

A simple model to describe the thixotropic behavior of paints

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Abstract

We propose a simple rheological model to describe the thixotropic behavior of paints, since the classical hysteresis area, which is usually used, is not enough to evaluate thixotropy. The model is based on the assumption that viscosity is a direct measure of the structural level of the paint. The model depends on two equations: the Cross-Carreau equation to describe the equilibrium viscosity and a second order kinetic equation to express the time dependence of viscosity. Two characteristic thixotropic times are differentiated: one for the net structure breakdown, which is defined as a power law function of shear rate, and an other for the net structure buildup, which is not dependent on the shear rate. The knowledge of both kinetic processes can be used to improve the quality and applicability of paints. Five representative commercial protective marine paints are tested. They are based on chlorinated rubber, acrylic, alkyd, vinyl, and epoxy resins. The temperature dependence of the rheological behavior is also studied with the temperature ranging from 5 °C to 35 °C. It is found that the paints exhibit both shear thinning and thixotropic behavior. The model fits satisfactorily the thixotropy of the studied paints. It is also able to predict the thixotropy dependence on temperature. Both viscosity and the degree of thixotropy increase as the temperature decreases.

Keywords: Rheology; Thixotropy; Thixotropic model; Hysteresis area; Marine paint; Temperature dependence.

1. Introduction

The rheology of paints depends mainly on the nature and concentration of the polymer matrix [1], and determines the performance of the paint during the whole handling cycle, from storage to application and drying [2]. The stability required on a paint to allow the storage of the dispersion without settling should be analyzed by dynamic rheology in the linear viscoelastic zone. The applicability, however, should be characterized by flow behavior tests, since it is related to the way of flow under the influence of an external shear rate; for example, low viscosity at intermediate shear rates and very low viscosity at high shear rates are needed to be easily pumped and sprayed, respectively. However, it is not enough to evaluate the dependence of viscosity on shear rate to examine the behavior of a coating during processing, the dependence of viscosity on time, i.e. the thixotropy, is also necessary. The rate at which the viscosity of a paint is recovered after its application is indeed directly related to the thixotropic behavior of the coating, which plays a determinant role in the occurrence of some common problems like leveling or sagging that evolve during or immediately after the paint application process. Most paints are non-Newtonian (usually shear thinning) and thixotropic fluids, whose viscosity is a function of shear rate and time, respectively.

Thixotropy describes the time-dependence of transient state viscosity at a given shear rate and the reversible and relatively slow breakdown of internal structure under shear. It is usually evaluated by measuring the area enclosed between the up- and down-curve obtained in a linear increasing and decreasing shear rate over time (named hysteresis loop test). This method was first developed by Green and Weltmann (1946) [3]. Strongly thixotropic behavior should exhibit large hysteresis areas since the time dependence of viscosity should be significant. The hysteresis area is a relative measure of thixotropy, since it depends on the nature of the paint and the parameters that define the hysteresis loop test: the maximum shear rate and the times of duration of the linear increasing and decreasing of shear rate. An alternative approach is more recently proposed by Dolz et al. (1995) [4]. It is based on the use of the relative hysteresis area, which is defined as the ratio of the hysteresis area to the area beneath the rising shear curve.

However, thixotropy is a complex behavior that can not be defined only by a single parameter. There are mathematical models that explain this behavior. They are based on the assumption of a structural parameter,

λ , which is defined as a numeric scalar measure of internal structure [5]: $\lambda = 0$ represents a completely broken down structure and corresponds to η_{∞} for pseudoplastic suspensions, $\lambda = 1$ represents a completely build up structure and corresponds to η_0 . Some theories associate the structural parameter to the number of bonds or links between the particles that form the internal structure [6].

The rheology of paints from the point of view of the steady-state viscosity profile (viscosity vs. shear rate) has been widely studied. However, their thixotropic behavior has been slightly reported in the literature [7-9]. Therefore, the purpose of this paper is to examine this basic rheological feature of paints. In contrast with the thixotropic models that can be found in the literature, often very sophisticated and dependent on many parameters, in this study we propose a simple model, whose main goal is to provide a useful tool to the industry to evaluate and easily control thixotropy by means of the rate of breakdown and buildup of internal structure.

