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SHORT COMMUNICATION

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Phase inversion of UV-curable anionic polyurethane in the presence of acetone solvent

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Abstract UV-curable self-emulsified polyurethane acrylates were synthesized in acetone and then dispersed in water. The effect of acetone's ratio on the emulsification of the polyurethane acrylate was investigated. With a proper amount of acetone as a solvent, stable emulsion with small particle size and narrow particle size distribution was successfully produced and the viscosity during the process of emulsification was greatly reduced. However, stable emulsion could not be obtained when the acetone level was larger than a critical value. A ternary phase diagram was mapped. It was found that only those systems experiencing a phase inversion process lead to a stable emulsion. The carboxylic content is another important factor influencing the properties of emulsion and the process of emulsification. The effect of the carboxylic content on the emulsification was also studied in the experiment. There was another critical carboxylic content for stability. Stable emulsions with small drop sizes less than 50 nm were produced.

Keywords Self-emulsification · Phase inversion · UV-curable latex · Rheology

Abbreviations PIP: Phase inversion point · SAD: Surfactant affinity difference

Introduction

Aqueous emulsion coatings have been widely used in recent decades, due to their advantages in improving occupational health and safety [1–4]. The aqueous polymer dispersions used in those coatings can be classified into natural, synthetic, and artificial dispersions. Synthetic dispersions are directly obtained by heterophase polymerizations, such as emulsion and miniemulsion polymerizations of vinyl monomers. However, for those polymers that cannot be synthesized by radical polymerization, like polyester or polyurethane, one has to turn to physical emulsification. The physical emulsification of polymer resin or polymer solvent solutions in water can prepare artificial dispersions of all kind of polymers synthesized by various polymerization mechanisms, including condensation polymerization. There are two routes of physical emulsification: direct emulsification and phase inversion emulsification. By direct emulsification, it is difficult to disperse a highly viscous component. Phase inversion emulsification is effective in producing emulsions of high viscosity component [5] with smaller droplet size distribution, greater storage stability and lower latex viscosity than direct emulsification [4]. In practice, phase inversion emulsification is widely used in the petroleum, food, pharmacy, cosmetics and coating industries and has become an important emulsification technique in the commercial production of polymer emulsion [6].

Most of the studies on the emulsion inversion of polymers were based on the experiments of polymer–water–surfactant systems, for the final polymer emulsion traditionally is stabilized by externally added surfactant [7, 9–10, 12–13]. Since the external surfactants can deteriorate the final properties of emulsion coatings, many self-emulsified polymers were synthesized and found to have many advantages such as better stability, easier dispersion and less foaming ability [14–15]. Recently, the phase inversion of self-emulsified polymer was investigated by several research groups, including Brooks and Chen [8, 16–17, 19–20].

In many cases, the use of solvents to reduce the viscosity of the polymer phase during the emulsification is inevitable [16–18]. In the present study, a UV-curable ionomeric polyurethane solution with varied amounts of acetone was chosen as the studying system. UV-curable self-emulsified polymers have relatively complex structures with both unsaturated C = C bond and hydrophilic group in the polymer [22–25]. The emulsification process of these polymers cannot be carried out at high temperatures to avoid the cross-linking of the C = C groups. Those solvents with low boiling point, such as acetone, were chosen as the viscosity reducer, because acetone in the O/W emulsion can be stripped off to give nonvolatile emulsion.

Studies on the effect of solvents on emulsification are limited. Shunji Kojima [21] has pointed out that some water-soluble solvents such as ethylene glycol monobutyl ether (EGBE) have adverse effects on emulsification and stable dispersions cannot be formed when the mixed solvent becomes more water-soluble. Reports studying the effects of the amount of solvents' on the emulsion inversion process are scarce .

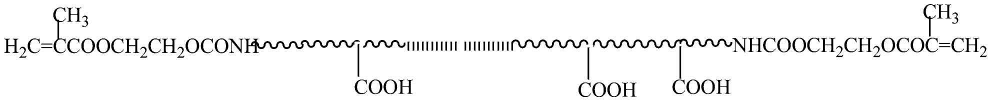
In this paper, how the amount of acetone solvent affects the process of emulsification has been investigated and the ultimate properties of emulsion have been studied. The changes of viscosity and conductivity were monitored during the emulsification. As a kind of self-emulsified polymer, it requires a certain amount of hydrophilic group on the polymer chain to form a stable emulsion. The effects of different carboxylic amounts on the phase inversion and the drop size of emulsion have also been studied.

