



Rheological Properties and Water-in-Oil Structural Stability of Emulsion Matrixes

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Abstract: The emulsion explosive is one of the important industrial explosives. The structural stability of the water-in-oil (W/O) emulsion matrix of an emulsion explosive determines the reliability of its initiation, safety and detonation performance. It is known that the emulsifier is one of the most important factors affecting W/O structural stability. In this paper, several emulsifiers with the functionalities of imide, amide, ester, salt, and sorbin monooleate (SMO) were selected. From the perspective of the rheological properties, the effects of the emulsifier structure and its functionality on the viscosity and visco-elastic properties of the emulsion matrix were analyzed and researched. The results show that emulsifiers with imide/amide functionality and their corresponding emulsion matrixes have higher viscosity at normal temperatures and better fluidity at high temperatures than those of the others. The linear visco-elastic region (LVR) for emulsion matrixes containing these emulsifiers is wider than that of the others. The effect of a change in ambient temperature on the viscosity for a complex emulsifier is small. The emulsion matrix containing the emulsifier named LZ2727B is the most stable, followed by the emulsifier named LZ2727D. This conclusion is consistent with the conclusions from tension tests and from high and low temperature cycling experiments. From the emulsifiers studied in this paper, LZ2727B and LZ2727D emulsifiers are very suitable for manufacturing packaged emulsion explosives. On the other hand emulsifiers based on SMO functionalities, named LZ2731 and LZ2735, are the best choices for manufacturing bulk emulsion explosives.

Keywords: emulsifier, emulsion matrix, rheological properties, visco-elasticity, water-in-oil structural stability

Introduction

An emulsion matrix is a water-in-oil (W/O) emulsion, in which the oxidant solution is named as the aqueous phase and the fuel oil is named as the oil phase [1]. Emulsion matrixes become emulsion explosives by sensitization. Compared with traditional industrial explosives, emulsion explosives have become leading industrial explosives because of their good explosive properties, their water-resistant nature, abundant raw materials, low cost, lower environmental pollution etc.

However, due to the super-saturated aqueous phase and the instability of the W/O structure itself of the emulsion matrix, it is easy for emulsion explosives to crystallize and to be affected by their surroundings, such as temperature, vibration and shearing, leading to misfires, semi-explosions or extinguishment.

There are many factors affecting the W/O structural stability of emulsion matrixes, such as emulsifying technique and temperature, and type, functionality, components, molecular weight, the addition rate of the emulsifier etc. Therefore research on the W/O stability of emulsion matrixes has recieved much attention. In 1994, Y. Otsubo [2] conducted experiments on the effect of interfacial tension on the rheology of emulsion matrixes. In 2003, I. Masalova [3] found that the rheological behavior of an emulsion matrix can change, that its Newton's flow region can be reduced, that the apparent viscosity can increase and show its yield characteristics during the shelf life. In 2004, Lydiane Becu *et al.* [4] proved that when the impacted tress is larger than the yield tress, the emulsifier shows obvious flowability. In 2006, I. Masalova [5] pointed out that the flow of super concentrated emulsion matrixes depends on the self rheological properties of the emulsion matrix and the time dependence produced by the self thermodynamic instability of the emulsion matrix. In 2010, S. Mudeme *et al.* [6] studied the dynamic emulsifying process of concentrated emulsion matrixes and found that emulsifiers with small molecules favour an accelerated emulsification process and reduced energy consumption. However, there are few scholars studying the rheological properties of emulsion matrixes in China [7-8].

For its extended application, a higher performance of emulsion explosives would be required. An emulsion matrix with different rheological properties can be applied in different occasions. An emulsion matrix with good W/O structural stability can be also adapted to extreme high and low temperature conditions.

The viscosity of an emulsion matrix may be affected by the internal phase ratio, the particle size, the components, the emulsifier and some other factors. The flow curves of different emulsion matrixes can be described by the power-law formula models, the Cross equation, the Herschel-Bulkley equation, the Prince-Kiss equation, and so on [3, 7]. Because of its complex structure, an emulsion matrix

could show rheological properties of viscous flow and elastic deformation under different conditions, such as non-Newtonian flow behavior, visco-elastic properties, thixotropic properties, rheopectic properties etc. Different conditions can cause changes in the emulsion matrix from a Newtonian fluid to a non-Newtonian fluid. The yield stress was proved to exist by the oscillation test. The visco-elastic properties will change with temperature, shear rate and oscillation conditions [9-12].

