

ICM11

Rheological Characterization of Clay-Polyester Composites

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Abstract

Polymer-clay composites, which consist of clay particles dispersed in a polymeric matrix, have been used in different applications. Clay fillers are widely used in polymers as ways to produce cost-effective, strong, and energy efficient materials. The compounding and inclusion of particulate fillers in the polymers to get a homogenous material is a rather complex process. The processing of these materials, like mixing and moulding is strongly dependent on the particle-particle and particle-polymer interactions. Therefore, the fundamental understanding of the rheological properties of the polymer-clay composites is very important in the design of their processing. In this study, the rheological behaviour of bentonite clay dispersed in unsaturated polyester was investigated. Herschel-Bulkley model and Structural Kinetic model were used to describe the dependence of the apparent viscosity of the composite on shear rate and shearing time, respectively. The effects of the filler/polyester ratio and filler size on the rheological properties of the composite were studied.

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Selection and peer-review under responsibility of ICM11

Keywords: bentonite; polyester; rheology; composite; shear thinning

1. Introduction

The use of polymers and polymeric materials has increased rapidly during the last few decades in different engineering applications by replacing other traditional materials like metals, wood and glasses. On the other hand, the use of polymer composite materials allowed the significant improvement of the physical, thermal and mechanical properties of polymeric materials [1]. Different filler materials, such as

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clay, carbon black, glass fibers, and silica, have been used in the formation of the polymer composite materials to achieve the desired properties.

Polymer-clay composites, which consist of clay particles dispersed in a polymeric matrix, have been prepared for different applications [1-3]. Clay fillers are widely used in polymers as ways to produce cost-effective, strong, and energy efficient materials. Because of their lower cost, ease of handling and a good balance of mechanical, electrical and chemical properties, the unsaturated polyester resins are more commonly used in composite materials. Ismail et al. [4] studied the mechanical and physical properties of sand/clay-unsaturated polyester composite. Different types of bentonite have been mixed with unsaturated polyester to form clay-based heat insulator composites [5-7]. Sangthong et al. [8] investigated the mechanical property improvement of unsaturated polyester composite reinforced with admicellar-treated sisal fibers.

The compounding and inclusion of particulate fillers in the polymers to get a homogenous material is a rather complex process. The processing of these materials, like mixing and molding is strongly dependent on the particle-particle and particle-polymer interactions [9]. In addition, the shrinkage and change in the final shape of the composite article depend on these interactions. Therefore, the fundamental understanding of the rheological properties of the polymer-clay composites is very important in the design of their processing. In the present work, the rheological properties of bentonite-unsaturated polyester (UP) resin composite were investigated. The effects of the filler content and size on the apparent viscosity of composite as a function of shear rate and shearing time were also studied.

2. Experimental methods

2.1. Materials

Polyester used in this study was obtained from the Intermediate Petrochemicals Co., Jordan. The type of polyester used was HM190 with a styrene content of 33–35%, and an acid content of 21–23%. The untreated bentonite sample obtained from Al-Azraq in Jordan was used in this study as filler. The sample has the following composition (wt%): Na_2O 4.58; K_2O 1.79; Fe_2O_3 11.58; MgO 2.65; Al_2O_3 16.10; SiO_2 51.64; CaO 1.98; H_2O 5.16. The filler was crushed and then screened into three batches with an average size of 1.0, 0.5 and 0.3 mm.

2.2. Sample preparation

A fresh sample of unsaturated polyester was poured into a vessel. Then specific amount of filler (0, 5, 10, 15, 20, 25, 30 or 40 wt%) was added to the sample. The vessel was equipped with an impeller mixer of a curved-blade turbine type. The mixing process was performed at 200 rpm for 10 min.

2.3. Rheological measurements

The rheological properties of filled polymer samples were measured at 25 °C using a concentric cylinder viscometer (Haake VT 500, MV3). The system has an inner cylinder rotating in a stationary outer cylinder. A bob with a length of 60 mm and radius of 15.2 mm and a cup with a radius of 21.0 mm were used to form a gap of width 5.8 mm. After the sample was transferred to the viscometer, it was allowed to rest for 5 min before the flow test was started. The viscometer was thermostatically controlled with a water circulator (Haake D8) at the desired temperature with a precision of ± 0.1 °C.

2.4. Methodology

The experiments performed to characterize the shear-, and time- dependency of the flow behavior of bentonite-polyester composites consisted of a series of two measurements:

- Flow curves: a fresh sample was loaded into the annular gap of the concentric-cylinder viscometer. Samples were left to reach the desired temperature. The shear stress was measured by continuous increasing of the shear rate in the range of 2.200 and 219.8 s^{-1} . The flow curves of the bentonite-polyester dispersion was modeled using the Herschel-Bulkley (H-B) model:

$$\tau = \tau_o + m\dot{\gamma}^n \quad (1)$$

where τ is the shear stress, τ_o is the yield stress, $\dot{\gamma}$ is the shear rate, m is the consistency coefficient and n is the flow behavior index. Typically, the Herschel-Bulkley model is used for many materials, as the Newtonian, shear thinning, shear thickening and Bingham plastic may be considered as special cases.