Experimental procedures

Materials and synthesis of UV-curable self-emulsified TDP400 polymers

Before use, 2,4-Tolylene diisocyanate (TDI) was vacuum distilled. Dimethylol propionic acid (DMPA, > 99%), polypropyleneoxide glycol (PPG400, $M_n = 400$) were maintained in vacuum at 80 °C for 2 h to remove the moisture. 2-Hydroxyethyl methacrylate (HEMA, > 98%), acetone (analytical pure) and triethylamine (TEA, analytical pure) were dried by molecular sieves. Dibutyltin dilaurate (DBTL, analytical pure) was used as catalyst. *p*-Hydroxyanisole (analytical pure) was used as an inhibitor. 1-Hydroxy-cyclohexyl-phenyl-ketone (IRGACURE184, Ciba) was used as an photoinitiator.

A series of UV-curable self-emulsified TDP400 polymers with different carboxyl amounts (as shown in Scheme 1) were synthesized in a glass reactor with a stirrer, a reflux condenser, and a thermometer. The reaction was carried out under N_2 purge. The amount of the –NCO during reaction was monitored using the dibutylamine back titration method and IR spectra.



$$H_2C{=}\overset{CH_3}{\overset{|}{C}}COOCH_2CH_2OCONH\sim\sim\underset{\underset{COOH}{|}}{\sim}\sim\cdots\cdots\sim\sim\underset{\underset{COOH}{|}}{\sim}\sim\underset{\underset{COOH}{|}}{\sim}\sim NHCOOCH_2CH_2OCO\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

TDP400 was synthesized in acetone solution under N_2 purge. PPG400 and TDI were reacted at 40 °C for 2 h. DMPA neutralized by a stoichiometric amount of TEA was dissolved in acetone. This solution of DMPA was then added to extend the polymer chain and incorporate the carboxyl as a hydrophilic group. Finally, HEMA was poured into the reactor to react with the residual –NCO and incorporate unsaturated C = C group into the polymer. The molecular weight and carboxyl amount were controlled by the ratio of the reactants. The molecular weight of the synthesized polymers was set to 4,000 g/mol and their carboxyl amounts were set to 0.2, 0.3, 0.4 and 0.5 mmol/g, respectively.

Emulsification procedure

The emulsification was carried out in a 250-ml glass flask with a two-bladed stirrer (diameter = 3 cm). The ratio of acetone in the polymer solution was adjusted to a given amount. Water was dropped into the TDP400 acetone solution at a rate of 50 ml/h to form an aqueous emulsion. The agitation speed was controlled at 1,050 ± 50 rpm. The temperature of emulsification was maintained at 25 °C. During this process, the TDP400 emulsion with water as the continuous

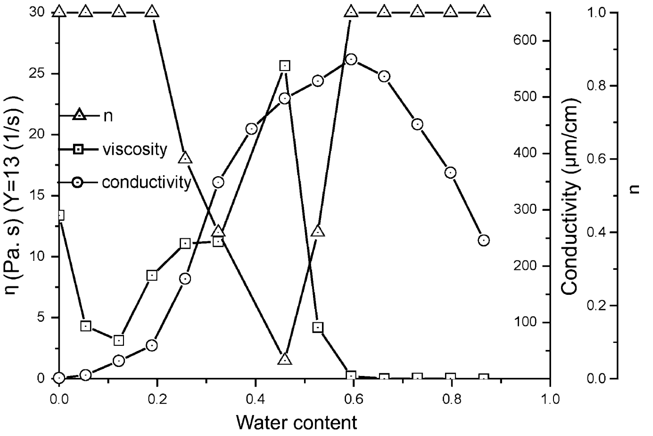


Fig. 1 Variation of conductivity, viscosity and non-Newtonian index with water content. (Water content $=m_{\text{water}}/m_{\text{water + acetone + polymer}}$. Ratio of acetone $=m_{\text{acetone}}/m_{\text{acetone + polymer}}$). Ratio of acetone = 0.26. $T = 25$ °C. The carboxylic content in TDP400 is 0.3 mmol/g

