The Effect of Shear Strength on Viscosity-Temperature Characteristics and Rheology Behavior of Emulsion Explosive Matrix

Jianmin Zhou, Xuguang Wang, Mingsheng Zhao, Min Gong, Dandan Tang

Abstract—In this work, the effect of shear strength on viscosity-temperature characteristics and rheological behavior of emulsion explosive matrix was investigated. It was demonstrated that the viscosity-temperature relationship of emulsion explosive matrix was in accordance with the Arrhenius equation. The increase of temperature leads to the decrease of viscosity and the value of $d\eta/dT$. Besides, the sensitivity of viscosity towards temperature increased under lower temperature condition. With the increased of shear strength, the value of $d\eta/dT$ decreased at the same temperature. In addition, the activation energy of emulsion explosive matrix varied with temperature, which decreased with the increase of shear strength. The temperature phase transition characteristics of the emulsion explosive matrix under dynamic oscillation mode were discussed. It was found that the crystallization temperature decreased with the increase of shear strength, which lead to the increase of peak storage modulus and peak composite viscosity.

Index Terms—Emulsion explosive matrix; Viscosity-temperature characteristics; Shear strength; Relative activation energy; Rheology behavior

I. INTRODUCTION

Emulsion is consisted of two insoluble liquids (such as water and oil) which are uniformly dispersed by a certain method (such as adding a surfactant or a stabilizer) in one liquid[1-3]. According to the type of continuous phase and dispersed phase, it can be divided into oil-in-water (O/W) and water-in-oil (W/O) emulsion. Emulsions have been widely used in industry, including food emulsions (such as salad cream, dessert), cosmetic emulsions (such as hand cream, lotion and sunscreen), petroleum emulsions, explosive emulsions, and so on[4-6]. The study of the structure and stable properties of emulsion have been the key content in previous publications[7-9].

The emulsion explosive matrix is a special type of highly concentrated emulsion with relatively high volume fraction of the dispersed phase which contains inorganic aqueous solutions such as ammonium nitrate, sodium nitrate and calcium nitrate[10-14]. The rheological properties of highly concentration emulsion have been the subject of numerous investigations in recent decades. Masalova et al. proposed that the energy storage modulus and yield stress of highly concentration emulsion varied with the type and concentration of emulsifier[15]. Tshilumbu et al. reported that the role of surfactant could improve the stability of highly concentrated emulsions with oversaturated dispersed phase[16]. Kovalchuk et al. proposed that there was an influence of electrolyte concentration on interface interaction, rheological and shear stability of emulsion. The results showed that the increase of electrolyte concentration has positive effects on the storage modulus and yield stress of highly concentration emulsion, while the shear stability of highly concentration emulsion was effectively improved with the decreased interfacial tension[17]. Zhang and Ni studied the influence of emulsifiers on the rheological properties and stability of highly concentrated water-in-oil emulsions. The results showed that the increase of the SMO concentration results in the increase of viscosity and storage modulus, and the stability of HCE with aging was also influenced by the nature of emulsifiers[18]. Malkin and Masalova considered that the instability of HCE was caused by the crystallization of supersaturated solution of the dispersed phase. They also investigated the relationship between the crystallization rate and normal stress[19]. Mudeme et al. showed the dynamics of droplet size evolution could be approximately expressed by a fitting iterative equation. The structural evolution of emulsion was determined by the energy loss in the shear process. The refinement of droplets was accompanied by the change of rheological energy, which is mainly manifested as the increase of yield stress and elastic modulus[20]. Temperature is the primary factor affecting the rheological properties of emulsion explosive matrix, and there are numerous investigations focusing on the viscosity-temperature and rheological properties of emulsion[21-23]. In this work, the viscose-temperature characteristic of emulsion explosive matrix under different

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shear strength was studied. The changing law of activation energy of emulsion explosive matrix under different temperature was analyzed, and the phase transition characteristics of emulsion explosive matrix under oscillatory mode were also investigated.

II. EXPERIMENTAL

A. Materials

Ammonium nitrate (AN) was supplied by the Poly Union Group Corporation, China. Diesel and lubricating oil were produced and supplied by the China National Petroleum Corporation. Sorbitan monooleate (SMO), which is a low-molecular weight surfactant supplied by ALADDIN Industries Corporation, China.

B. Sample preparation

The emulsification process was conducted in 500g batches by RW20 mixer (manufactured and supplied by the IKA Corporation, Germany). The oil phase, comprised of oil and surfactant, was placed in a bowl firstly, and then mixed evenly and heated to 80°C. Afterwards, the oxidizer solution was prepared in a large bowl, which was heated to approximately 85°C and then slowly added into the above oil phase at an agitation speed of 500 rpm/min for 5 min. Meanwhile, several parallel experiments were carried out under different shear strength. The schematic of the emulsification system is shown in Fig. 1.