2. Theory

The thixotropic models are composed of two equations, an equation of state and a kinetic equation (Equations 1 and 2, respectively) [10]:

$$\eta = f(\lambda, \dot{\gamma}) \quad (1)$$

$$\frac{\partial \lambda}{\partial t} = g(\lambda, \dot{\gamma}) \quad (2)$$

The equation of state (Eq. 1) relates the viscosity, η , with the structure parameter, λ , and the shear rate, $\dot{\gamma}$, while the kinetic equation, which is defined as the time derivation of structural parameter, depends on the net rate of breakdown and the net rate of build-up of the structure. These net processes are a result of the single rate of breakdown and the single rate of build-up, which are observed simultaneously at a given shear rate. A state of dynamic equilibrium is reached when both single rates are equal or when the net kinetic

process becomes zero. Each net kinetic process is defined by a kinetic equation which depends on the n -th power of departure between equilibrium and current structural parameter and the net kinetic parameter.

The proposed model is based on the assumption that viscosity is a direct measure of internal structure and therefore no theoretical parameter such as the structural parameter is needed [11]. A second order kinetic equation is proposed to describe the net kinetic process. It is defined as:

$$\frac{\partial \eta}{\partial t} = \frac{(\eta - \eta_e)^2}{t_s} \quad (3)$$

where η_e is the equilibrium viscosity and t_s is the thixotropic time, which is defined as the time that the structure delays in adapting its structure to the steady state. Two thixotropic times are defined: the thixotropic time for the net breakdown process, t_s^{break} , and the thixotropic time for the net build-up process, t_s^{build} . High thixotropic time values mean higher viscosity dependence with time, thus slow net kinetic processes.

The evolution of the viscosity with time is obtained by integrating the kinetic equation (3):

$$\eta(t) = \frac{\eta_i - \eta_e}{1 + t_s(\eta_e - \eta_i)(t - t_i)} + \eta_e \quad (4)$$

where η_i is the viscosity at the time $t_i = t - \Delta t$. The equation (4) shows the evolution of viscosity with time only under constant shear rate condition for the net breakdown process when $\eta > \eta_e$ and $t_s = t_s^{break}$, and for the net build-up process when $\eta < \eta_e$ and $t_s = t_s^{build}$. The net breakdown process usually shows shear rate dependence [12].

The equilibrium viscosity of most colloidal suspensions follows shear-thinning behavior, i.e. viscosity decreases with increasing shear rate. The equilibrium viscosity obeys an empirical power law model, even at very low shear rates. Below a critical shear rate the viscosity tends to approach an asymptotic value, which is

the maximum viscosity or zero-shear-rate viscosity, η_0 . Therefore, the equilibrium viscosity as a function of shear rate can be calculated from the generalized Cross-Carreau model [13-14]:

$$\frac{\eta_e - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{\left[1 + (k \cdot \dot{\gamma})^a\right]^{1-n/a}} \quad (5)$$

where η_∞ is the infinite-shear-rate viscosity, k is a characteristic time, and a and n are exponents of the shear rate. In this study we take $a = 2$, according to the Carreau model. Eq. (5) can be converted to a power law at intermediate shear rates, where the product $(\eta_0 \cdot k^{n-1})$ is the consistency index.

Finally, the shear stress, σ , for inelastic systems can be obtained from the Newton equation, which relates the shear stress with viscosity and shear rate as follows:

$$\sigma = \eta \cdot \dot{\gamma} \quad (6)$$

The proposed model has been developed to predict the thixotropy that the coatings manifest both by shear rate steps-change test and by hysteresis loop test. The latter test consists in a linear increasing and decreasing of shear rate over time although it can also be conceived as the first one when it is considered as a succession of very short steps where each shear rate is kept constant only for a few seconds.

3. Experimental

3.1. Materials

Commercial coatings for marine and protective uses kindly supplied by Pinturas Hempel S.A. (Barcelona) have been studied in this work. They are based on chlorinated rubber, acrylic, alkyd, vinyl, and epoxy resins. Some of their main characteristics are summarized in Table 1.

3.2. Rheological measurements

The rheological characterization was carried out using a shear rate-controlled rotational rheometer (Haake Rotovisco RV20/CV20N) (Couette flow) fitted with a Mooney-Ewart coaxial cylinder sensor (inner cylinder diameter 28.93 mm, outer cylinder diameter 30.0 mm, length 24.0 mm, and sample volume 1.8 cm³). The temperature was controlled with an accuracy of $\pm 0.1^\circ\text{C}$ by circulating water in the jacket of the outer cylinder arrangement.

