

Role of polymer components of mixture as Non-Newtonian fluids

C. Moskalova, O. Popov, E. Rozhnyuk

Abstract – Analyzed are viscosity functions for model mixes – the emulsions of three polymers. Effective viscosity of the mixes is described with sufficient exactness by power rheological equation of Ostwald-de Waele. Parameters of the equations were determined by the data of rheological measurements for each mix according the design of experiment. To analyze the rheological behavior of the model mixes used the differences of logarithms of viscosity functions when mix proportions of emulsions are varied.

Keywords - Concentration of polymer, difference of function logarithms, effective viscosity, emulsion, model mix, Ostwald-de Waele model.

1. INTRODUCTION

Rheometry creates a base of information on the flow of Non-Newtonian fluids [1]. The results of the analysis and synthesis of information - part of rheology, which solves problems in the various fields of science, technology and medicine. As an analysis tool of structure of Non-Newtonian fluids the rheometry is used in science of building materials with the 50-ies (P.A. Reh binder, N.B.Urev, N.N. Kruglitsky, Y.P. Ivanov [2-3]). For more than twenty years to assess the impact of compounding and technology (CT-factors) on the parameters of rheological models used experimental-statistically (ES) modelling and methods of computer materials science [4-6].

For compositions with different polymeric matrixes, depending on the factors for CT-factors by the model were analyzed effective viscosity η (Pa·s) at a constant shear strain rate $\dot{\gamma}$ (s^{-1}) usually, $\dot{\gamma} = 1$, as $\eta_1 = K$ – parameter of one of the most commonly used simple rheological models, the law of exponent . This is equation of Ostwald-de Waele (1), which, after taking the logarithm of (2) becomes linear in the parameters.

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C. Moskalova is with the Odessa State Academy of Civil Engineering and Architecture, Ukraine (krisogasa@gmail.com)

O. Popov is with the Odessa State Academy of Civil Engineering and Architecture, Ukraine

E. Rozhnyuk is with the Odessa State Academy of Civil Engineering and Architecture, Ukraine

$$\eta = K m \gamma' \quad (1)$$

$$\text{and also, } \ln \eta = \ln K + m \cdot \ln \gamma' \quad (2)$$

In parallel, by the ES - model was described and analyzed parameter $m < 0$ - the pace of destruction structured Non-Newtonian fluid under increase γ' .

Function (2) is make on the obtained on rotational viscometers values of effective viscosity by a change of shift speed and it well describes of building mixes with the maximum grain size of up to 2 – 2.5 mm in small and medium range $\gamma' \leq 20 \text{ s}^{-1}$ (it is typical, in particular for the mixing and pouring of solutions of dry building mixes (DBM)). The error of inadequacy in the area of $\gamma' = 1$ does not exceed 5%. This allows us to consider (1-2) as a model, admitting those or other engineering calculations and transformation.

The method of comparative analysis of variability under influence of CT - factors of viscosity using the differences of described models of logarithmic functions (2) is devised. One of the functions – for «E» of the mixture, regarded as a reference. For other mixtures «U» is defined by the represented straight functions (3) differences of the logarithms.

$$\exp([\ln K_U - m_U \ln \gamma'] - [\ln K_E - m_E \ln \gamma']) = \exp(\ln \eta_U - \ln \eta_E) = \eta_U / \eta_E \quad (3)$$

The methodology has applied in the multivariate comparative analysis of the influence components on the function of viscosity of model mixes for plaster from DBM in the early stages of hardening.

2. EXPERIMENT DESCRIPTION

The effective viscosity in the shear rate range of 0.045 to 8.406 s^{-1} was determined by for polymer emulsions. Polymer emulsions (index P) contained 3 polymer component in the saturated solution of $\text{Ca}(\text{OH})_2$, which dosage (factors X, by weight parts per 100 w.p. solution) ranged at 3 levels (Table. 1) in accordance with a 15-point's plan of experiment B_3 in ranges wich produced in Ukraine DBM for plastering. The minimum concentration of polymer is 4.17% by weight solution CaOH_2 ; this mixture is considered as the reference «E». The maximum concentration of three polymers is 12.85%.