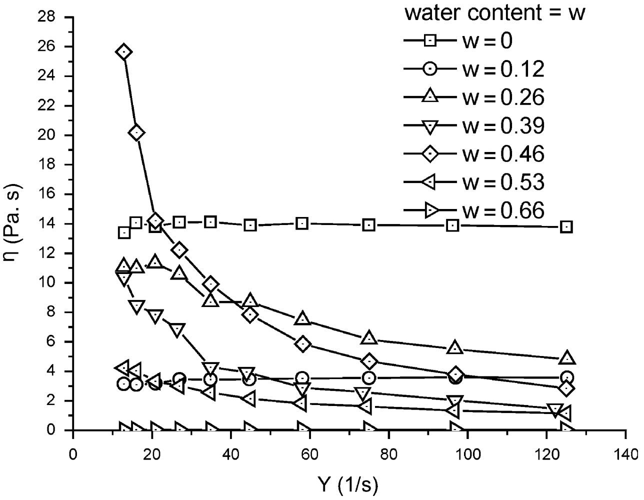


Fig. 2 Viscosity versus shear rate for TDP400 of different water contents. (Water content $=m_{\text{water}}/m_{\text{water + acetone + polymer}}$. Ratio of acetone $=m_{\text{acetone}}/m_{\text{acetone + polymer}}$.) Ratio of acetone = 0.26. $T = 25$ °C. The carboxylic content in TDP400 is 0.3 mmol/g

phase was produced. Finally, the emulsions were distilled with a rotary vacuum evaporator to remove the acetone solvent.

Measurements and apparatus

Rheological behavior during the phase inversion process was monitored using a Rheolab MC1 Rheometer. Electric conductivity was monitored using a DDS-11A Digital Conductivity Meter. Emulsion particle size and distribution were measured by a two particle size analyzer, namely, Coulter LS-230 and Malvern Zetasizer 3000HSA.

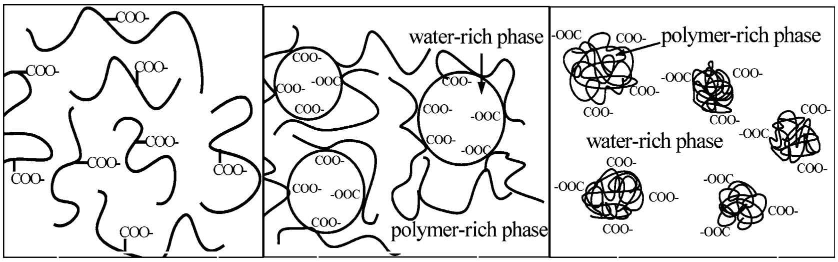
Results and discussion

A typical emulsification process

The process of emulsification is illustrated by a typical system with acetone ratio 0.26 (as shown in Fig.1). Figure 2 shows viscosity curves at different water contents. The viscosity decreases slightly after the initial addition of water. Further addition of water causes a sharp increase in viscosity. After reaching a maximum, the viscosity falls quickly by the dilution with water. The maximum point of viscosity is considered as the phase inversion point (PIP). The system was found to be one of the Newtonian fluids but they exhibited pseudoplastic behavior in the vicinity of PIP. The curves of the emulsion are coincided with power-law. The emulsion at PIP has the lowest non-Newtonian index (*n*) value (as shown in Fig.1). The rheological behavior of emulsions is influenced by many factors. The shear-induced deformation and alignment of the droplets may contribute to the shear-thinning behavior.

It was observed that the dispersion system began to become turbid as *n* became lower than 1, which was indicated that the system became heterogeneous and phase separation happened. Actually, the system appeared white with a bluish cast when the dispersion system became turbid. Phase separation happened before the maximum of viscosity, and it may be considered that the water-rich liquid phase formed into the dispersed phase and the polymer swollen with the acetone solvent was the continuous phase. Since there is no external surfactant in the system, the water-rich phase is actually stabilized by anionic polyurethane that constitutes the continuous phase. Addition of water made the viscosity increase before the maximum value, and decrease after the maximum, showing that the W/O structure was switched to O/W structure at the point of PIP and the polymer particles enclosed by a continuous water-rich phase. This is why the maximum point of viscosity is considered as PIP in this paper.

As shown in the viscosity graphs of the emulsification, the phase inversion process can be clearly divided into three stages. In stage 1, the viscosity drops slightly and, as described in Fig. 3a, the dispersion system looked clear. The system exhibits Newtonian behavior. The carboxyl groups are partly neutralized. In stage 2, the viscosity begins to rise and reaches the maximum. In this stage, the non-Newtonian index *n* is lower than 1 and decreases to the lowest value. Phase separation occurs and W/O structure formes, as shown in Fig.3b. It is difficult to divide the conductivity graphs of TDP400 into three stages. The conductivity rises steadily in stages 1and 2. In stage 3, where the phase inversion was com-



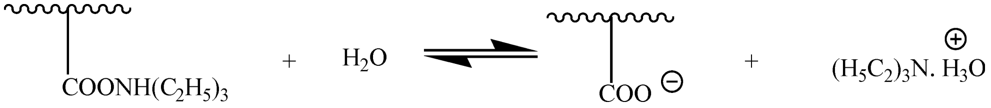
(a) stage 1 (b) stage 2 (c) stage 3

Fig. 3 Schematic emulsion morphologies during the process of emulsification

pleted, the adding of water dilutes the highly concentrated emulsion and makes the viscosity decrease sharply. The conductivity increases to the maximum at first and then begins to fall in this stage. The water content at the maximum of conductivity is not same as that at PIP, which is also observed in other systems with different amounts of acetone.

