

Application of the Navarro Rheological Model to Polyester-Attapulgite and Polyester-Alumina Composites in a Liquid State

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Abstract

Composites where the filler has no activity, that is, where there is not a transient interface between the matrix and filler particles, can be considered, at liquid or molten state, as suspensions. Several rheological models have been developed relating the behaviour under shear of suspensions with the filler content. Frequently these models predicting a critical value for filler content, above which the suspension initially newtonian changes its rheological behaviour to a non-newtonian one. In this paper is applied a new rheological model to experimental data of apparent viscosity versus filler content from polyester composites with attapulgite and alumina, without coupling agent, that remain newtonian up to 25-30 g of filler per dl of liquid matrix. The proposed model shows to be suitable to explain the uncommon behaviour of these systems.

Introduction

Suspensions of mineral fillers in newtonian media are generally newtonian up to a critical concentration. This concentration, which generally lies in a range of 2-15 g of filler by dl of dispersion media, depends upon several factors related to filler and dispersion media, which are largely mentioned in the literature [1,2]. Above this critical concentration almost all suspensions change their initial newtonian rheological behaviour to a shear rate and/or time dependent one. When the dispersion media is a polymeric fluid, the shape and length of its chains at rest in association with filler content must be considered. Accordingly to Navarro [3] suspensions of mineral fillers in polymeric fluids, of linear and flexible like chains such as poly(dimethylsiloxane), can become non-newtonian even at low filler concentration. On the other hand, if the polymer has chains that are linear but rigid such as unsaturated polyester, the suspension could remain newtonian up to a concentration where it can still flow like a liquid. In the first case, the space between the chains allow the particles to form

agglomerates (see Figure 1a). In the last, this space is insufficient and the particles remain dispersed (see Figure 1b). Since the dispersion media is newtonian and the particles don't agglomerate even at filler contents up to 20-30g/dl, the suspension doesn't change its newtonian behaviour.

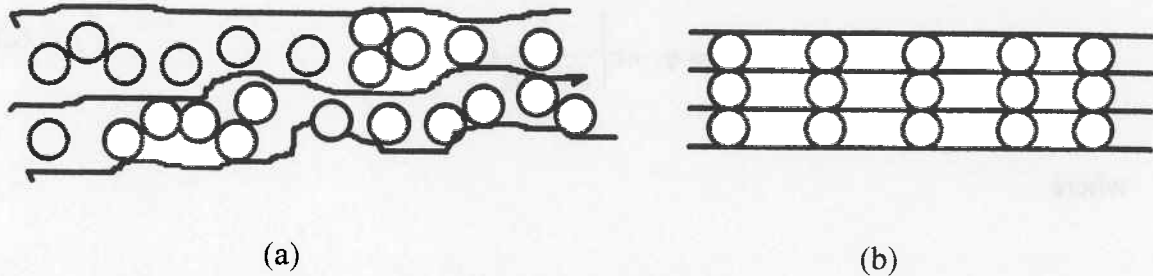


Figure 1. Polymeric suspension with linear and flexible chains (a) and linear and rigid chains (b).

In a recent paper, Navarro [3] based on De Genes' reptation model [4,5] developed a rheological model (equation 1) that relates the concentration dependence of the rheological behaviour of highly concentrated suspensions with the mobility of polymeric chains.

$$\eta_s = \eta_o + c \left[\frac{1}{2kTf_v \rho} \left(\frac{X_s^2 E_s}{m_s} - \frac{X_o^2 E_o}{m_o} \right) \right] \quad (1)$$

where: s and o indicate suspension and polymer, respectively;

η - apparent viscosity (Pa.s);

k - Boltzmann constant (N/m.K);

T - absolute temperature (K);

ρ - filler density (g/cm³);

f_v - volumetric factor = volume of filler/volume of polymer;

c - filler content (g/dl);

E - modulus dependent of the distance between two adjacent obstaculus (Pa);

X - mean distance of chains dislocation among the obstaculus (m);

m - chain mobility (m/s.N).