The viscosities of each model mixture were described by functions (2). The values of $\ln K$ and tempo $|m|$ for each of the 15 types of the mixes allowed to build non-linear three-factor ES-model of dependency of parameter rheological model on the composition of the emulsion. Models describe field of rheological parameters in 3 coordinates of compositions.

The minimum values of effective viscosity for test solutions is correspond to the low level of polymer concentration ($x_i = -1$), while the maximum is correspond to the upper level ($x_1 = x_3 = 1, x_2 = 0.8 \approx 1$).

Table 1 Levels of varying the polymer components

Components		X_{imin} $x_i = -1$	X_{i0} $x_i = 0$	X_{imax} $x_i = +1$
X_1	Redispersible polymer powder Vinnapas 5034 (V) – ethylene-vinyl acetate copolymer (brand <i>Wacker Polymer Systems</i>)	3.5	8	12.5
X_2	Hostapur OSB (H) – multifunctional surfactants based on high molecular sulfonate olefin, sodium salt (<i>ShinEtsu</i>)	0.05	0.15	0.25
X_3	Tylose MH60010 (T) – methylhydroxyethylcellulose, water-soluble, nonionic cellulose ethers (<i>ShinEtsu</i>)	0.8	1.4	2

Within the field η_1 of emulsion increases 18 times. This is due, firstly, with the increasing concentration of polymer powders in 2.5-5 times by weight and with decrease of specific volume $Ca(OH)_2$; secondly - with increasing proportion of physically bound water (by dispersing, swelling and dissolution of polymer powders).

3. RESULTS AND SIGNIFICANCES

Effect of concentrations of the polymer components on $\ln K$ and $|m|$ emulsions based on calcium hydrate. The total field of viscosity at a shear rate $\gamma' = 1$ in the coordinates of contents of the three polymer powders shows in Fig.1a. Along the direction of the average gradient of this field (dashed line on the diagonal of prescriptions cube), the viscosity η_1 increases by 18 times; the increasing almost proportionally.

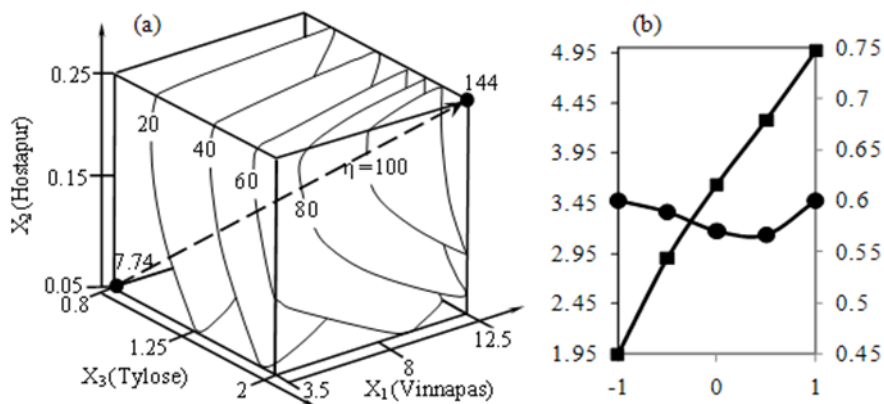


Fig.1. Field of emulsion viscosity by $\gamma' = 1 \text{ s}^{-1}$ in coordinates of polymer concentration (a) and their generalizing impact (b) on $\ln K$ (■) and $|m|$ (●)

Figure 1b shows the integral influence of all three polymeric components on η_1 and the pace of destruction. Their individual influence in the area of maximum and minimum $\ln K$ is shown single-factor dependence to Fig.2. It is seen that the greatest influence on viscosity when $\gamma' = 1$ provides the introduction of water-holding Tylose; with an increase in a concentration of 0.8 to 2 w.p. the viscosity in the zone of minimum increases up to 6 times, and in the zone of maximum of 11 times, indicating a sufficiently "strong" frame which produced by cellulose ethers.

Sensitivity $\ln K$ to the amount of Vinnapas slightly lower; this parameter varies only in 2 - 3 times in maximum zone, and in minimum zone; viscosity increase is occur due to strong membrane formed by dispersing. Hostapur slightly increases the viscosity of the mixture; its plasticizing effect does not explicitly detected.