It was reported that the conductivity curve had a sudden jump at PIP in the case of conventional external emulsification. Low conductivity readings in the conventional case indicate that the continuous phase is the polymer or oil phase, because the conductivity of the oil phase is much lower than that of the aqueous phase with electrolyte. The aqueous phase of the external emulsified system may contain a salt to improve the conductivity in order to monitor the process of phase inversion. Thus, high conductivity readings indicate that the phase inversion has been completed and the aqueous phase becomes the continuous phase. So the PIP in conventional external emulsified system can be identified easily by the conductivity graph [21]. But the anionic self-emulsified polymer synthesized in this study alone can make the aqueous phase conductive since the polymer itself contains ionized carboxylic group. Therefore, it is unnecessary to add move salt during the conductivity measurement. The conductivity of TDP400 in the present experiment increases steadily (as shown in Fig. 1), just like those of ionomeric polymer systems without solvent [8, 17–18].

There was an ionization equilibrium in the anionomer solution as water was added (see Structure 1):



$$\mathrm{\sim COONH(C_2H_5)_3 + H_2O \rightleftharpoons \sim COO^{\ominus} + (H_5C_2)_3N.\,H_3O^{\oplus}}$$

The ionization equilibrium moved to the right and the electrolytic concentration became larger as water was added. As a result, the conductivity increased with the increasing of water content. After formation of the O/W emulsion, more ion was released as more water was added, but the dilution by water became the main factor to influence the conductivity. No additional electrolyte was also responsible for the decreasing of the conductivity after the formation of O/W emulsion. There was no sudden change in the conductivity graph of TDP400 phase inversion. Therefore, the PIP of TDP400 cannot be determined with the conductivity graph alone.

Emulsification process with different acetone levels

Viscosity evolution curves with different acetone levels

The level of acetone was found to have great effect on the emulsification. The viscosity curves were greatly influenced by the acetone level, as shown in Fig. 5. Too much use of acetone can damage the emulsions' stability. Actually, stable emulsion cannot be obtained when the ratio of acetone is larger than a critical value, which is 0.55 for TDP400 (as shown in Table 1). From the results of the experiment, stable emulsions were obtained as the acetone's ratio varied from 0.26 to 0.45; when the solvent's ratio was larger than 0.55, the final dispersions were partly or totally precipitated. Within the critical value for stable emulsion, the drop size and distribution of emulsion didnot change much. The emulsions could keep stable for more than 12 months.

All of the curves in Fig.4 except the totally precipitated system show that the viscosity rises before the viscosity maximum and falls sharply after that. The same changing trend of viscosity as the water phase increases, is found in external-emulsified dispersion systems, which can be seen in the study of Szelag and Pauzder [26]. It can be seen from Fig. 4 that the viscosity decreases sharply with the increasing acetone ratio. When the ratio of acetone rose from 0.26 to 0.45, the maximum viscosity fell from 26 Pa s to 7 Pa s.

The observation of the non-Newtonian index *n* being the lowest at PIP is found at various acetone ratios during the emulsification process (as shown in Fig. 5). Furthermore, it seems that the lowest *n* value decreases

Table 1 The emulsion drop size and appearance as the ratio of acetone is changed

Ratio of acetone	Volume average particle size (μm)	Volume average particle size/number average particle size	Emulsion appearance	Size analyzer
0.90			Totally precipitable	
0.65	8.501	22.31	Totally precipitable	Coulter LS-230
0.55	0.440	6.73	Partly precipitable	Coulter LS-230
0.45	0.127	1.05	Stable	Zetasizer 3000HSA
0.35	0.124	1.05	Stable	Zetasizer 3000HSA
0.26	0.120	1.04	Stable	Zetasizer 3000HSA