Generally, for small molecule emulsifiers, the Hydrophile Lipophile Balance (HLB) is an important reference for selecting the emulsifier. For polymeric or complex emulsifiers, it is necessary to develop a new method for evaluating the emulsifier. In this paper, the variation of viscosity, elastic modulus and viscous modulus of emulsion matrixes will be systematically and accurately studied under different conditions using an automatic rheometer to give rheology regulation, water-in-oil structural stability of complex emulsifiers and the emulsion matrixes.

Experimental conditions

Emulsifiers and emulsion matrixes

The 9 emulsifiers shown in Table 1 were selected to prepare the emulsion matrixes at a concentration of 2.0%.

Table 1. Description of emulsifiers

Sample	Trade name	Category	Main functionality	PIB ^③ /g mol ⁻¹	Maleic anhydride /No.	HLB
1#	LZ2731 ^①	I	ester/salt+SMO (>30%)	1850	2	2.8
2#	LZ2735 ^①		ester/salt-1+ ester/salt-2 (>60%)	940 1850	1 2	2.7
3#	LZ2725 ^①	II	imide/amide	940	5	4-6
4#	LZ2727B ^①		imide/amide	1850	5	1-3
5#	LZ2727D ^①		imide/amide	1850	6	4-6
6#	LZ2820 ^①	III	ester/salt /amide+SMO (>50%)	940	1	4.7
7#	LZ2820A ^①		ester/salt /amide+SMO (>30%)	940	1	2.6
8#	LZ2820B ^①		ester/salt /amide+SMO (>10%)	940	1	2.3
9#	Span-80 ^②		SMO ^⑤	251 ^④	1	4.3

^① trade name of the emulsifiers by The Lubrizol Corporation ^②Span-80 made in China

^③polyisobutylene ^④oleic molecule weight ^⑤sorbin monooleate

In this paper, the emulsifiers are divided into three categories according to the differences between their functionalities. Category I emulsifiers *e.g.* LZ2731 and LZ2735, are mixed emulsifiers formed by a polymer with ester/salt functionality in addition SMO and other ester/salt, respectively. Category II emulsifiers *e.g.* LZ2725, LZ2727B and LZ2727D, are polymers containing imide/amide functionality, namely polyolefin amide alkeneamines with different molecular weights and maleic anhydride. Category III emulsifiers *e.g.* LZ2820, LZ2820A and LZ2820B, are three mixed emulsifiers formed by a polymer with ester/salt/amide functionality in addition more than 50%, 30% and 10% SMO functionality respectively. Span-80 emulsifier is 100% SMO, an emulsifier with small molecules, as a carboxylic ester.

The emulsion matrix with W/O structure is composed of an aqueous phase (supersaturated solution, 16.0% water, 70.0% ammonium nitrate and 7.0% sodium nitrate by weight) 93.0% by weight and an oil phase, including mineral diesel oil and emulsifier, 7.0% by weight.

Rheological experimental conditions

The equipment used in the rheological experiments was a Gemini HR Nano200 automatic rheometer (see Figure 1), coupled with a CP4°/40 cone-plate and a PP20 flat. The tests were conducted in both the steady-state and the dynamic-state modes.



Figure 1. Rheometer.

The viscosity-temperature characteristic was tested at a shear rate ($\dot{\gamma}$) = 20 s⁻¹.

The viscosity was tested with a change in shear rate from 10 s^{-1} to 0.00015 s^{-1} at $25 \text{ }^{\circ}\text{C}$ in the steady-state mode. The visco-elastic properties were tested in the dynamic-state mode as follows.

- (1) Strain from 0.05 to 50% at $25 \text{ }^{\circ}\text{C}$ and 1 Hz;
- (2) Stress from 50 to 500 Pa at $25 \text{ }^{\circ}\text{C}$ and 1 Hz;
- (3) Under 100 Pa external force with 1 Hz, at temperatures from 25 to $80 \text{ }^{\circ}\text{C}$ during 1200 s, then maintained at $80 \text{ }^{\circ}\text{C}$ for 100 s, and finally at temperatures from 80 to $25 \text{ }^{\circ}\text{C}$ for 1200 s.