Figure 2 shows the extreme nature of the influence of content of Vinnapas on the $|m|$, most intensively destroyed under shear deformations a mixture with an average content V. Above this concentration Vinnapas begins to rapidly stabilize the mixture. Increased dosage Hostapur promotes destruction of the structure, and most intensively in mixes with a high viscosity.

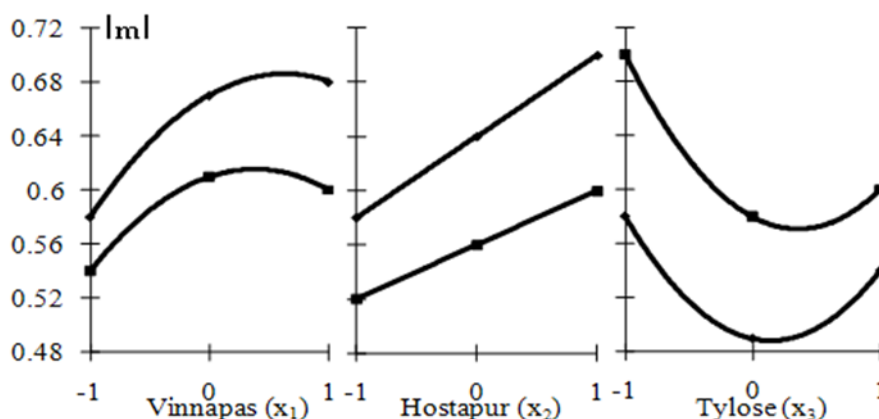


Fig.2. The single-factor dependency of concentrations of polymer in the emulsion from the rate of destruction $|m|$ and at zone of minimum and maximum

Fundamentally important results obtained for methyl cellulose - an increase in its concentration to $X_3 = 1.25$ w.p. plays a role of reinforcement and the pace of destruction of mixture structure is significantly reduced, and with increasing concentrations of $|m|$ it remains constant or increases slightly.

In this way, it can be considered as a reliable conclusion that for polymer emulsions (to indicated in Table 1 dosage ranges.) the main factor determining the effective viscosity η_1 and the rate of destruction $|m|$ is the content of Tylose.

The transformation of the emulsion viscosity functions during the transition of the concentrations polymer components from lower to the upper level. Extended information about the role of the components of the polymer

emulsion was obtained by using special methods of analysis of logarithmic viscosity function (2). In contrast to the previous analysis, it allows you to visualize the nature of viscosity as a processes associated with time through a gradient speed of deformation.

Logarithmic function which used in analysis are obtained from the shown in Table 2 ES - models by substituting $x_i = \text{const}$ ($i = 1, 2, 3$). Discusses five boundary functions: emulsions with minimum (4.17%) and the maximum concentration (12.85% by weight) of the three components (reference $P\{E\}$ and $P\{VHT\}$ respectively) and with an extremely high content of a component ($P\{V\}$, $P\{H\}$ and $P\{T\}$). The calculation of algorithm is reflects in the Table 3: it has five lines which correspond to the five functions of the boundary viscosity (2). Graphs of five logarithmic function $P\{U\}$ (where $U = E, V, H, T$ and VHT) has shown on Fig. 3 a, b.