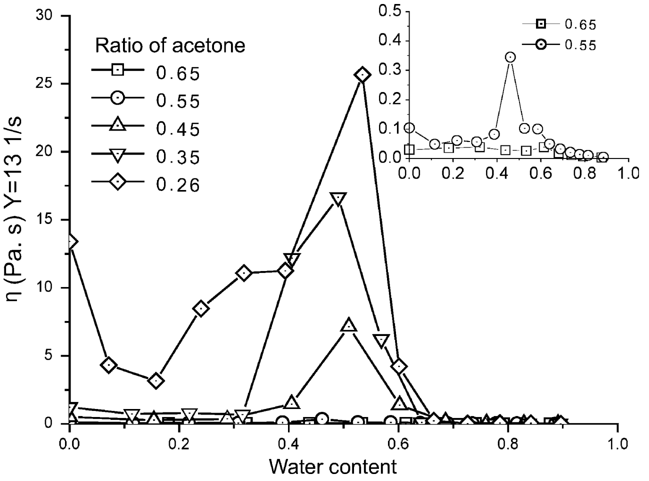


Fig. 4 Viscosity evolution of TDP400 at different acetone ratios. (Water content $= m_{\text{water}}/m_{\text{water + acetone + polymer}}$. Ratio of acetone $= m_{\text{acetone}}/m_{\text{acetone + polymer}}$). The carboxylic content in TDP400 is 0.3 mmol/g

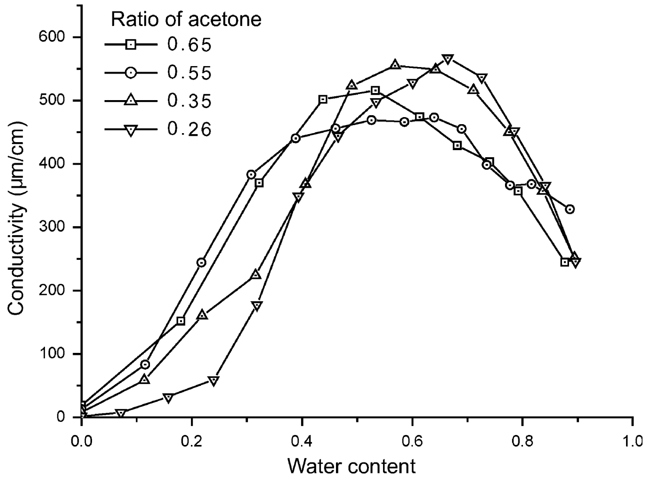


Fig. 6 Conductivity evolution of TDP400 at different acetone ratios. (Water content $= m_{\text{water}}/m_{\text{water + acetone + polymer}}$. Ratio of acetone $= m_{\text{acetone}}/m_{\text{acetone + polymer}}$.) The carboxylic content in TDP400 is 0.3 mmol/g

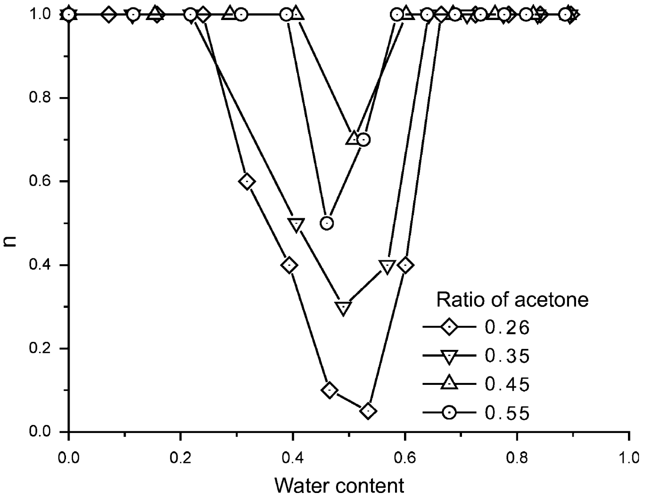


Fig. 5 Non-Newtonian index evolution at different acetone ratios. (Water content $= m_{\text{water}}/m_{\text{water + acetone + polymer}}$. Ratio of acetone $= m_{\text{acetone}}/m_{\text{acetone + polymer}}$.) The carboxylic content in TDP400 is 0.3 mmol/g

with the reduction of acetone level. Again, the dispersion systems began to become turbid as *n* became lower than 1, which indicated that the system became heterogeneous and phase separation occurred. Here too, the stable emulsion systems appeared white with a bluish cast and the precipitated system was purely white when the dispersion system became turbid. Non-Newtonian behavior occurred earlier in those cases of low acetone level. Since acetone and water are miscible, more water is needed to make phase separation occur as the acetone level becomes higher.