Fig. 1. The schematic of the emulsification system

Three emulsion samples with different shear strength were prepared and the compositions of the obtained samples were shown in Table I.

TABLE I
COMPOSITIONS OF THE EMULSION EXPLOSIVE MATRIX (BY MASS)

Sample	AN	H_2O	Surfactants (SMO)	Oil	shear strength （rpm）
A1	77%	17%	1.2%	Diesel 3.6% Lubricating oil 1.2%	1400
A2	77%	17%	1.2%	Diesel 3.6% Lubricating oil 1.2%	1600
A3	77%	17%	1.2%	Diesel 3.6% Lubricating oil 1.2%	1800

C. Instrumentation and Methodology

(1) Rheological test

Viscosity-temperature characteristics tests were conducted using a rotational rheometer physical MCR 102 (Anton Paar, Austria) with a PP50 flat and 1 mm gap. The experiments were conducted under the condition of 50 s^{-1} shear rate with the frequency of 1 Hz. The temperature was firstly set at 80 ^{o}C for 10 min. Then, the temperature was continuously decreased to 20 ^{o}C at the rate of 1 ^{o}C/min. The viscosity of emulsion matrix was recorded under different temperatures.

Temperature phase transition characteristics test was conducted using a rotational rheometer physical MCR 102 (Anton Paar, Austria) with a PP50 flat and 1 mm gap. The experiments were conducted under the condition of 1% strain rate with the angular frequency of 10 rad/s. The temperature was firstly kept at 25°C for 10 min. Then, the temperature was continuously raised to 80 ^{o}C by rate of 1 ^{o}C/min. The storage modulus and loss modulus of emulsion matrix were recorded under different temperatures.

(2) The droplet size distributions (DSD) test and microstructure observation

The droplet size distributions (DSD) were measured using the Malvern Mastersizer 2000 instrument. This method is based on measuring the angle distribution of the He–Ne laser light scattered by dispersed droplets in diluted form. The scattering angle is inversely proportional to the size of the particles. The samples were diluted in the oil of the continuous phase, just before the measurements were taken.

Microstructure of emulsion was measured using the Motic Biological Microscope under the magnification of 400.

III. RESULTS AND DISCUSSION

A. Evolution of average droplet size and droplet size distribution

The microstructures of emulsion explosive matrix under different shear strength were shown in Fig. 2. As can be seen from the Fig. 2, the droplet of emulsion matrix presented a polyhedral structure. In addition, the samples obtained under greater shear strength were founded to be equipped with smaller and more uniform particle size. The increase of shear strength resulted in the decrease of average droplet size and narrower size distribution.
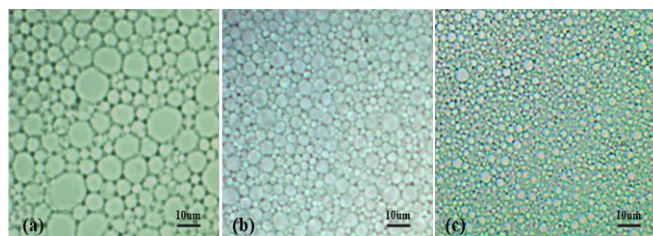

Fig. 2. The microstructures of emulsion explosive matrix under 1400rpm (a), 1600rpm (b) and 1800rpm (c) shear strength

B. Evolution of rheological properties

(1) Analysis on the viscosity-temperature characteristics of emulsion explosive matrix under steady shear mode

The results of viscosities of emulsion explosive matrix in different temperature were obtained in this work. The

viscosity-temperature curve in different temperature under different shear strength is shown in Fig. 3.
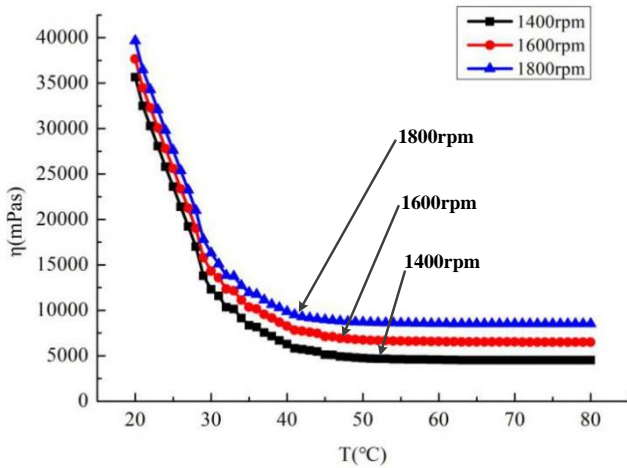