Experimental Results and Discussion

The change of mean viscosity (η_{mean}) with temperature ($\dot{\gamma} = 20 \text{ s}^{-1}$) for several emulsifiers was obtained from Figure 2, and showed that the viscosity of the emulsifiers decreases with an increase in temperature. At ambient temperatures, the viscosity of LZ2727B or LZ2727D emulsifiers, with imide/amide functionality and large molecules, is much higher than for the others. Their viscosities at high temperatures are close to each other.

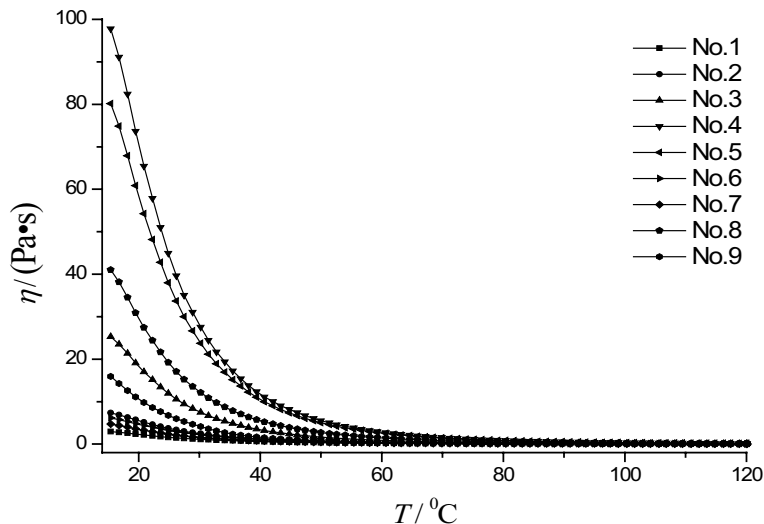
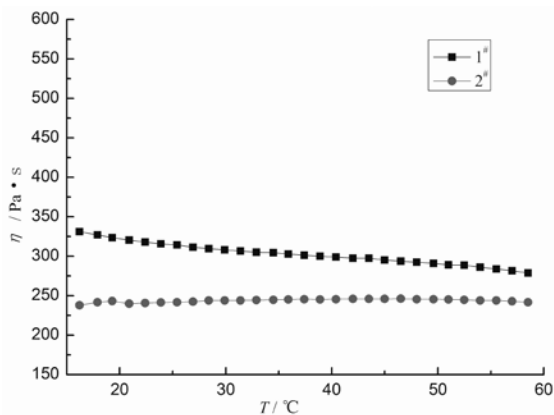


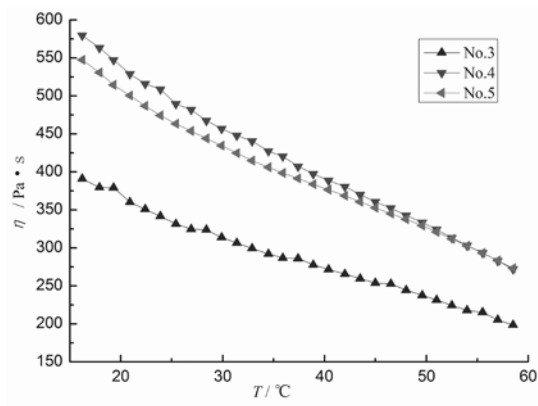
Figure 2. Viscosity-temperature curves for the emulsifiers ($\dot{\gamma} = 20 \text{ s}^{-1}$).