Conductivity evolution curves with different acetone levels

Changing the amount of acetone does not have great effect on the shapes and values of the conductivity (as shown in Fig. 6). Since the conductivity is also influenced by other factors such as viscosity and solvent, it is hard to find an apparent changing trend in the conductivity graphs. Before phase inversion, the conductivity of these systems with higher acetone concentration

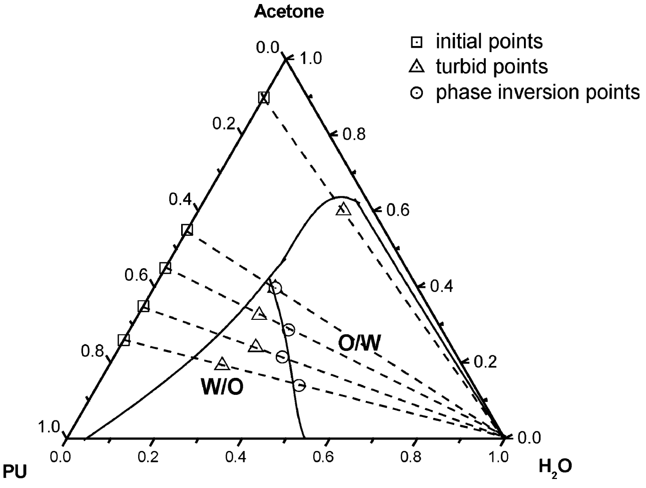


Fig. 7 Schematic ternary phase diagram for the system TDP400-acetone-water

is higher than that of those with lower acetone concentration, the reason might be that the viscosity becomes lower and the ionized polymers move more freely when more acetone is used.

The critical ratio of acetone for stability

Emulsification was carried out by adding water into the acetone solution of polyurethane. Initially, a limited amount of water can dissolve in the PU/acetone solution. As more water is added, phase separation occurs. We can describe this process by a ternary phase diagram, as shown in Fig. 7. Turbid points can be approximately considered as phase separation points. Connecting turbid points, we can divide the diagram into homogeneous and heterogeneous regions. The heterogeneous region can be further divided into W/O emulsion and O/W emulsion parts by the PIP line which connects PIPs. Since the ratio of PU to acetone is invariable during emulsification, the composition points changes along the straight dash line towards pure H_2O with the addition of water. As seen in Fig. 7, those composition lines with lower acetone ratios would go from the homogeneous region through the W/O emulsion region into the O/W region, experiencing a phase inversion process. However, in the cases of higher acetone ratios, the composition lines would go directly from the homogeneous region to the O/W emulsion. In such a case, PU would precipitate from PU/acetone/H_2O solution. It was found that a stable emulsion could be obtained only in those systems experiencing phase inversion. The process of adding water into these higher-acetone-amount systems was likely to be a precipitation process. The polymer directly precipitated from acetone and water solvent and coalesced into a large bulk that could not disperse stably in the solvent. But the ternary phase diagram cannot describe the phenomena of decreasing viscosity at the PIP. The formulation–composition bidimensional diagram was used to describe the phenomena of the emulsion inversions. The ordinate is a generalized parameter SAD, which is surfactant affinity difference, and the abscissa is the water/oil content.

The Formulation–composition diagram

In fact, on changing the ratio of acetone, the formation of the system was different. The numerical expression for SAD [27] of the ionic surfactant system was utilized to discuss the phenomena in the experiment. SAD is the difference between the standard chemical potentials of the surfactant in the oil and water phase,

$$\mathrm{SAD} = \mu^*_{\mathrm{W}} - \mu^*_{\mathrm{O}} = \Delta G_{\text{oil-water}} = -RT \ln K_p \tag{1}$$

where K_p is the partition coefficient of the surfactant between water and oil at the corresponding temperature. Salager showed that the numerical expression as a function of the formulation variables is given by:

$$\mathrm{SAD}/RT = \ln(S) - K \times \mathrm{ACN} - f(\mathrm{A}) + \sigma - \sigma_T \Delta T + \mathrm{Constant} \tag{2}$$

where S is the salinity, ACN (alkane carbon number) is a characteristic parameter of the oil phase, f(A) is the function of the alcohol type and concentration, σ is the characteristic parameter of the surfactant structure and ΔT is the temperature deviation from the ambient reference temperature (25 °C). K and α_T are empirical constants that depend on the nature of the system. The "Constant" is the value of SAD/RT for a reference system that is at "optimum formulation."