Two kind of tests were designed to evaluate the thixotropy of the samples: a step-change of shear rate test and a hysteresis loop test. The step-change of shear rate consisted in a sequence of various shear rates (0.1, 0.5, 1, 5, 10, 50, 100 and 200 s⁻¹) applied for 10 minutes, time enough to reach the steady-state value (equilibrium value). Hysteresis loop tests involved the following steps: (a) to keep the sample at rest, i.e. undisturbed, for 10 minutes; (b) to increase linearly the shear rate from zero to a maximum value, $\dot{\gamma}_{max}$, within the running process time, t_{run} ; (c) to decrease linearly the shear rate from maximum shear rate to zero within t_{run} . Four different tests were carried out: (1) $t_{run} = 120$ s and $\dot{\gamma}_{max} = 50$ s⁻¹; (2) $t_{run} = 120$ s and $\dot{\gamma}_{max} = 200$ s⁻¹; (3) $t_{run} = 600$ s and $\dot{\gamma}_{max} = 50$ s⁻¹; (4) $t_{run} = 600$ s and $\dot{\gamma}_{max} = 200$ s⁻¹. All these rheological measurements were performed at five different temperatures: 5, 10, 15, 25 and 35 °C. It was found that all paints were inelastic, thus the viscosities were calculated according to Equation (6).

4. Results and discussion

4.1. Equilibrium viscosity

Equilibrium viscosities were determined by applying different shear rates and waiting for reaching the steady state value at each of the applied shear rates. Figure 1 shows the evolution of equilibrium viscosity at 25 °C as a function of shear rate for the five polymer emulsions. The symbols correspond to the experimental equilibrium viscosity, and the lines correspond to the fitting of experimental data to Equation (5). All paints show shear thinning behavior, since viscosity decreases as shear rate is increased. The lowest viscosity is observed for alkyd paint at intermediate and high shear rate, and for alkyd and vinyl paints at low shear rate.

Chlorinated rubber and alkyd resins are characterized by shear thinning at intermediate shear rates and a Newtonian viscosity plateau at moderately high shear rate corresponding to infinite-shear-rate viscosity. The equilibrium viscosity for acrylic, epoxy and vinyl paints follows power law dependence with shear rate. The same shear rate dependence of the equilibrium viscosity was observed for the other temperatures. Table 2 shows the values of equilibrium parameters that better fit the experimental data as a function of temperature. The zero-shear-rate viscosity, η_o , was calculated from Equation (5) since no Newtonian viscosity plateau region was observed at very low shear rates. As it was expected the zero-shear-rate viscosity decreases with temperature, as well as the consistency index ($\eta_o \cdot k^{n-1}$). This temperature dependence of η_o will be analyzed further. On the other hand, the power law index, n , increases with temperature for all paints, although the power law index for vinyl paint is almost independent of temperature. The lowest power law value was showed by chlorinated rubber paint at 5 °C and the highest value by vinyl paint at 35 °C. In all cases, the power law index is minor to 1, what corresponds to a shear thinning fluid. The increase of n with temperature indicates that the rheological behavior of the polymer emulsions is the farthest from Newtonian behavior as the lowest is the temperature.

Figure 2 shows the temperature ($1/T$) dependence of the zero-shear-rate viscosity obtained from Equation (5). The zero-shear-rate viscosity increases as temperature is decreased for all paints. The highest values are shown by epoxy paints. Zero-shear-rate viscosity values (symbols) were fitted to the Arrhenius equation, which describes the viscosity exponential dependence over the activation energy of viscous flow, ΔE_a ,

$$\eta_o = A \cdot \exp\left(\frac{\Delta E_a}{R \cdot T}\right) \quad (7)$$

where R is the gas constant and A is the Arrhenius pre-exponential factor. Table 3 shows the values of the activation energy and the pre-exponential factor A for all paints. As it is shown in Figure 2, the zero-shear-rate viscosity for the epoxy-based paint is less sensitive to temperature due to the low activation energy value, while the effect of temperature for the acrylic-based paint is more significant due to the high activation energy value.