- Apparent viscosity measurements as a function of shearing time at constant shear rate: in transient measurements, a fresh sample was sheared at constant shear rate of 6.116 s^{-1} , for 40 min. Most of the samples reached the equilibrium state in 30 min. The time-dependent flow properties could be modeled by applying the structural kinetic (SK) model, which is adopted by using the analogy with chemical reactions. The final form of the model [10] is:

$$\left[\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} \right]^{1-n} = (n - 1)kt + 1 \quad (2)$$

where η is the apparent viscosity, η_0 is the initial apparent viscosity at $t = 0$, η_∞ is the equilibrium apparent viscosity as $t \rightarrow \infty$, k is the rate constant, and n is the order of the structure breakdown reaction.

3. Results and discussion

Figure 1 shows the typical effect of solid concentration on the apparent viscosity of the bentonite-polyester composites. An increase in the solid concentration, as would be expected, increased the apparent viscosity. The bentonite-polyester samples tested here exhibited significant increase in apparent viscosity at solid concentration of 25 wt%. The effects of solid concentration on the flow curves of bentonite-polyester dispersions were quantified using the H-B model, which fitted well the τ versus $\dot{\gamma}$ data for bentonite-polyester suspensions giving correlation coefficients between 0.980 and 0.999, and as indicated in Figure 1. The polyester used behaved as a Newtonian fluid. On the other hand, all bentonite-polyester suspensions tested here exhibited both Newtonian and non-Newtonian behaviours at low and high solid concentration, respectively, as can be seen in Table 1. The obtained H-B model parameters reported in Table 1 show that the filler of 0.3 mm size with 15 wt% solid concentration and below show Newtonian behaviour without yield stress. However, significant yield stress was observed when the solid concentration increased above 20 wt%. On the other hand, 0.3 mm suspension with 20 wt% solid concentration, was found to behave like Bingham fluid, where n in Eq. 1 equals one. At high solid concentration (25 – 40 wt%) 0.3 mm suspensions exhibited shear thinning behaviour with a yield stress.

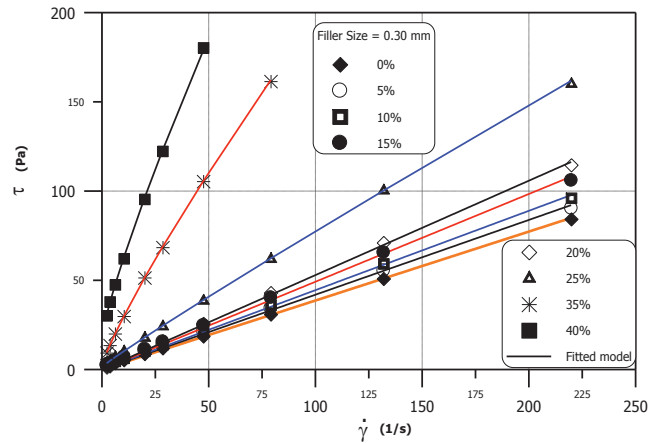


Fig. 1. Flow curves of bentonite-polyester dispersions at different solid concentration

The same transition from Newtonian to Bingham and then to shear thinning behaviour has also been observed in suspensions with higher particle size. However, the transition was shifted with increasing the particle size, where the Bingham behaviour observed in the 0.5 mm suspension at 25 wt%, and in 1.0 mm suspension at 35 wt%. For 1.0 mm suspension, only the 40 wt% showed shear thinning behaviour.

Table 1. Herschel-Bulkley parameters of bentonite suspensions at different solid concentrations. S1= 0.3 mm particle size, S2= 0.5 mm particle size, S3= 1.0 mm particle size

Solid Conc. (wt%)	τ_0 (Pa)			$m (Pa \cdot s^n)$			n		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
0	0	0	0	0.386	0.386	0.386	1.0	1.0	1.0
5	0	0	0	0.419	0.441	0.521	1.0	1.0	1.0
10	0	0	0	0.445	0.450	0.570	1.0	1.0	1.0
15	0	0	0	0.492	0.456	0.630	1.0	1.0	1.0
20	0.74	0	0	0.523	0.460	0.842	1.0	1.0	1.0
25	1.50	0.33	0	0.960	0.554	1.150	0.95	1.0	1.0
35	1.97	1.60	2.93	3.820	3.542	6.529	0.86	0.80	1.0
40	18.30	6.5	6.05	6.420	8.517	10.352	0.83	0.78	0.99