Figure 3 shows the viscosity-temperature curves of the emulsion matrixes formed. The viscosity of the emulsion matrixes formed by adding LZ2727B or LZ2727D emulsifier is high. This means that for these emulsifiers, it is difficult to

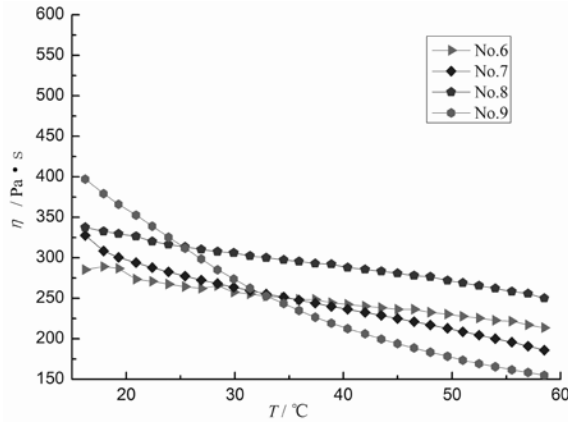
emulsify at normal temperatures, and that there is more stability for the emulsion matrixes formed by these emulsifiers.



(a) Category I



(b) Category II



(c) Category III

Figure 3. Viscosity-temperature curves for the emulsion matrixes formed with the 9 emulsifiers.

It was found that although at ambient temperatures the viscosity of the emulsion matrix created by the emulsifier formed by mixing LZ2727B and Span-80 emulsifiers is lower than that by LZ2727B emulsifier alone, the sensitivity of the viscosity to ambient temperature also decreases. It was demonstrated that the complex emulsifier has a strong adaptability to changes in environmental temperature. The viscosity-temperature curves for emulsion matrixes with different proportions of LZ2727B and Span-80 is shown in Figure 4.

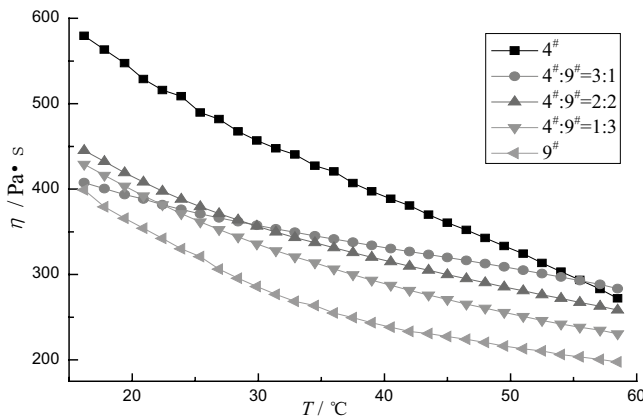


Figure 4. Viscosity-temperature curves for emulsion matrixes with different proportions of LZ2727B and Span-80.

The change of viscosity η and stress σ for the emulsion matrix containing only one emulsifier, such as LZ2727B emulsifier, were tested with changes of shear rate from 10 to 0.00015 s^{-1} at 25 °C in the steady-state mode, and are shown in Figure 5.

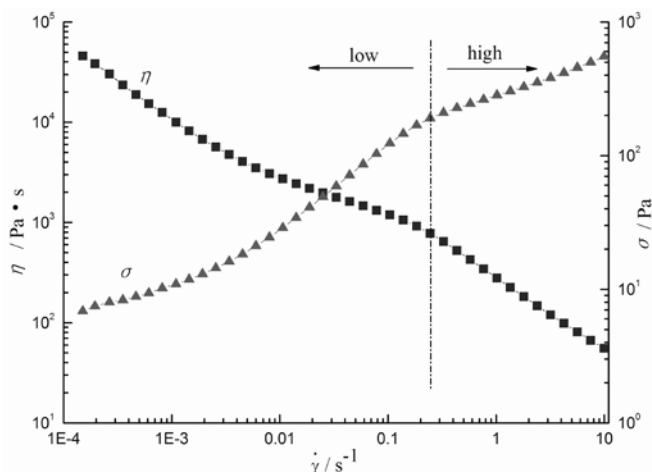


Figure 5. Viscosity-shear rate, and stress-shear rate curves for the emulsion matrix with LZ2727B.

From Figure 5, the viscosity decreases, whilst the stress increases with the increase in shear rate. This shows that the emulsion matrix is a shear-thinning fluid and presents clear non-Newtonian behavior. However, compared with emulsions in general, its flow curve can be divided into two regions at the transition shear rate of 0.18 s^{-1} , that is, into low and high shear rate regions. There is also a similar situation for other emulsifiers.