Actually, T is constant and S is zero in the system we studied. We can now write the following expression for the current system:

$$\mathrm{SAD}/RT = -K \times \mathrm{ACN} - f(\mathrm{A}) + \mathrm{Constant}' \tag{3}$$

when the ratio of acetone increases, the polymer phase is swollen with more acetone solvent and ACN decreases according to its definition [28]. Both acetone and alcohol can be dissolved in water and partition into the oil phase. Acetone makes a similar effect on SAD as alcohol does in the system. Since f(A) is a degressive function of alcohol concentration [29], the value of f(A) also decreases with the increase of acetone ratio. So it can be deduced that the SAD in our system rises with the increase of acetone ratio and approaches "optimum formulation" where the SAD = 0 (as shown in Fig. 8). It is known that at optimum formulation the emulsion stability, viscosity and the interfacial tension become minimum [11]. Therefore, increasing the ratio of acetone makes the emulsion more and more unstable and the viscosity at PIP decreases as the formulation is approaching the "optimum formulation." The interfa-

Table 2 The emulsion drop size and appearance as the amount of carboxylic group is changed

Carboxylic content (mmol/g)	Volume average particle size (μm)	Volume average particle size/number average particle size	Emulsion appearance	Size analyzer
0.20			Totally precipitable	
0.30	0.127	1.05	Stable, opaque	Zetasizer 3000HSA
0.40	0.021	1.17	Stable, semitransparent	Zetasizer 3000HSA
0.50	0.021	1.5	Stable, semitransparent	Zetasizer 3000HSA

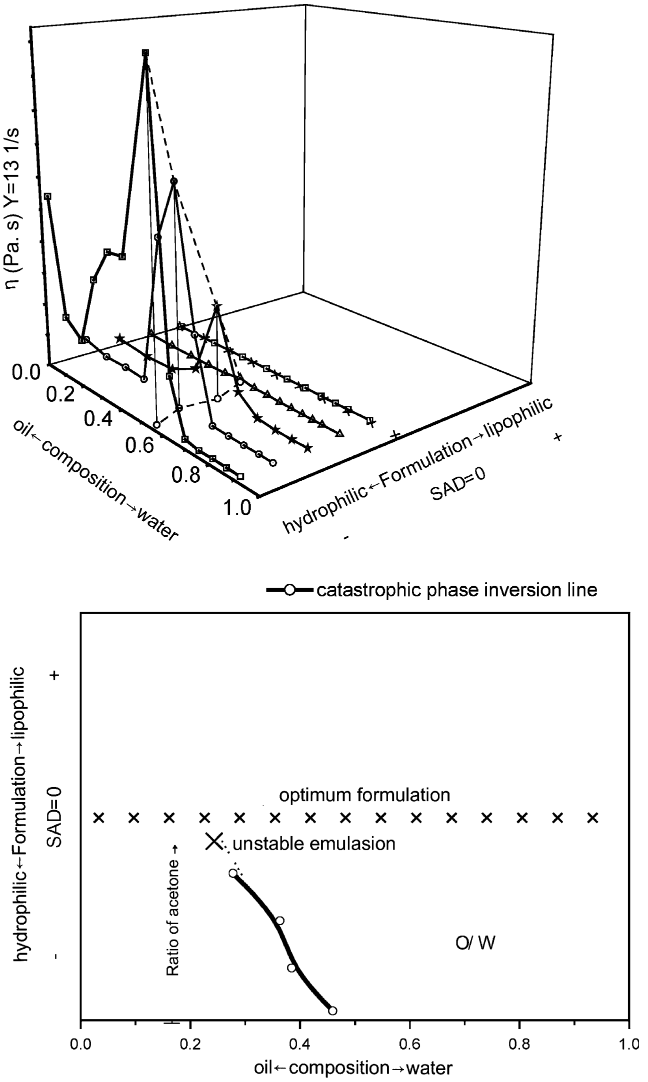


Fig. 8 Formulation—water fraction schematic diagram for TDP400—water dispersions, showing the emulsion inversion line as the amount of acetone is changed. The carboxylic content in TDP400 is 0.3 mmol/g

cial tension becomes lower and lower as the acetone amount increases. The cause may be that stable emulsion could not be obtained by catastrophic phase inversion when the acetone amount was larger than a critical value.

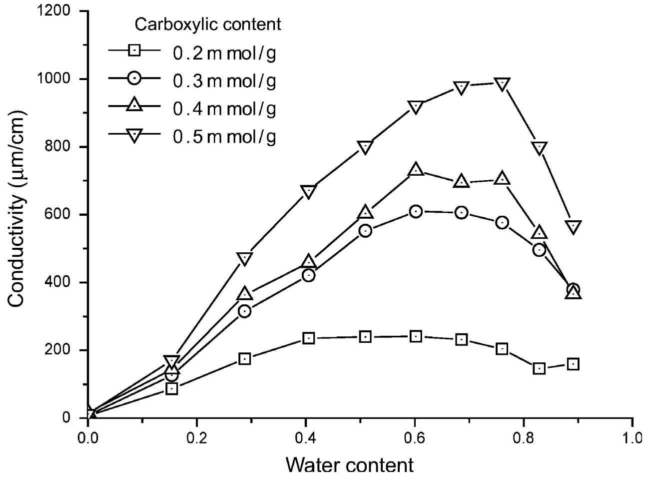


Fig. 9 Conductivity graphs of TDP400 with different carboxylic contents. (Water content = $m_{\mathrm{water}}/m_{\mathrm{water}\ +\mathrm{acetone}\ +\mathrm{polymer}}$.) Ratio of acetone = 0.45