Fig. 3. Viscosity temperature curve of emulsion explosive matrix under different shear strength

The viscosity-temperature curve of emulsion explosive matrix can be closely fitted to the Arrhenius equation，which is consistent with the reports in relevant literature[24, 25]:

$$\eta = 1000Ae^{\Delta E/(RT)} = 1000Ae^{B/T} \qquad (1)$$

Where η is the viscosity, A is characteristic parameter of curve, R is Platt's gas constant, T is thermodynamic temperature, ΔE is activation energy, B is another characteristic parameter of curve which equal to ΔE divided by R.

Fig. 3 shows that the viscosity changes gently with the temperature when the temperature is above 50°C. However, the viscosity increases rapidly with the decrease of temperature when the temperature is lower than 50°C. The lower the temperature was, the more drastic the viscosity changed.

MATLAB was used for regression analysis of the curve results in Fig. 3, and the following equation was obtained.

The viscosity-temperature equation of emulsion explosive matrix under 1400 rpm shear strength:

$$\eta = 1000*1.49*e^{65.42/T} \qquad (2)$$

The viscosity-temperature equation of emulsion explosive matrix under 1600 rpm shear strength:

$$\eta = 1000*2.45*e^{55.98/T} \qquad (3)$$

The viscosity-temperature equation of emulsion explosive matrix under 1800 rpm shear strength:

$$\eta = 1000*3.44*e^{49.71/T} \qquad (4)$$

Derivative of formula (1) can be obtained as follows:

$$d\eta/dT = -Ae^{B/T}B/T^2 = -B\eta/T^2 \qquad (5)$$

Where the absolutely value of dη/dT reflects the change rate of viscosity with temperature. In the above equation, Bη is the slope of viscosity-temperature curve at a temperature point which physical significance reflects the rate of viscosity change when the temperature varies. The larger the value is, the more sensitive the viscosity is to the temperature. According to Equation (5), the values in different temperature can be calculated, and the results are shown in Fig. 4.
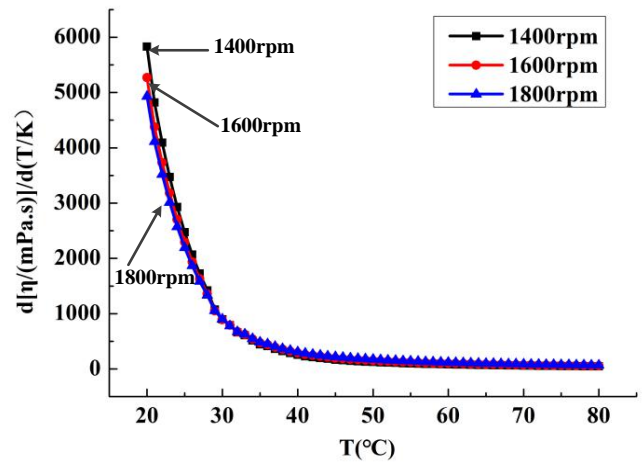

Fig. 4. The curve of relationship between dη/dT and temperature for emulsion explosive matrix

Fig. 4 shows that the increase of temperature leads to the decrease of viscosity and the value of dη/dT. The lower the temperature is, the more sensitive of viscosity changes. With the increase of shear strength, the value of dη/dT decreases at the same temperature.

Logarithms of both sides of the Arrhenius equation are obtained as follows:

$$\ln\eta = A + B/T \qquad (6)$$

The viscosity-temperature curve of emulsion explosive matrix was transformed into a lnη~(1/T) curve. Fig. 5 shows the curve is not a strictly straight line, but changes along with the increasing value of 1/T. It indicates that during the heating process of the emulsion explosive matrix, not only the Van Der Waals force plays a role in the interaction between particles inside the emulsion explosive matrix, but also the microstructure of the emulsion explosive matrix changes, which resulting in the sharp increase of the viscosity of the emulsion explosive matrix with the decrease of temperature. The curve increased upward smoothly with the increase of 1/T, indicating that the internal microstructure of the emulsion explosive matrix gradually changed during the decreased of temperature without obvious phase transformation point.
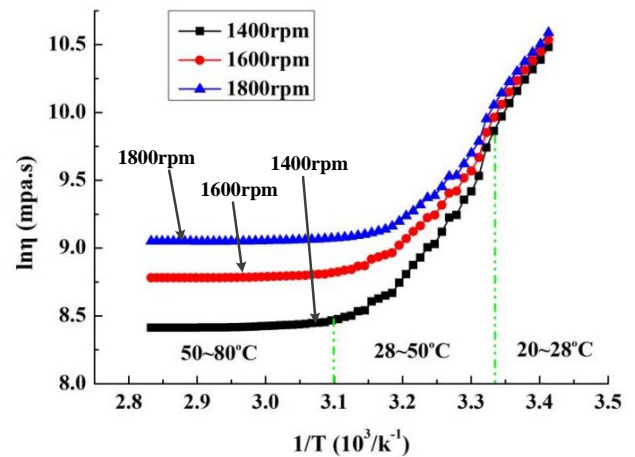

