The effect of carrier molecular weight and pigment particle concentration on the rheological properties of suspension systems in polymeric medium

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ABSTRACT

In this research study, the prediction and analysis of the flow behavior in the particulate suspension systems of polymers is investigated in wide ranges of shear rates using rheometry technique.

Our findings indicate both polymer molecular weight and particle concentration play important roles in controlling the properties of the flow. The details of the changes in flow behavior are elaborated by relating to interactions among the components and microstructure of the systems.

INTRODUCTION

Suspension systems have found many applications in the production of paints, and other polymeric compounds and pigments have been used extensively for colouring of thermoplastics. However, it has been found that in most cases, the presence of pigment particle may alter the physical, chemical, mechanical, flow behaviour of polymer.

Investigations have revealed that the incorporation of particles to the polymer system highly affect the flow behavior of polymer. There abound many factors associated with fine particles such as concentration, size, shape, size distribution as well as suspension stability which play the part in governing the properties of flow. Many research studies have been carried out to develop the fundamental understanding of aspects of particulate systems and uncover the complexities of the system.

The main objective of this work is to investigate the rheological properties of poly(ethylene terephthalate) suspension systems containing coloring pigments under different shear rates.

EXPERIMENTAL

Poly(ethylene terephthalate) granules (YPC, Iran) underwent hydrolytic degradation in order to prepare polymeric carriers having different molecular weights. Pigment particles (Cromophtal red 214 BN, Ciba) were dispersed in a batch process using an internal mixer by compounding four range of carrier molecular weights (9,319~24,209) with different pigment concentration (4~16 v/v%).

The molecular weight of degraded polymers was measured by viscometry analysis according to the standard method of ASTM D 4603. The intrinsic viscosity of the samples was calculated using the Billmeyer equation[1]:

$$\eta = 0.25\frac{(\eta_r - 1 + 3\ln\eta_r)}{C} \quad (1)$$

where $\eta_r = \eta / \eta_0$, and η_0, η and η_r are the viscosities of the solvent, polymer solution and relative viscosity values, respectively.

The molecular weight of the polymers was calculated using the Mark-Houwink equation: $\eta = K[M_v]^a$ with the following constants of $K = 7.44 \times 10^{-6}$ mL/g and $a = 0.648$ [2]. The results of the viscometry analysis are summarized in Table 1. Due to high tendency of PET toward hydrolytic degradation, viscometry analysis was conducted in the solution state.

In addition, analysis of the samples was carried out in a unique regime which was determined according to polymer solution theory[3]. The first critical concentration of PET solutions c* was calculated based on the results of viscometry and using Eq. (2).

$$c^* = \frac{1}{[\eta]} \qquad (2)$$

where $[\eta]$ is the intrinsic viscosity of solution[4]. Rheological properties of suspensions were evaluated at 25 ± 0.1°C using a HAAKE RV12 rotational viscometer.

Table 1. The results of viscometry analysis and molecular weight determination for hydrolytically degraded polymers.

Sample	Degradation period (days)	(dL/g)	*Mv*	C* (g/dL)
1	0	0.5156	24,209	1.939
2	5	0.4728	21,179	2.115
3	15	0.3316	1,2252	3.016
4	25	0.2776	9,309	3.602

RESULTS AND DISCUSSION

The fundamental method for identification of the nature of the flow is establishing the relationship between the shear stress or viscosity and shear rates. Findings show that in majority of the cases, the suspension systems follow the common trend of the flow of pure polymeric materials which is the shear-thinning behaviour [5-7].

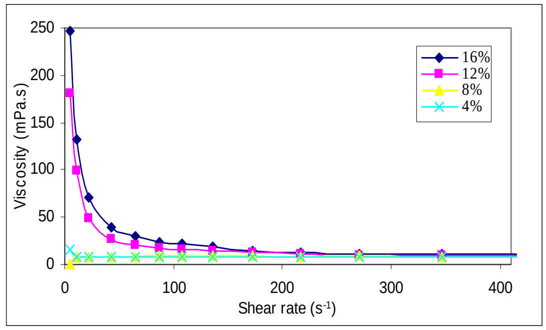

Fig.1. The effect of shear rate and pigment concentration on viscosity of dispersion system (carrier molecular weight: 24,209).

Figs. 1 to 4 exhibit plots of changes in viscosity versus shear rate for samples containing various loadings of pigments. It can be seen that increase of the shear rate applied to the system is followed by decrease in viscosity values. According to Power-law model, this characteristic is interpreted as the pseudo plastic behaviour of the pigmented PET suspensions which was observed for all the samples. Interestingly this behaviour was substituted by Newtonian behaviour at higher shear rates.

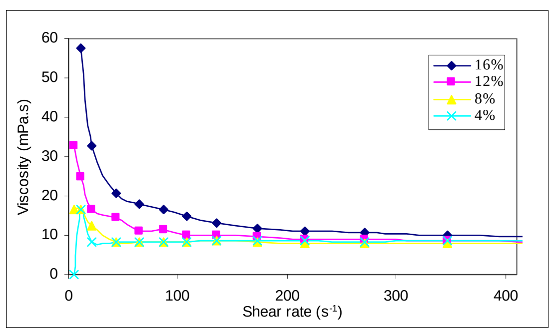

Fig.2. The effect of shear rate and pigment concentration on viscosity of dispersion system (carrier molecular weight: 20,179).