The stress-shear rate curve in both low and high regions can be closely fitted to the Herschel-Bulkley equation (1).

$$\sigma = \sigma_y + K \dot{\gamma}^n . \quad (1)$$

Where σ means stress, Pa; σ_y – yield stress, Pa; K – coefficients; $\dot{\gamma}$ – shear rate, s^{-1} ; n – index. The fitting result is shown in Figure 6 and compared with the testing results. The correlation coefficients of the two regions are 0.9994 and 0.9996, respectively.

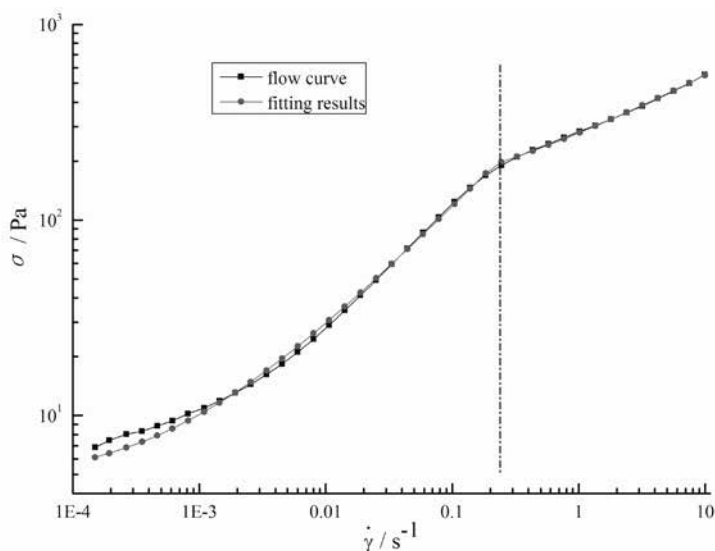


Figure 6. Stress-shear rate curves for the testing results and for the fitting results.

It can be seen that the emulsion matrix is a kind of Bingham plastic body, and that there is a yield stress. When the applied stress is less than the yield stress, the emulsion matrix cannot flow, showing infinite viscosity. However, when emulsion matrix flows, there is a double yield phenomenon, yield stress and transition stress, because of the special structure of the emulsion matrix.

Figure 7 shows the changes of viscosity η and stress σ with shear rate on adding different ratios of LZ2727B emulsifier. The higher the ratio is, the higher is the viscosity of emulsion matrix. Figure 8 shows the changes of viscosity η and stress σ with shear rate for the emulsion matrix formed on adding different ratios of LZ2727B and Span-80. After LZ2727B emulsifier is added to Span-80 emulsifier with low viscosity, there is an obvious increase in the viscosity. For other emulsifiers, there is also a similar situation with LZ2727B emulsifier.

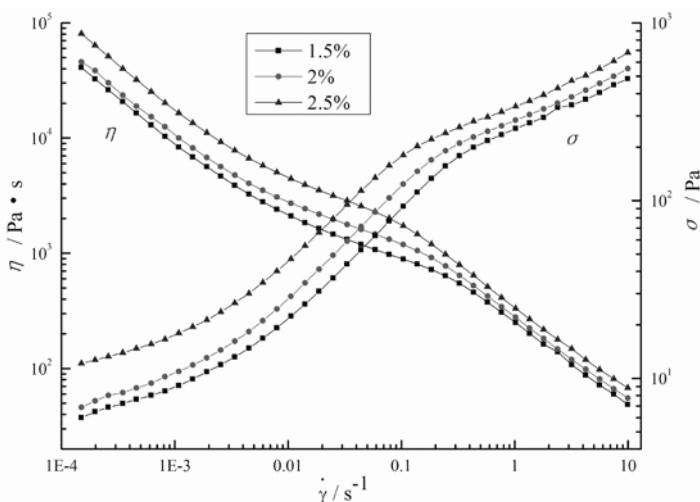


Figure 7. Viscosity-shear rate, stress-shear rate curves for the emulsion matrixes formed by adding different ratios of LZ2727B.