Fig. 5. The curve of relationship between logarithm of viscosity and reciprocal temperature for emulsion explosive matrix

According to the changing trend of 1/T on the curve, 1/T is roughly divided into three intervals, and the regression of lnη~(1/T) is carried out in each interval according to Formula (6). The regression results are shown in Table II.

TABLE II
THE RELATION BETWEEN LOGARITHM OF VISCOSITY AND RECIPROCAL OF
TEMPERATURE

Shear Strength /rpm	The regression equation		
	20~28°C	28~50°C	50~80°C
1400	lnη=-16.57+7.93/T	lnη=-7.09+4.98/T	lnη=8.01+0.14/T
1600	lnη=-14.48+7.33/T	lnη=-3.43+3.92/T	lnη=8.49+0.09/T
1800	lnη=-12.68+6.82/T	lnη=-0.98+3.21/T	lnη=8.88+0.06/T

Table II show that lnη~(1/T) curve can be well regressed by equation (6), indicating that the curve can well conform to the Arrhenius equation in each temperature range. ΔE/R can be used to represent the relative activation energy which refers to the energy barrier that must be overcome before the particle of fluid begins to move. It is a measure of the friction between the fluid particles, which depends on the polarity of emulsion droplets, as well as the size and configuration of the droplet.

The relative activation energy of emulsion explosive varies at different temperature ranges. In the higher temperature range, the relative activation energy of emulsion explosive matrix is lower than that in the lower temperature range. Specifically, on the condition of 1400 rpm shear strength, the relative activation energy in the low temperature range (28~20°C) increases from 5.28 to 79.06 than that in the high temperature range (80~55°C). Analyses about the causes of relative activation energy increases under low-temperature are as follow: 1) In the process of temperature decrease, the intensity of thermal motion and solubility of droplets is restrained. Thus, droplets are constantly separated from the emulsion, resulting in the coalescence of the emulsion matrix. The lower temperature would lead to the more obvious coalescence. 2) In the process of temperature decrease, the aggregation of inner phase droplet will formulate a certain thickness of layer, which makes the volume of the inner phase droplet increase continuously, and the interaction force between them is also greater. Under low temperature condition, with the increase of the aggregate volume of the inner phase droplet, the distance between the particles decreases, which makes the emulsion more unstable. 3) Ammonium nitrate contained in emulsion explosive matrix is crystallized at low temperature and interacts with the internal phase droplets in the process of precipitation, which will lead to a sharp increase in the viscosity of the internal phase droplets. It is also the reason for the large upward deviation of the curve at low temperature.

The relative activation energy of emulsion explosive varied under different shear strength. The results showed that the relative activation energies of emulsion explosive matrix under 1400 rpm and 1800 rpm shear strength are 79.06 and 53.19 respectively in the low temperature range (28~20°C). Analysis results on the causes of activation energy decreases under high shear strength are as follows: 1) The droplet size of high shear emulsion matrix is small, which make the emulsion more stable. The interaction force between the droplets of emulsion is lower, the effect of coalescence is prevented. 2) The droplet distribution of high shear emulsion matrix is more homogeneous, which make the structure of emulsion more stable.

(2) Analysis of temperature phase transition characteristics of emulsion explosive matrix under dynamic oscillation mode

