors on the gelation by critical gel equation (9)

3.4.1. Effect of functionality of carboxyl acrylic polymer

The functionality (f_{AP}) of performed carboxyl acrylic polymer is about 25–500 according to the determination of molecular weight by GPC method and the concentration of methacrylic acid in the polymer. If the f_{AP} is changed from 25 to 500, the coefficient of m_{AP} in Eq. (9) is changed correspondingly, but the maximal difference of coefficient is no more than 10%. It means the great change of molecular weight of acrylic polymer in some extent has not much important influence on the gelling effect. This conclusion is consistent with the experimental result. If we assume that $p(K_s/K_b) = 7$, $f_{EP} = 2$, $S^* = 0.1$, $f_{AP} = 25$ or 500, the simulated curves are shown in Fig. 7.

3.4.2. Effect of base intensity

When dimethylaminoethanol is replaced with another tertiary amine-triethylamine, the danger of gel increases, and the original critical gel point turns to gel point during the reaction process. This experimental phenomenon has not been well understood until the base dissociation constant of triethylamine is determined as $p(K_s/K_b) = 7.7$ by nonaqueous potentiometric titration method. It means that the base intensity of triethylamine is stronger than dimethylaminoethanol. Based on Eq. (9) and $\frac{K_S}{K_a \cdot K_b} = 0.2$ of triethylamine, we can estimate the effect of the base intensity on the gel area in the condition of $f_{AP} = 25$, $f_{EP} = 2$, $S^* = 0.1$. The result is shown in Fig. 8. It clearly indicates that a little change of base intensity has a great effect on the esterification process. The stronger the base is, the easier it is to induce the gel of system. Because the concentration of free tertiary amine is determined by the value of pH, it also suggests that the pH of reaction system is also an important factor to influence gel in the same way as base intensity.

3.4.3. Effect of molecular weight of epoxy resin

The previous discussion has related the value of f_{EP} to the reaction extent of self-polymerization (R4, R7 in Fig. 5). As we have known, the reaction extent (reactivity) can further relate to the molecular weight of difunctional epoxy resin. The lower f_{EP} is, the higher the molecular weight of epoxy resin. Fig. 9 shows the effect of molecular weight of epoxy resin on the critical gel curve. Compared with the effect of molecular weight of acrylate polymer in Fig. 7, the effect of molecular weight of epoxy resin is much more important. There are two ways to lower the value of f_{EP}, one is to increase the molecular weight of epoxy resin in the reaction. However, an excessively high molecular weight introduces problems of incompatibility which can only be resolved by reacting a considerable proportion of oxirane functionality, and this leads to gelation. The other way is

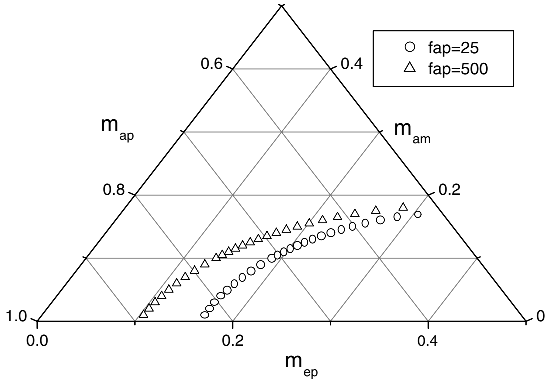

Fig. 7. The simulated critical gel curves by Eq. (9) when $p(K_s/K_b) = 7$, $f_{EP} = 2$, $S^* = 0.1$, $f_{AP} = 25$ or 500.

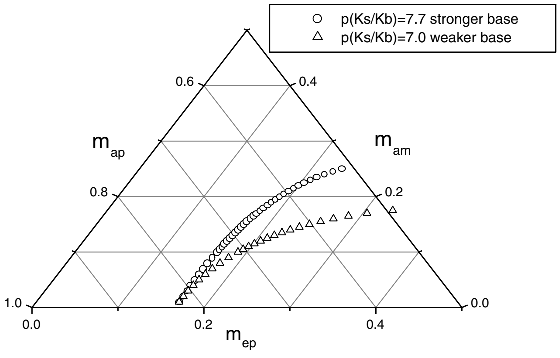

Fig. 8. The simulated critical gel curves by Eq. (9) when $f_{AP} = 25$, $f_{EP} = 2$, $S^* = 0.1$, $p(K_s/K_b) = 7.7$ or 7.0.