4.2. Thixotropy

The evolution of viscosity as a function of shear rate resulting from the hysteresis loop tests has been analyzed. Fig. 3 shows some representative results obtained at 25 °C. The filled circles correspond to the up-curve resulting from the linear increase of shear rate with time, while the open circles correspond to the down-curve due to the linear decrease of shear rate with time. The lines correspond to the fitted data by the proposed model. Analogous results have been obtained for the rest of loop tests and temperatures investigated. It has to be pointed out that the thixotropic times, t_s^{break} and t_s^{build} , have been obtained analyzing simultaneously the four hysteresis loop tests examined for each paint. All paints show a hysteresis area, except the chlorinated rubber-based paint, for which a collapse between the up- and down-curves is observed. The presence of a hysteresis area means that the sample shows time dependence rheological behavior, i.e. thixotropy. Therefore, all the polymer emulsions studied are thixotropic fluids, except the chlorinated rubber, which is almost not thixotropic. From Fig. 3 it can be concluded that all hysteresis loops are well represented by the model calculations taking into account the shear rate dependence of the net breakdown thixotropic time. Figure 3a shows the hysteresis area for the vinyl-based paint obtained from the loop test defined by 600 s as increasing time and 200 s⁻¹ as maximum shear rate. Vinyl-based paint shows a high degree of thixotropy because of the high hysteresis area, which depends on shear rate. The difference between viscosities of up and down curve at the same shear rate is decreased gradually upon shear rates. High hysteresis area is also observed in Figure 3d for the epoxy-based paint at $t_{run} = 120$ s and $\dot{\gamma}_{max} = 50$ s⁻¹. Figure 3b shows the hysteresis area for alkyd-based paint at $t_{run} = 120$ s and $\dot{\gamma}_{max} = 200$ s⁻¹. Thixotropy is only observed at low shear rates, viscosities of up- and down-curves are nearly identical and equal to infinite-shear-rate viscosity. Figure 3c shows the hysteresis area for acrylic-based paint at $t_{run} = 600$ s and $\dot{\gamma}_{max} = 50$ s⁻¹. Shear thinning behavior is observed over the entire range of shear rate, whereas thixotropy is only showed at low shear rates. Chlorinated rubber does not show thixotropy at any hysteresis loop test.

The temperature dependence of thixotropy has also been analyzed. Table 4 shows the hysteresis area at the different temperatures at $t_{run} = 600$ s and $\dot{\gamma}_{max} = 50$ s⁻¹. In addition, Figure 4 shows the evolution of viscosity as a function of shear rate when the hysteresis loop test at 120 s as increasing time and 50 s⁻¹ as

maximum shear rate was applied at different temperatures for acrylic-based paint. An increase on thixotropy is observed as temperature decreases. From the hysteresis area, both viscosity and the degree of thixotropy gradually increase when the temperature decreases from 35 °C to 5 °C. The degree of thixotropy observed for the rest of paints was less dependent upon temperature.

The fitting of experimental data for all paints and temperatures by the proposed model was very satisfactory. The fitted thixotropic times listed in Table 2 describe the net structure breakdown and the net structure buildup processes. The net breakdown thixotropic time shows shear rate dependence while the net buildup thixotropic time is shear rate independent. Figure 5 shows the evolution with shear rate of thixotropic time (in absolute value) for the net breakdown process at two differentiated temperatures (5 °C and 25 °C). It can be observed that the breakdown thixotropic time decreases with shear rate for all paints, especially for acrylic, alkyd and vinyl paints at 25 °C, which means that the net kinetic process of breakdown becomes faster with shear rate. Similarly, the rate of the structure breakdown increases with temperature. The higher values are shown by the acrylic paint at 5 °C, therefore the rate of breakdown is the slowest one. On the other hand, the epoxy-based paint shows fast net kinetic process of buildup because of the low thixotropic time (see Table 2), which shows slight dependence with temperature. Both thixotropic times are important to improve the quality of the paint. For example, relatively slow rate of net breakdown and fast rate of the net buildup is required to brush properly the paint onto a surface.

5. Conclusions

The proposed model based on assumption that viscosity is a direct measure of the structural level can explain the rheological behavior under flow observed in paints. The equilibrium viscosity is defined following shear thinning behavior by the Cross-Carreau equation, and the time dependence of viscosity is introduced by a kinetic equation. The model depends only on two equilibrium parameters (k and n) and two thixotropic times (t_s^{break} and t_s^{build}). The net breakdown thixotropic time is defined as a function of shear rate, whereas the net buildup thixotropic time is considered independent of shear rate. Therefore, the proposed model is very simple and suitable for determining easily and accurately the thixotropy of paints. In comparison with the classical method used to evaluate thixotropy, the calculation of the hysteresis area, the proposed method is

able to better describe the thixotropic behavior since it is an absolute method which does not depend on the hysteresis loop test applied such as the hysteresis area does.