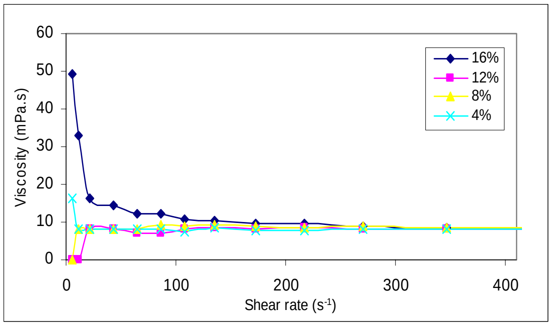

Fig.3. The effect of shear rate and pigment concentration on viscosity of dispersion system (carrier molecular weight: 12,252).

Moreover, all samples were found to exhibit the yield stress. For instance, the plot of changes in shear stress with the variation of shear rate for the suspension system having the carrier molecular weight of 24,209 is shown in Fig. 5. This figure clearly reveals that the magnitude of yield stress is dependent on the pigment concentration. The largest yield stress was observed for the sample containing 16 v/v% of particle loading. This is possibly due to the tendency of particles and polymer macromolecules for formation of agglomerates leading to an interacting network which occurs at certain levels of pigment content. The yield stress was gradually diminished at the concentrations below 8% which may indicate the rupture of the spanning network and finite clusters at relatively high shear rates [8,9].

Results in Fig. 1 to 4 also show that the viscosity of the suspension is highly affected

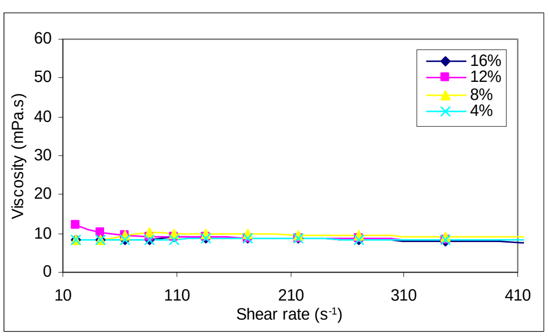

Fig.4. The effect of shear rate and pigment concentration on viscosity of dispersion system (carrier molecular weight: 9,319).

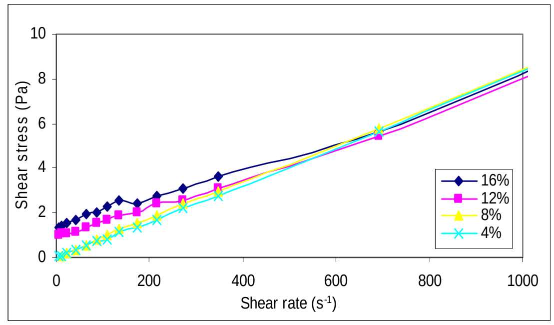

Fig.5. The effect of variations in shear rate on the shear stress for the samples containing different pigment contents. (carrier molecular weight: 24,209)

by amount of pigment loading. It can be seen that at lower shear rates the effect of pigment concentration is more sensible; increase in pigment concentration results is higher viscosity values. This mainly denotes that the presence of agglomerates imposes higher resistance to flow. The inorganic nature of the particles may also contribute to this behaviour through the induction of friction between the components. The effect of pigment loading levels off by exceeding a certain shear rates. This implies that at higher shear rates, the network structure has been broken and no difference can be distinguished between pigment particles and macromolecules.

Similarly, the effect of pigment concentration is more tangible for samples containing higher molecular weight career. As the molecular weight decreases, the system loses its network integrity due to the severe decrease in the length of macromolecules. As a result, the suspension behaves rather like Newtonian fluids by possessing a constant viscosity value for different shear rates. These figures similarly show that the effect of molecular weight on the flow behavior is more sensible at low shear rate values. It should be noted that this is valid only for the suspension systems carrying 16 v/v% and 12 v/v% pigment loadings. The higher viscosity values for higher molecular weights are expected since the presence of macromolecules with long chains that are entangled into each other. Subsequently, the flow behavior of the system is mainly governed by non-

Newtonian nature of the polymer medium. The extent of entanglements gradually decreases by depletion in carrier molecular; as a result the behavior of macromolecules tends more toward single elements. In addition, the fold effects caused from the increase in pigment concentration can contribute to this behavior. The trend is completely different by considering the systems composed of low pigment concentration.

CONCLUSIONS

The rheometry analysis reveal the pseudoplastic characteristic of the suspension systems show the characteristics of PET/pigment suspension system at low shear rate values However, suspensions turn to a Newtonian fluid after exceeding a certain shear rate value. The tinctures of yield stress were detected as a consequence of formation of semi-stable network within the system for samples with high molecular weight and high pigment concentration. However, the integrity of the network was disrupted by increase in shear rate. The effect of pigment flow behavior was more pronounced in lower shear rates and for samples with high molecular weight. Similarly the high viscosity was observed for the samples with high molecular weight carrier. The overall analysis reveals that the effect of molecular weight is more pronounced than the effect of pigment loading.

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