Since the experimental determination of the quantities X , E and m is very difficult, a new parameter called motion perturbation number ($\Psi = X^2 E/m$), which increases with filler content and is related to motion hindrance, must be introduced in equation 1. This way the equation 1 becomes:

$$\eta_s = \eta_o + c \left[\frac{1}{2kTf_v \rho} (\Psi_s - \Psi_o) \right] \quad (2)$$

where

$$\left[\frac{1}{2kTf_v \rho} (\Psi_s - \Psi_o) \right] = \alpha \quad (3)$$

where α (Pa.s.dl/g) is a constant that represents the effect that the filler plays to increase the apparent viscosity of the suspension. Since α is independent of filler concentration, the ratio, $\frac{\Psi_s - \Psi_o}{f_v \rho} = \xi$, must be constant for all filler content at each temperature of analysis. This must occur even though $\Delta\Psi = \Psi_s - \Psi_o$, called perturbation degree, increases as c is increased.

After the introduction of ξ and $\Delta\Psi$ we have:

$$\alpha = \frac{\Delta\Psi}{2kTf_v \rho} \quad (4)$$

$$\alpha = \frac{\xi}{2kT} \quad (5)$$

since

$$\eta_s = \eta_o + \alpha \cdot c \quad (6)$$

then

$$\eta_s = \eta_o + \frac{\xi}{2kT} c \quad (7)$$

In this paper the equations 3-7 are applied to experimental data of polyester-attapulgite composites (PEATC) [6] and polyester-alumina composites (PEALC) [7] to obtain the experimental values of α , $\Delta\Psi$ and ξ and to compare them with the theoretically estimated values.

Materials

The characteristics of the materials used to obtain the composites PEALC [7] and PEATC [6] are listed at table 1.

PEATC polyester attapulgite	reference Alpolit LP8121 UBM	μ_0 (Pa.s) 0,509 -	ρ (g/cm ³) 1,13 2,6547	α_e (Pa.s.dl/g) 0,0116±0,0003 [6]
PEALC polyester alumina	Alpolit LP8121* Alcoa 710	0,803 -	1,13 3,975	0,028±0,001 [7]

* - pre-polymerized - e - estimated value.

Table 1. Materials characteristics.

Results and Discussion

Table 2 presents the values of f_v , $\Delta\Psi$, ξ and α as filler content function for the two composites systems after the application of the proposed model. The comparison of experimental data with theoretically predicted results are best verified at Figures 2-5.

System	c (g/dl)	α (Pa.s.dl/g)	$\Delta\Psi$ (Pa ² .s.m ³)	ξ (Pa ² .s.m ⁶ /kg)
PEALC	5	0,031	12,75 x 10 ⁻²²	2,5 x 10 ⁻²²
	10	0,029	23.85	2,4
	15	0,027	33.3	2,2
	20	0,029	47.7	2,4
	25	0,028	57.6	2,3
PEATC	10	0,01150	9.4 x 10 ⁻²²	9.4 x 10 ⁻²²
	20	0,01175	19.3	9.6
	25	0,01110	22.8	9.1

Table 2. α , $\Delta\Psi$ and ξ experimental values for PEALC and PEATC systems.

Figure 2 shows the best fit between the experimental and estimated data for $\Delta\Psi(c)$ dependence for PEALC system. This occur for all alumina content, even tough

the model proposed consider the particles of the filler to act as a barrier similar to each polymeric chain in the De Gennes reptation model. Of course this is only true as the filler content is sufficiently high to produce significant chain motion perturbation. without changes the rheological behaviour of the suspension.

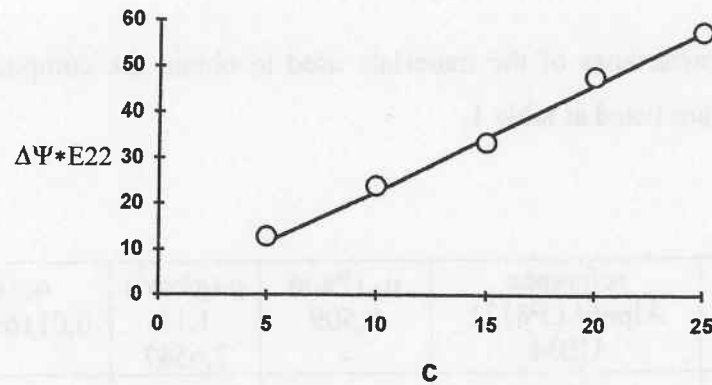


Figure 2. $\Delta\Psi(c)$ dependence for PEALC (— estimated value; O experimental data).