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References

- [1] C.K. Schoff, in: Encyclopedia of Polymer Science and Engineering, vol. 14, Wiley, New York, 1988, p. 454.
- [2] C.K. Schoff, Prog. Org. Coat. 52 (2005) 21.
- [3] H. Green, R.N. Weltmann Ind. Eng. Chem. Anal. Ed. 18 (1946) 167.
- [4] M. Dolz, M.J. Hernández, J. Pellicer, J. Delegido J. Pharm. Sci. 84 (1995) 728.
- [5] F. Moore Trans. Br. Ceramics Soc. 58 (1959) 470.
- [6] M.M. Cross J. Colloid Sci. 20 (1965) 417.
- [7] O. Cohu O, A. Magnin Prog. Org. Coat. 28 (1996) 89.
- [8] L.J. Boggs, D. Law, H. Taniguchi Eur. Coat. J. 5 (1998) 350.
- [9] J. Xu, K.W. Koelling Prog. Org. Coat. 53 (2005) 169.
- [10] D.-H. Cheng, F. Evans Br. J. Appl. Phys. 16 (1965) 1599.
- [11] J. Labanda, J. Llorens J. Colloid Interf. Sci. 289 (2005) 86.
- [12] J. Labanda, J. Llorens Colloid. Surfaces A, 249 (2004) 123.
- [13] K. Yasuda, R.C. Armstrong, R.E. Cohen Rheol. Acta 20 (1981) 163.
- [14] C.A. Hieber, H.H. Chiang Polym. Eng. Sci. 32 (1992) 931.

Nomenclature

a : shear rate exponent in Eq. (5), [-]

A : Arrhenius pre-exponential factor, [Pa·s]

Ea : activation energy of viscous flow, [kJ/mol]

k : characteristic time in Eq. (5), [s]

n : shear rate exponent in Eq. (5), [-]

t_S : thixotropic time, [s].

t_S^{break} : thixotropic time for the net breakdown process, [s].

t_S^{build} : thixotropic time for the net buildup process, [s].

t_{run} : running process time, [s].

$\dot{\gamma}$: shear rate, [s⁻¹]

$\dot{\gamma}_{max}$: maximum shear rate in the hysteresis loop, [s⁻¹]

η : viscosity, [Pa·s]

η_0 : zero-shear-rate viscosity, [Pa·s]

η_∞ : infinite-shear-rate viscosity, [Pa·s]

η_e : equilibrium viscosity, [Pa·s]

η_i : viscosity at the time $t_i = t - \Delta t$, [Pa·s]

λ : relaxation time, [s]

σ : shear stress, [Pa]

Table legends

Table 1 Some of the main characteristics of the paint resins.

Table 2. Parameters of the model.

Table 3. Parameters of the Arrhenius equation.

Table 4. Hysteresis area at $t_{run} = 600$ s and $\dot{\gamma}_{max} = 50$ s⁻¹.

Figure legends

Fig. 1. Evolution of equilibrium viscosity at 25 °C as a function of shear rate. Symbols represent experimental equilibrium viscosity data, while lines show the fittings of experimental data to Eq. (5).

Fig. 2. Dependence of the zero-shear-rate viscosity on temperature. The lines show the dependence predicted by Arrhenius equation.

Fig. 3. Evolution of viscosity as a function of shear rate resulting from the hysteresis loop test at a temperature of 25°C. The filled circles correspond to the up-curve resulting from the linear increase of shear rate with time, the open circles correspond to the down-curve due to the linear decrease of shear rate with time. The lines correspond to the fitted data by the proposed model. (a) Vinyl-based paint: $t_{run} = 600$ s and $\dot{\gamma}_{max} = 200$ s⁻¹; (b) Alkyd-based paint: $t_{run} = 120$ s and $\dot{\gamma}_{max} = 200$ s⁻¹; (c) Acrylic-based paint: $t_{run} = 600$ s and $\dot{\gamma}_{max} = 50$ s⁻¹; (d) Epoxy-based paint: $t_{run} = 120$ s and $\dot{\gamma}_{max} = 50$ s⁻¹; (e) Chlorinated rubber paint: $t_{run} = 600$ s and $\dot{\gamma}_{max} = 50$ s⁻¹.

Fig. 4. Evolution of viscosity as a function of shear rate when the hysteresis loop test ($t_{run} = 120$ s and $\dot{\gamma}_{max} = 50$ s⁻¹) was applied for acrylic-based paint at 5 °C (filled circles), 15 °C (open triangles) and 35 °C (filled squares). Lines correspond to the fitted data by the proposed model.

Fig. 5. Dependence of net breakdown thixotropic time (in absolute value) on shear rate and temperature. Big symbols and continuous lines correspond to thixotropic time at 25 °C, while small symbols and discontinuous lines correspond to thixotropic time at 5 °C.