Increasing the particle size of solids led to an increase in the apparent viscosity of bentonite-polyester dispersion. However this enhancement in the apparent viscosity decreased with the solid concentration to reach negligible level at 40 wt% concentration. The presence of the yield stress in bentonite-polyester suspensions, which was significant at highly concentrated suspensions (40 wt%), is due to the resistance solid particles show against deformation, until the applied stress exceeds the yield strength of the solid phase and that the suspension likes a show flow. It is commonly admitted that the yield stress of suspensions is linked to the existence of an interconnected three dimensional network of flocks. The value of the yield stress corresponds to the stress needed to be applied to overcome the cohesion Van der-Waals forces and induce the flow of the suspension. As can be seen in Table 1, increasing the particle size decreased the yield stress and increased the consistency coefficient, which is a measure of the shear viscosity. This means that after the yield stress is exceeded, suspensions with low particle size would flow

easily. In addition, Table 1 shows that the shear thinning behaviour was more pronounced at low particle size, which means that the bentonite dispersion tends to behave like a shear thinning material rather than plastic material at small particle size. The shear thinning often evident in mineral suspensions is attributed to the alignment of particles or flocks. An increase in the shear rate from rest results in the alignment of particles in the direction of shear, therefore, provides a lower resistance to flow [11].

Thixotropy, which is a decrease in the apparent viscosity with time under constant shearing, followed by a gradual recovery when the shear is removed, has been detected in many bentonite suspensions [12]. The effect is time dependent. If the viscosity is reduced and immediately returned after shearing, the material is not thixotropic but just shear thinning. In order to evaluate the effect of shearing time on the rheological behaviour of the bentonite-polyester suspension, the apparent viscosity was determined as a function of shearing time at constant value of shear rate. All samples exhibited a time-independent behaviour expect the 35 and 40 wt% suspensions with 0.3 and 0.5 mm particle size. Typical thixotropic behaviour obtained for these samples is shown in Figure 2. The observed time-dependent flow behaviour of bentonite-polyester suspension was modelled using the structural kinetics approach [10]. This model postulates that the change in the rheological properties is associated with shear-induced breakdown of the internal fluid structure in the clay suspension. Using the analogy with chemical reactions, the final form of the structural breakdown process can be expressed as in Eq. 2. For all samples exhibited thixotropic behaviour, it was found that their apparent viscosity data at constant shear rate could be correlated with Eq. 2 using $n = 2$, i.e., with a 2nd order irreversible kinetic model. A good comparison between the model fitted results (solid lines) and the experimental apparent viscosity - time data for bentonite-polyester suspensions can be seen in Figure 2.

The rate constant, k , is a measure of the rate of thixotropic breakdown, meanwhile the ratio of the initial to equilibrium viscosity, η_0/η_∞ , can be considered as a relative measure of the amount of structure breakdown, or in other words as a relative measure of the extent of thixotropy. The values of k and η_0/η_∞ as a function of solid concentration and particle size are reported in Table 2. It can be seen, that k and the amount of structure breakdown increased with solid concentration and particle size.

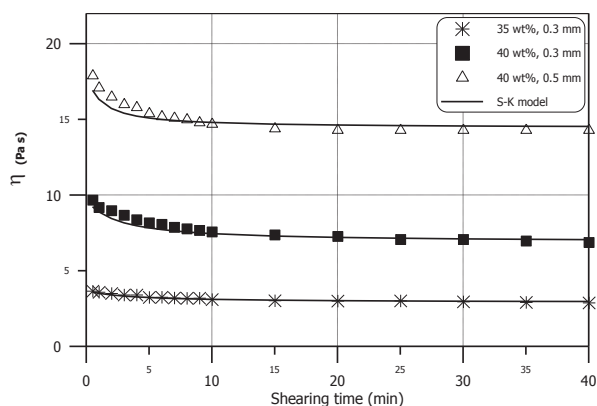


Fig. 2. Dependence of the apparent viscosity of suspension on the shearing time

Table 2. S-K model regressed parameters for bentonite-polyester dispersions

Particle size (mm)	Soild conc. (wt%)	η_0 (Pa)	η_∞ (Pa)	η_0/η_∞	k (1/min)
0.30	35	3.663	2.893	1.266	0.267
	40	9.683	6.883	1.407	0.397
0.50	35	9.338	8.088	1.154	0.974
	40	17.898	14.200	1.26	1.295

4. Conclusions

Bentonite-polyester suspension was found to exhibit non-Newtonian behavior starting from 20 wt% solid concentration. The transition from Newtonian to Bingham plastic and then to shear thinning material with yield stress was found to depend on the solid concentration and the particle size. The suspension with the lowest particle size was observed to show the earliest transition to pseudoplastic behavior, which was well described by the Herschel-Bulkley model. In addition, a thixotropic behavior was detected in bentonite-polyester suspensions at high solid concentration and low particle size.

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