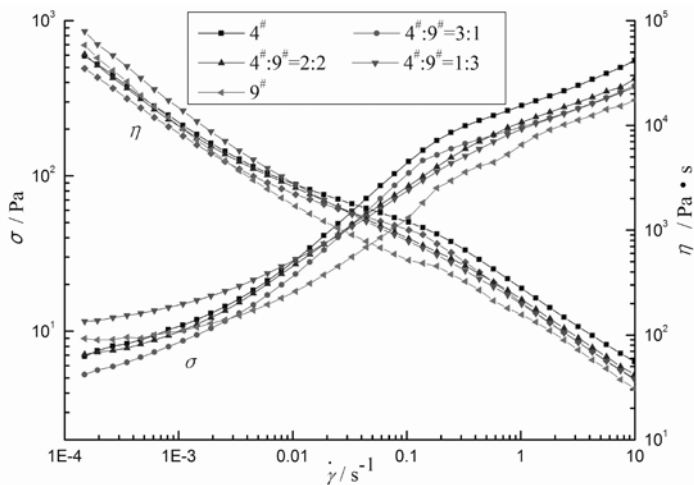
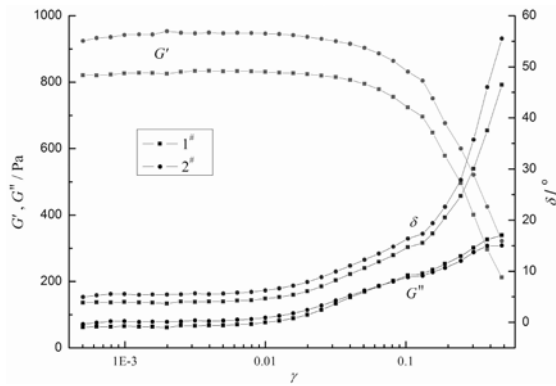
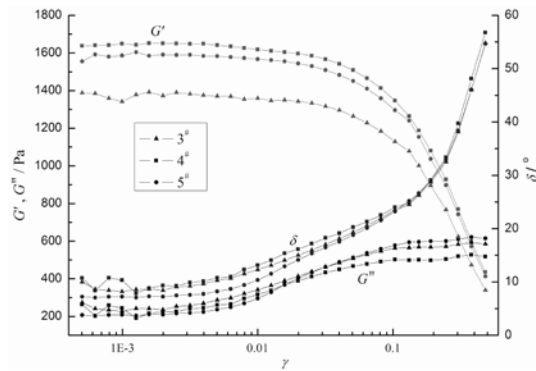


Figure 8. Viscosity-shear rate, stress-shear rate curves for the emulsion matrixes formed by adding different ratios of LZ2727B and Span-80.

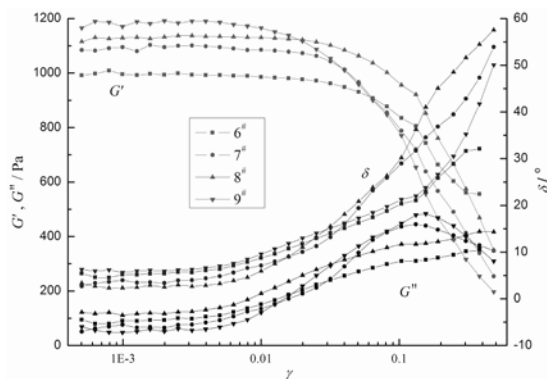
The visco-elasticity of an emulsion matrix, such as the elastic modulus G' , the viscous modulus G'' and the phase angle δ , was studied for strains from 0.05 to 50% under oscillation. The amplitude sweep curves are shown in Figure 9 for the three categories of emulsion matrix.



(a) Category I



(b) Category II



(c) Category III

Figure 9. Amplitude sweep curves of the emulsion matrixes: elastic modulus-strain, viscous modulus-strain and phase angle-strain curves of the emulsion matrixes for categories I, II and III.

In Figure 9, there is a special linear, visco-elastic region (LVR) with increase of strain on the emulsion matrix, that is, there is a critical strain γ_{cr} . Within the LVR, the elastic modulus keeps almost constant. The interfacial film shows elasticity. The film can absorb external energy and elastic deformation occurs. When the external force is withdrawn, the interfacial film can completely release the energy and the initial state is restored. But when the strain is outside the LVR, the interfacial film cannot endure such high energy and deforms irreversibly. As a result, the emulsion matrix shows less elasticity, and elastic modulus decreases rapidly. Generally, the broader the LVR is, the bigger γ_{cr} is, and the more stable the matrix formed is. However, in this paper, although γ_{cr} of LZ2731 and LZ2735 is higher than that of LZ2725, LZ2727B and LZ2727D, the elastic modulus of LZ2731 and LZ2735 is much less than that of LZ2725, LZ2727B and LZ2727D. So the emulsifiers in category II have better elasticity than the others and are easy to mould.