Emulsification process of PU with different carboxylic content

The minimum carboxylic content

Many researches indicate that incorporating hydrophilic groups into the polymer is an effective way to render a polymer water dispersible without an external emulsifier [30]. The effects of different carboxyl amounts in the presence of acetone on the emulsification process was studied. It can be seen from Table 2 that stable emulsion cannot be obtained below about 0.2 mmol/g of neutralized carboxylic groups, which is in good agreement with that reported by Brooks [8]. Above the minimum carboxylic content, the drop size of emulsion decreases and the drop size distribution increases with the increasing of carboxylic content. The emulsions stayed for more than 12 months.

Conductivity changes during emulsification

Figure 9 shows the conductivity changes of TDP400 with different carboxylic contents during emulsification. Obviously, the conductivity increases with the increasing

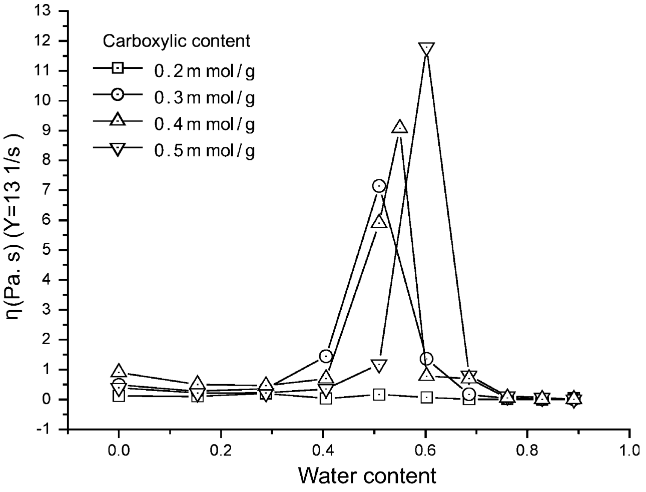


Fig. 10 Viscosity changes graphs of TDP400 with different carboxylic contents. (Water content = $m_{\mathrm{water}}/m_{\mathrm{water+acetone+polymer}}$). Ratio of acetone = 0.45

of the carboxylic content. More carboxylic groups could release more mobile ions. As a consequence, the conductivity increased. The water content at the maximum of conductivity increased as the carboxylic content of the TDP400 increased.

Viscosity changes during emulsification

Figure 10 shows the viscosity change of TDP400 with different carboxylic contents. The maximum of viscosity rises with increase of carboxylic content. More carboxylic groups strengthen the interaction between the anionic polymers and the water-rich phase. The ionized carboxylic groups on the polymer chain produce polymer hydration, causing the polymer backbones to assume a more extended conformation also contributing to the viscosity enhancement. Water content at PIP shows a slight increase with increasing carboxylic content. This is ascribed to more water being needed to dissociate the ionic aggregation in the solution as carboxylic content [19] increases. In the case of the 0.2 mmol/g carboxylic group, viscosity of the system did not change much during the whole emulsification process and the emulsions formed were not stable.

Conclusions

A proper amount of acetone as solvent can help to reduce the viscosity during the self-emulsification process of UV-curable anionic polyurethane. However, there was a critical acetone ratio used in the emulsification, which was 0.55 for TDP400 synthesized in the current studies. Below this critical value of the acetone ratio, stable emulsion with narrow drop size distribution could be successfully produced. When the acetone ratio was higher than the critical value, with water added, polyurethane would precipitate. A ternary phase diagram was used to describe the emulsification process. It was found that those stable emulsion systems with lower acetone ratios would go the from homogeneous region through the W/O emulsion region into the O/W region, experiencing a phase inversion process. However, in the cases of higher acetone ratios, the composition lines would go directly from the homogeneous to O/W emulsion. In such a case, stable polyurethane latex would not be obtained. The formulation–composition bidimensional diagram can complement the ternary phase diagram and describe the viscosity-decrease phenomenon. The carboxylic content is another important factor influencing the properties of emulsion and the process of emulsification. There was a lowest lever of carboxylic content also, which was 0.2 mmol/g for TDP400 in the experiment, to get a stable emulsion.

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