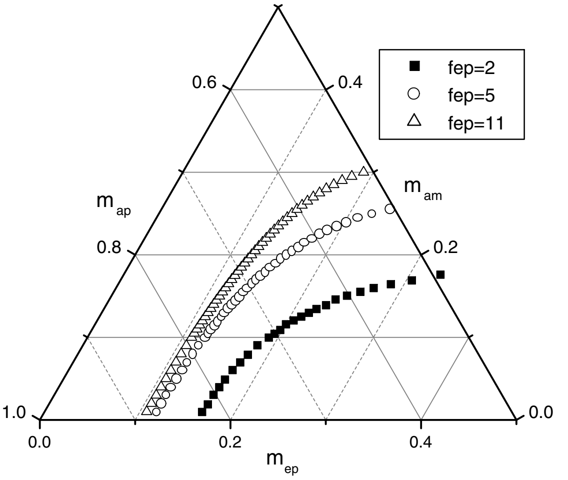

Fig. 9. The simulated critical gel curves by Eq. (9) when $f_{AP} = 25$, $S^* = 0.1$, $p(K_s/K_b) = 7$, $f_{EP} = 2$, 5 or 11.

to modify the epoxy resin to reduce the proportion of diepoxide as well as the value of f_{EP}. It is often practical to start with lower molecular weight epoxy resins and merely chain extend the same in a known manner with divalent compounds such as bisphenol A. In this way, the preferred molecular weight of epoxy resin is obtained and epoxy functionality decreases at the same time. Fig. 3 shows the experimental critical gel point of modified Ep618#.

3.4.4. Effect of solid content of system

From the point of protecting the environment, it is desirable to use as little solvent as possible to minimize the solvent content of the final aqueous emulsions. However, experiments told us the less solvent, the greater the danger of gelation is. This regulation can be simulated in Fig. 10 by adjusting the value of S^* in Eq. (9) that is consistent with the experiments. The practical solid content of the solution containing two resins is between 40% and 65%.

4. Conclusions

Based on the designed fixed gel/nongel point and critical gel point experiments, the relations between the gelation and the reactants are disclosed in tertiary diagram. The critical gel equation is concluded. The simulated critical gel curve upon the equation accords very well with the experiment data. All this work illustrates that the suggested reaction process is reasonable. The possible reaction details can be summarized as following. First, self-polymerization of epoxy resin which is always ignored before may take place in some extent in the epoxy resin/amine/acrylic polymer reaction system. Secondly, the tertiary amine is not only utilized as a esterification catalyst to accelerate the esterification, but also as a mono-functional material reacting with a part of oxirane functions to avoid gelling of the reaction system. Furthermore, the organic solvent is not only a medium where the esterification process is carried in, but also a reactant which terminates some oligomeric ionic groups to prevent gelling of the reaction system.

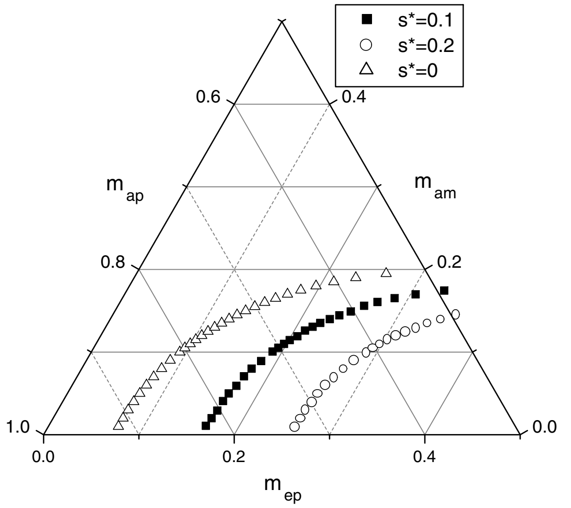

Fig. 10. The simulated critical gel curves by Eq. (9) when $f_{AP} = 25$, $p(K_s/K_b) = 7$, $f_{EP} = 2$, $S^* = 0$, 0.1 or 0.2.

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