The visco-elasticity of the emulsion matrixes was tested under 1 Hz oscillation frequency at 25 °C as the stress was changed from 50 to 500 Pa and then back down to 50 Pa. Figure 10 shows the results for the variation of the elastic modulus for the emulsion matrix with LZ2727B emulsifier, with the stress in the up and down stages.

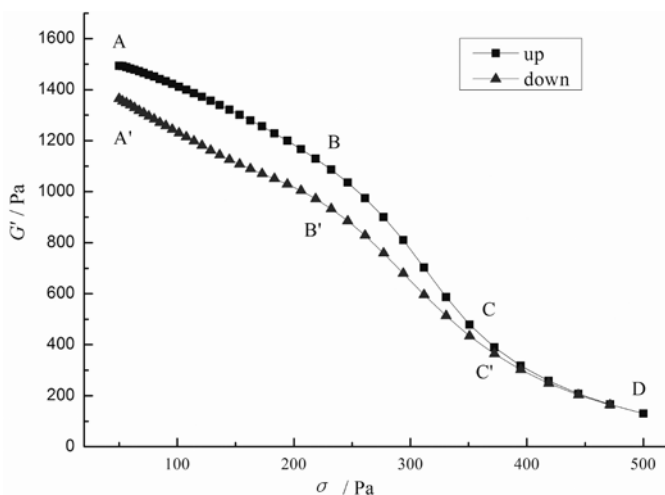


Figure 10. Variation of elastic modulus-stress in the up and down phases.

When the applied stress increases, the elastic modulus decreases. The deformation process includes three zones, an interfacial film deformation zone (AB), a dispersed phase deformation zone (BC) and a complete deformation

zone (CD). When the external energy is beyond the energy needed for plastic deformation, the elastic modulus decreases and would cause plastic deformation of the interfacial film. In the AB phase, the elastic modulus decreases slowly, whilst the strain is obviously beyond γ_{cr} . In the BC phase, some of the aqueous phase particles decrease leading to a more rapid reduction of the elastic modulus. In the CD phase, most particles deform, and the elastic modulus gradually decreases to a limiting constant value.

When the stress decreases, there are also three deformation zones, A'B', B'C' and C'D. But it is clear that with the continuous decrease of the stress, the system cannot return to the initial state. The elastic modulus becomes smaller than that of the initial state. So the deformation of the emulsion matrix is irreversible.

Figure 11 shows the changes of the elastic modulus, the viscous modulus and the phase angle with the stress in the up phase.

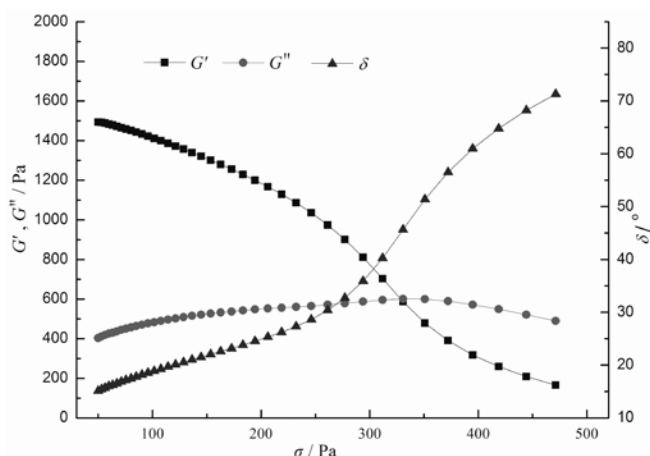


Figure 11. Variation of elastic modulus-stress, viscous modulus-stress, phase-stress in the up phase.