The results of storage modulus G' and composite viscosity Δη of emulsion explosive matrix in different temperature were obtained in this work. The temperature T_n is set as crystal evolution temperature when storage modulus mutates with the increase of temperature, which means that the phase transition of emulsion explosive matrix occurs at this temperature, leading to crystal evolution of emulsion explosive matrix. The temperature transformation curves of emulsion explosive matrix under different shear strength are shown in Fig. 6. The composite viscosity of emulsion explosive matrix varies with temperature under different shear strength are shown in Fig. 7.
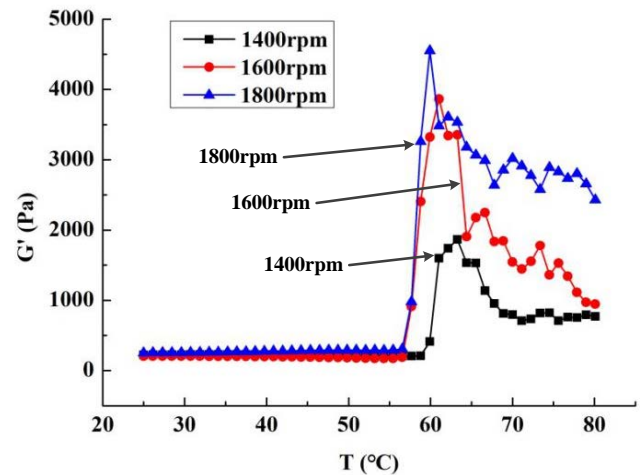

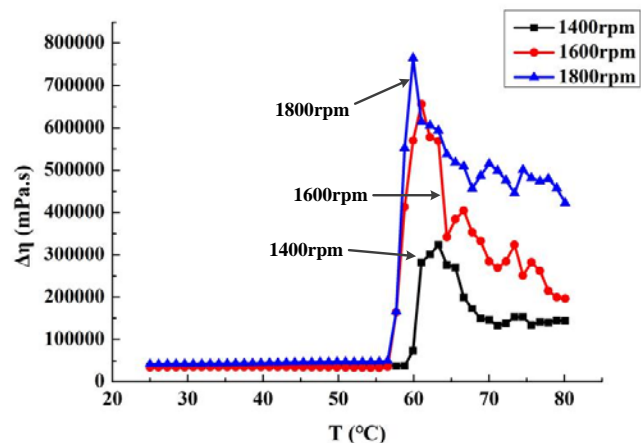Fig. 6. Temperature phase transition curve of emulsion explosive matrix under different shear strength

Fig. 7. The composite viscosity of emulsion explosive matrix varies with temperature under different shear strength

As illustrated in the Fig. 6 and Fig. 7, in a certain temperature range, with the increase of temperature, the storage modulus, loss modulus and composite viscosity of emulsion matrix remain basically constant. When the temperature increases to the crystallizing temperature, the storage modulus and composite viscosity increase abruptly, indicating that the physical phase transition has occurred in

the emulsion matrix, which lead to the crystallization of the emulsion matrix.

The influence of shear strength on the physical structure of emulsion matrix and its structure change were studied by measuring the crystallization temperature of emulsion explosive matrix. The results of temperature phase transition characteristics of emulsion explosive matrix under different shear strength are shown in Table III.

TABLE III
THE RESULTS OF TEMPERATURE PHASE TRANSITION CHARACTERISTICS OF EMULSION EXPLOSIVE MATRIX UNDER DIFFERENT SHEAR STRENGTH

Shear strength/ rpm	Peak energy storage modulus G'/Pa	Crystallization temperature T_n /°C	Peak composite viscosity $\Delta\eta$/ mPa·s
1400	1866.4	61.04	324460
1600	3864.9	58.83	655760
1800	4552.2	57.69	764540

As exhibited in the Table III, with the increase of shear strength, the crystallization temperature decreased from 61.06°C to 57.69°C. It indicates that the smaller the particle size of emulsion explosive matrix is, the more sensitive it is to temperature, and the lower the temperature of phase transition crystal evolution is. The peak energy storage modulus and peak composite viscosity increased with the increase of shear strength.

IV. CONCLUSION

This work demonstrated the influence of shear strength on viscosity-temperature characteristics and rheology behavior of emulsion explosive matrix. Combined with rheology test, microstructure observation and particle size analysis, we found that the increase of temperature lead to the decrease of viscosity and the value of dη/dT. The relative activation energy of emulsion varies under different temperature ranges, which increase with the decrease of temperature. In the low temperature, the intensity of thermal motion and solubility of droplets is restrained, which lead to the coalescence and crystallization of droplets. The relative activation energy of emulsion varies under different shear strength, which decreases with the increase of shear strength. The samples obtained under greater shear strength are founded to be equipped with smaller and more uniform particle size, which make the lower of the interaction force between the droplets as well as the higher the stability of the emulsion. In addition, the crystallization temperature decreases with the increase of shear strength. The results indicate that the smaller the droplet size of emulsion explosive matrix is, the lower the temperature of phase transition crystal evolution is. Besides, the increase of shear strength leads to the increase of peak storage modulus and peak composite viscosity of emulsion explosive matrix.

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