The $\alpha(c)$ dependence for PEALC (Figure 3) agrees with the proposed model, since the α values that lie in the theoretical range correspond to concentrations above 10g/dl where the motion perturbation becomes dramatic. This way, α can be consider independent of alumina concentration in the range of 10-25g/dl.

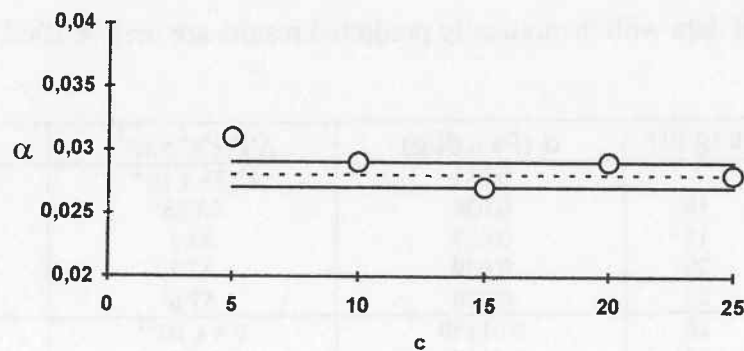


Figure 3. α versus c for PEALC (— theoretical range; --- estimated mean value; O experimental data).

The $\Delta\Psi(c)$ dependence for PEATC (Figure 4) was exactly as expected and although on first sight α seems to deviate from the expected behaviour at 25g/dl (Figure

5), further analysis shows that this value is just 4.3% lower than the mean estimated value and, therefore, α can be considered to be constant and independent of c .

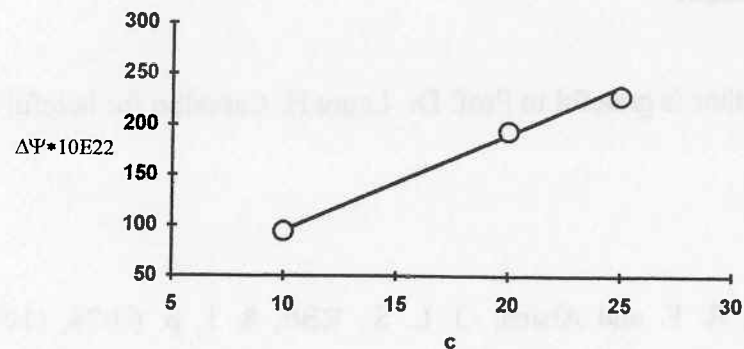


Figure 4. $\Delta\Psi(c)$ dependence for PEATC (— estimated values; O experimental data).

Since ξ is a multiple of α (see Table 2), identical behaviour will be achieved for this quantity with respect to filler content in both PEALC and PEATC systems.

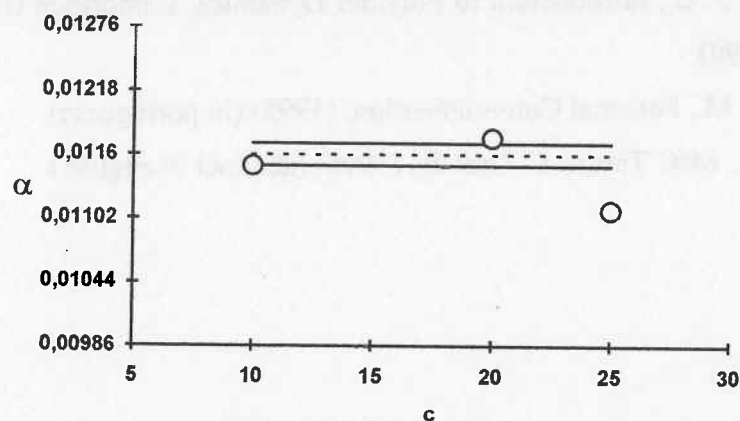


Figure 5. α versus c for PEATC (— theoretical range; --- estimated mean value; O experimental data).

Conclusion

The proposed model is suitable to adjust the experimental data for both PEALC and PEATC systems, specially in relation to $\Delta\Psi(c)$ dependence. Studies with PEATC system with alumina content higher than 25g/dl are necessary to confirm if α will or

will not lie in the theoretical range and considered to be constant like for PEALC system.

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