Table 1

Commercial product	Recommended use	Product information¹
Acrylic-based paint	Varnish for steel	<i>Color: white</i> <i>Solids content: 42±2%</i> <i>Application method: Air spray, brush, roller</i>
Alkyd-based paint	Primer for steel plates	<i>Color: green</i> <i>Solids content: 49±2%</i> <i>Application method: airless spray, air spray, brush, roller</i>
Chlorinated rubber-based paint	Primer for steel plates	<i>Color: brown</i> <i>Solids content: 46%</i> <i>Application method: airless spray, air spray, brush</i>
Epoxy-based paint	Primer for steel plates	<i>Color: grey</i> <i>Solids content: 65±2%</i> <i>Application method: airless spray, air spray, brush</i>
Vinyl-based paint	Primer for steel plates	<i>Color: grey</i> <i>Solids content: 42±2%</i> <i>Application method: airless spray, air spray, brush</i>

¹All the paints have one component except the epoxy-based resin which consists of two components: the base and the curing agent, in a proportion of 4:1 in volume.

Table 2

Sample	T =	5 °C	10 °C	15 °C	25 °C	35 °C
Acrylic	η_o [Pa·s] =	332	251	194	102	73
	η_∞ [Pa·s] =	0.017	0.017	0.017	0.017	0.017
	k [s] =	15.3	16.8	18	19.2	20
	n [-] =	0.343	0.37	0.399	0.438	0.44
	$(\eta_o k^{n-1})$ [Pa·s] =	55.3	42.4	34.1	19.4	13.6
	t_s^{break} [s] =	$-9.14 \cdot \dot{\gamma}^{-0.53}$	$-4.18 \cdot \dot{\gamma}^{-0.78}$	$-2.08 \cdot \dot{\gamma}^{-1.06}$	$-0.78 \cdot \dot{\gamma}^{-1.79}$	$-0.23 \cdot \dot{\gamma}^{-2.35}$
	t_s^{build} [s] =	0.00225	0.00297	0.00381	0.00761	0.01126
Alkyd	η_o [Pa·s] =	10	9	8	6	5
	η_∞ [Pa·s] =	0.818	0.725	0.581	0.316	0.238
	k [s] =	3.7	3.6	3.55	3.53	3.5
	n [-] =	0.132	0.14	0.15	0.178	0.18
	$(\eta_o k^{n-1})$ [Pa·s] =	3.2	3.0	2.7	2.1	1.8
	t_s^{break} [s] =	$-0.33 \cdot \dot{\gamma}^{-0.94}$	$-0.18 \cdot \dot{\gamma}^{-1.32}$	$-0.14 \cdot \dot{\gamma}^{-1.45}$	$-0.11 \cdot \dot{\gamma}^{-1.54}$	$-0.067 \cdot \dot{\gamma}^{-1.91}$
	t_s^{build} [s] =	0.0211	0.0216	0.0219	0.0222	0.0225
Chlorinated rubber	η_o [Pa·s] =	40	27	18	16	12
	η_∞ [Pa·s] =	2.1	1.67	1.25	0.66	0.49
	k [s] =	5	5.5	5.63	6.44	8.23
	n [-] =	0.039	0.13	0.16	0.191	0.2
	$(\eta_o k^{n-1})$ [Pa·s] =	8.5	6.1	4.2	3.5	2.2
	t_s^{break} [s] =	0	0	0	0	0
	t_s^{build} [s] =	0	0	0	0	0
Epoxy	η_o [Pa·s] =	361	330	310	299	295
	η_∞ [Pa·s] =	0.205	0.01	0.013	0.013	0.013
	k [s] =	16	15.3	16.2	20.1	22.1
	n [-] =	0.147	0.16	0.18	0.208	0.21
	$(\eta_o k^{n-1})$ [Pa·s] =	33.9	33.4	31.6	27.8	25.6
	t_s^{break} [s] =	$-0.36 \cdot \dot{\gamma}^{-0.58}$	$-0.27 \cdot \dot{\gamma}^{-0.59}$	$-0.26 \cdot \dot{\gamma}^{-0.59}$	$-0.25 \cdot \dot{\gamma}^{-0.58}$	$-0.23 \cdot \dot{\gamma}^{-0.56}$
	t_s^{build} [s] =	0.0833	0.0877	0.0877	0.0877	0.0877
Vinyl	η_o [Pa·s] =	16	12	12	10	8
	η_∞ [Pa·s] =	0.00046	0.00046	0.00045	0.00044	0.00043
	k [s] =	63.6	41.8	50	44	33.3
	n [-] =	0.632	0.635	0.636	0.637	0.638
	$(\eta_o k^{n-1})$ [Pa·s] =	3.5	3.1	2.9	2.5	2.2
	t_s^{break} [s] =	$-1.76 \cdot \dot{\gamma}^{-0.76}$	$-1.99 \cdot \dot{\gamma}^{-0.88}$	$-2.07 \cdot \dot{\gamma}^{-1.29}$	$-2.84 \cdot \dot{\gamma}^{-1.54}$	$-4.4 \cdot \dot{\gamma}^{-1.69}$
	t_s^{build} [s] =	0.0083	0.0093	0.0113	0.0136	0.0183