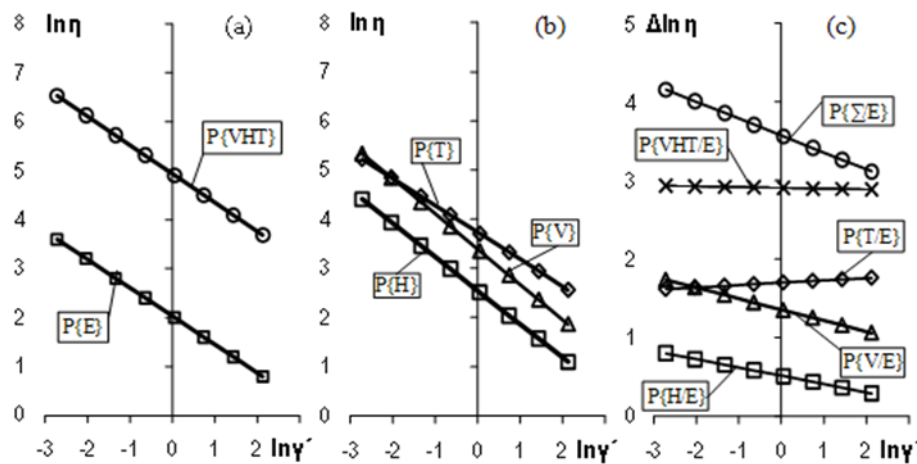


Fig.3. The logarithmic functions of emulsion viscosity (a, b) and the augmentation of logarithm of viscosity in relation to the reference emulsion $P\{E\}$ (c)

The bottom line in Fig. 3a is a reference. Effective viscosity varies with shear rate increasing from 2.4 to 46, and falling almost 20 times. The top line corresponds to the maximum concentrations of the components. The viscosity decreased from 871 to 42.3 Pa·s - fall in 20.6 times.

Increasing η_1 the mixture $P\{VHT\}$ compared to $P\{E\}$ approximately 18 times this is presumably because the chemical reactions in the system P does not occur, it can be assumed that the reference emulsion has a mosaic structure with weak intermolecular bonds, which at higher concentrations of polymers are enhanced, but with growth γ' failure mechanism remains unchanged, due to the heterogeneity of the structure. Graphs of viscosity of emulsions with an increased concentration of one of the components (Fig. 3b) lie between the functions in Fig. 3a. Changes $\ln \eta(\gamma')$ in relation to the reference model mixture reflect graphs in Fig. 3c.

Table 2 Models of viscosity emulsion and augmentation of viscosity relatively lowconcentrated of the reference emulsion

Conditions	Model	Number of formula
The emulsion viscosity with different content of polymer		
The minimum concentration of polymers	$2.03 - 0.58 \ln \gamma'$	(4)
The maximum concentration of polymers	$4.94 - 0.59 \ln \gamma'$	(5)
The maximum content of Vinnapas ($x_1 = 1$)	$3.39 - 0.72 \ln \gamma'$	(6)
The maximum content of Hostapur ($x_2 = 1$)	$2.55 - 0.68 \ln \gamma'$	(7)
The maximum content of Tylose ($x_3 = 1$)	$3.73 - 0.55 \ln \gamma'$	(8)
Relative augmentation of emulsion viscosity		
(5) – (4)	$2.91 - 0.01 \ln \gamma'$	(9)
(6) – (4)	$1.36 - 0.14 \ln \gamma'$	(10)
(7) – (4)	$0.52 - 0.11 \ln \gamma'$	(11)
(8) – (4)	$1.70 - 0.03 \ln \gamma'$	(12)
(10) + (11) + (12)	$3.58 - 0.21 \ln \gamma'$	(13)

The biggest increase (3.6 times) was observed with increasing concentration of Tylose (while maintaining the two other components to the model level), this effect (12) does not depend on γ' (graphics is parallel graphics P {E}, $\Delta[m]$ for P {T} little different of zero). Increased viscosity connected to the increase in the proportion of physically bound water, while maintaining the mosaic structure and its destruction under shear deformations. Vinnapas, with small γ' is increases viscosity like Tylose, with increasing γ' structure collapses faster than the model blend. Hostapur gives a smaller increase η_1 (equal to $\exp(0.52) = 1.7$ times) concerning to the model, which declining with increase γ' . Simultaneous administration of increased concentrations of components the increase (5) for P {VHT} and corresponding effective viscosity is lower than in the case of a hypothetical increase P { Σ / E} from adding the individual effects (13); hypothesis of additivity is not confirmed.

4. CONCLUSIONS

In studies of multicomponent polimermineral mixtures, which when mixed with water, transporting, pouring and moulding begins intensive hardening mineral binders, useful information could be given by model liquid phase systems - emulsions. In their study, it is advisable to employ methods rheometry, the results of which are summarized and analyzed using methods of computer materials science. For systems, effective viscosity of which with sufficient engineering accuracy, describes the exponent functions of Ostwald-de Waele, useful analysis of the differences of logarithms functions at change of structure of emulsions.

5. REFERENCES

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