It can be seen that, the viscous modulus of the emulsion matrix initially increases and then decreases as the stress increases, whilst the phase angle continuously increases. When the stress is low, the elastic modulus is larger than the viscous modulus. The emulsion matrix shows elasticity. The elastic modulus equals the viscous modulus when the viscous modulus reaches a maximum. Beyond that point, the elastic modulus becomes smaller than the viscous modulus. The emulsion matrix becomes viscous. This point is called the transition point. The corresponding stress and modulus are called the transition stress and the transition modulus respectively.

From the above analysis it can be seen that the change from an interfacial film deformation zone to a dispersed phase deformation zone is similar to the change in the flow curve. When the stress is large enough, the visco-elasticity of the emulsion matrix would change. The range of application of the emulsion matrix would be affected.

To study the effect of temperature on the visco-elasticity of the emulsion matrix with LZ2727B emulsifier, the behavior of the elastic modulus, the viscous modulus and the phase angle with time under 100 Pa external force at 1Hz, as the temperature was increased from 25 to 80 °C during 1200 s, then maintained at 80 °C for 100 s, and finally decreased from 80 to 25 °C during 1200 s was obtained, as seen in Figure 12.

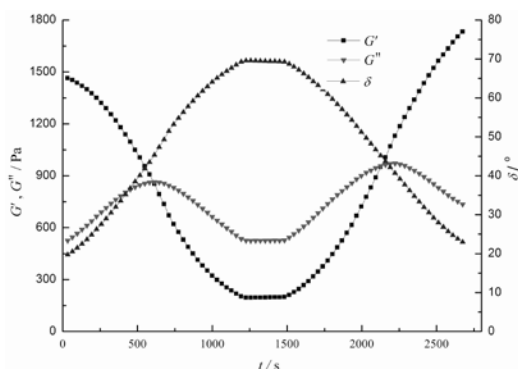


Figure 12. Behaviour of elastic modulus, viscous modulus and phase angle with time for emulsion matrix with LZ2727B at different temperatures.

It is observed that at the temperature increasing stage, the phase angle continues to increase, that between 25 °C and 60 °C the elastic modulus is larger than the viscous modulus, that above 60 °C the emulsion matrix begins to change from elastic deformation to viscous flow and that the viscous modulus continues to increase and the system becomes viscous. At the constant temperature stage, the elastic modulus and the viscous modulus remain constant. A change of visco-elastic parameters for the emulsion matrix at the temperature decreasing stage is the opposite to that at the temperature increasing stage. It is found that there is good elasticity of the emulsion matrix at normal temperatures and good fluidity, easily emulsified at high temperatures. This means that the emulsion matrix has good W/O structural stability at normal temperatures.

From the references [13, 14], and from the tension tests, the surface tension of LZ2727B emulsifier is the largest, followed by LZ2727D emulsifier. According to the results from the high and low temperature cycle experiments,

the emulsion matrix with LZ2727B emulsifier attained 30 cycles. This is the most stable system, followed by the emulsion matrix with LZ2727D emulsifier, which attained 25 cycles. More details can be seen in the related references.

In summary, from the present experiments, we can see that the W/O structural stability of the emulsion matrixes with LZ2727B and LZ2727D emulsifiers, having imide/amide functionality and with a molecular weight larger than 1000, is better than for the others. This conclusion is consistent with the conclusion from the tension tests and from the high and low temperature cycle experiments.

Conclusions

From the above experiments, it is clear that the emulsifiers with amide/imide functionality, such as LZ2727B and LZ2727D, and their corresponding emulsion matrixes, have higher viscosity at normal temperatures and better fluidity at high temperatures than the others. The linear visco-elastic region (LVR) for the emulsion matrixes containing LZ2727B and LZ2727D emulsifiers is wider than for the others. When shear rate and impacted strain are larger than a certain value, the visco-elasticity of the system changes from elastic to viscous.

The emulsion matrix containing LZ2727B emulsifier has a high viscosity, a high elasticity modulus and a large LVR, and is considered the most stable emulsion matrix in this study, followed by that containing LZ2727D. This conclusion is consistent with the conclusions from the tension tests and from the high and low temperature cycle experiments [13, 14]. For the emulsifiers studied in this paper, LZ2727B and LZ2727D are very suitable for manufacturing packaged emulsion explosives. On the other hand emulsifiers based on SMO functionalities, namely LZ2731 and LZ2735, are the best choices for manufacturing bulk emulsion explosives.

Acknowledgments

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