Table 3

Sample	A (Pa·s)	Ea (kJ/mol)
Acrylic	3.4E-05	37.17
Alkyd	7.0E-03	16.80
Chlorinated rubber	3.0E-04	26.94
Epoxy	50	4.47
Vinyl	1.9E-02	15.38

Table 4

	Hysteresis area (Pa·s ⁻¹)				
	T = 5 °C	T = 10 °C	T = 15 °C	T = 25 °C	T = 35 °C
Acrylic	230	124	51.7	6.3	8.8
Alkyd	9.25	4.29	2.34	1.62	2.78
Chlorinated rubber	1.91	1.52	1.21	1.18	0.87
Epoxy	18.9	11.7	11.3	10.0	9.9
Vinyl	28.5	30.0	22.4	23.1	22.5

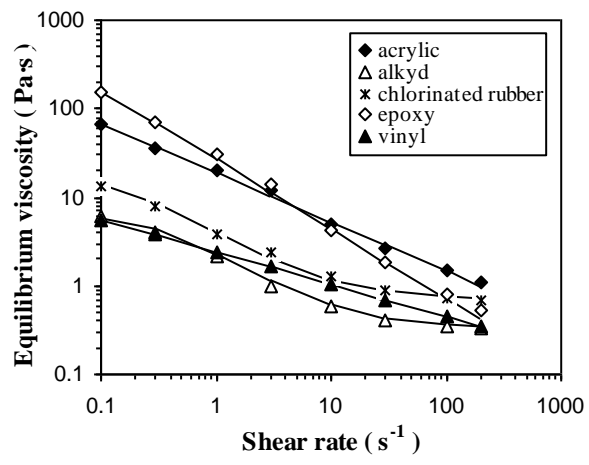


Fig. 1

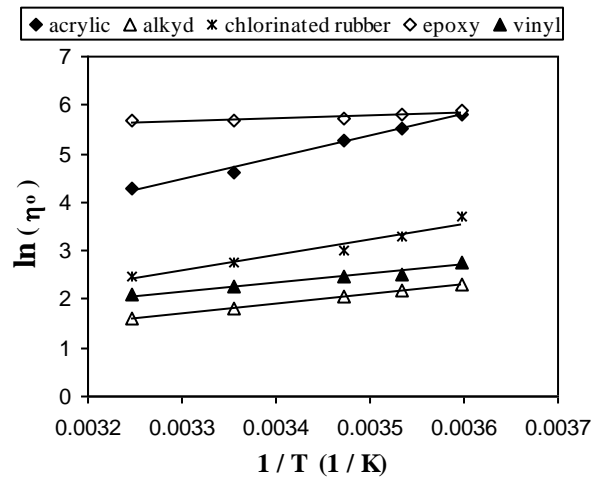


Fig. 2

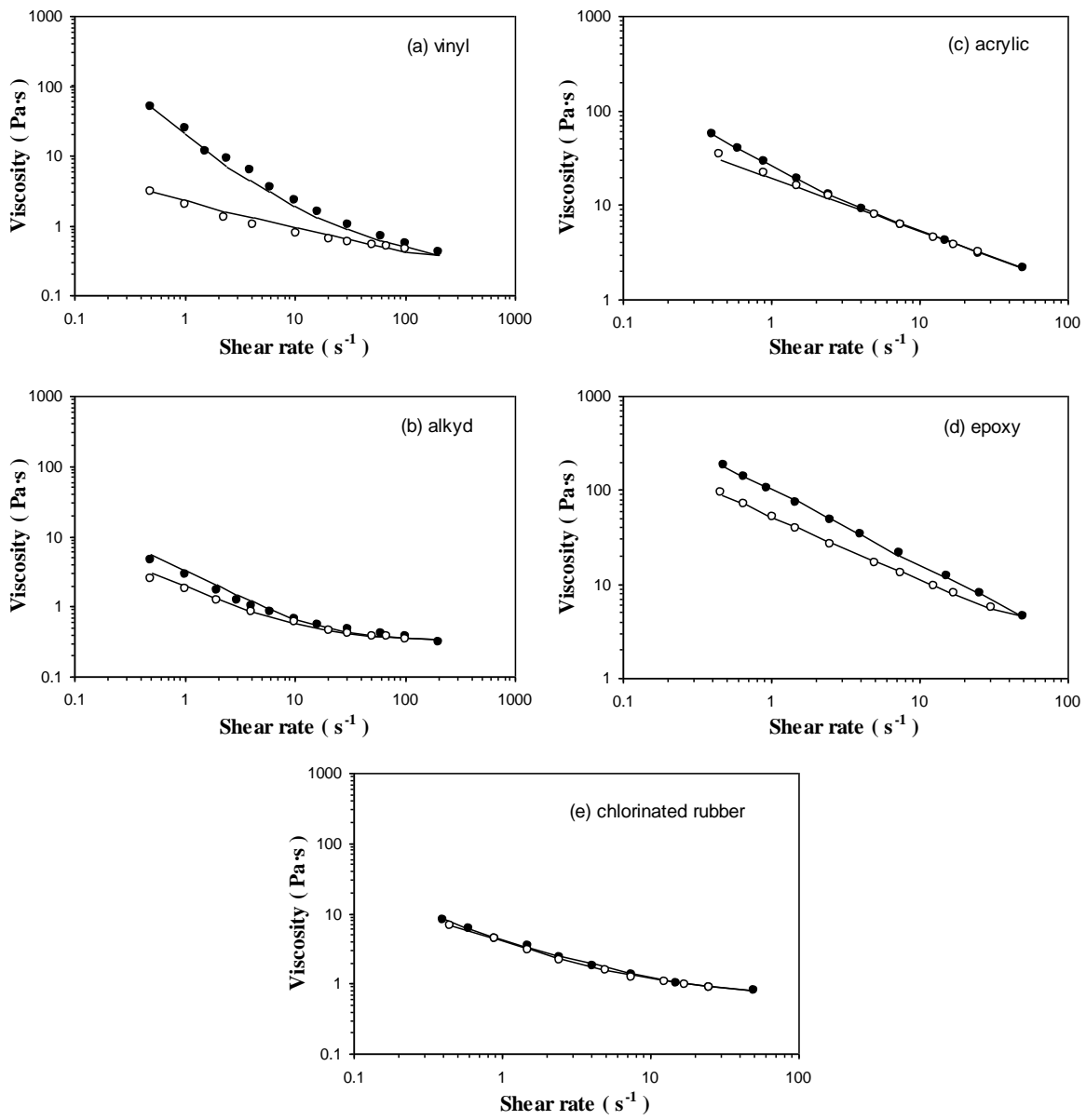


Fig. 3

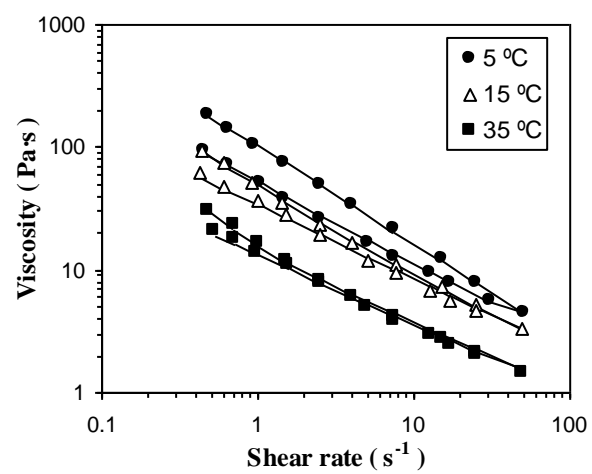


Fig. 4

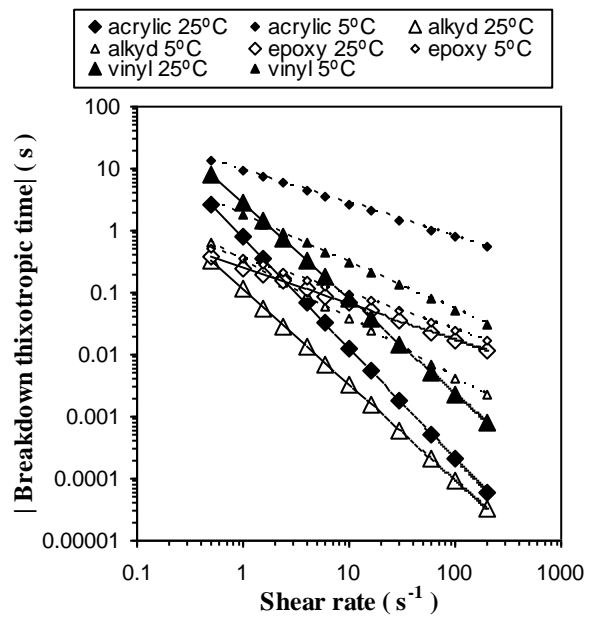


Fig. 5