Rheological behavior of the composite matrix Diglycidylether of bisphenol-A (DGEBA/ wt% blast furnace slag (BFS))

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Abstract. This paper reports experiments on the rheological behavior of DGEBA epoxy resin filled with blast furnace slag nanoparticles. The study of the variation of stress and viscosity as a function of shear rate is emphasized.

The purpose of this study is to investigate the rheological behavior of DGEBA loaded with blast furnace slag (BFS), the selected mixtures cannot exceed 10% in wt%, given the fineness of grinding which SSB= 44.5 m2.g-1. We tested the compositions of DGEBA/%wt blast furnace slag (BFS) at filling ratios of (10, 20, 30, 40and 50%). Viscosity and shear stress as a function of temperature and filler rate were investigated. In this study, formulations were developed to test the best compositions with favorable rheological behavior for better processing of these matrices.

Keywords: DGEBA, blast furnace slag, FTIR, rheological behavior, viscosity

1. Introduction

The search for new and improved components for coating systems requires a better understanding of the structure-property relationships of materials [1-2]. Although some properties of coating systems can be obtained experimentally, the ability to predict the properties of new coatings prior to laboratory synthesis will greatly facilitate the design of new coatings [3-4].

Resins reinforced with inorganic fillers have recently attracted considerable interest due to their potential application in a wide variety of technological fields [1-4].

The rheological behavior of resins has always played a role in understanding and controlling the processing when used in the manufacture of complex shaped composite materials [5].

The epoxy resin is usually considered as a complex fluid that exhibits various rheological behaviors under shear, most often rheofluidizing, but also rheo-thickening, or even both behaviors if the range of shear rates examined is sufficiently large. This type of resin can also show solids and threshold stress. However, the rheofluidizing behavior is by far the most frequently encountered.

In the case of using fillers as reinforcement, several authors underline the importance of the microstructure (anisotropic, isotropic) on the rheological behavior of the composite. Studies of S. Ménio (2000) [6] and Dumont et al. (2003) [7], during shear and simple compression tests on a filled epoxy matrix, showed that the elongational viscosity of these products is more than 100 times the shear viscosity, whereas for a Newtonian isotropic fluid the ratio between these two quantities is only three. R.Blanc [8] stresses the
importance of taking into account the orientation and distribution of loads imposed by the experiment carried out.
In this study, we will test the contribution of the blast furnace slag type mineral filler on the rheological behavior of the epoxy resin and the influence of temperature on the fluidity of the resin/filler system. After curing we will study the distribution and morphology of the filler in the matrix.

2. Materials and Methods

2.1. Materials

The epoxy resin [diglycidyl ether of bisphenol A (DGEBA)] with a density (ISO 758): 1.1 ± 0.05 and an epoxy equivalent weight of 171 g.eq\(^{-1}\). Infrared absorption spectroscopy (IR) provides very valuable information about the chemical structure of the compositions. Besides, IR is available especially for the cross-linking analysis, and it has been used for the estimation of both epoxy and hydroxyl functional groups in polymeric materials [9-11]. Aliphatic amines are well known quenchers of the aromatic hydrocarbons. It has been reported that the quenching of the fluorescence of the aromatic hydrocarbons by aliphatic amines increase with electron-donating ability of the amine groups [12]. In FT-IR spectra (Fig. 1), peaks at 890 cm\(^{-1}\) to 910 cm\(^{-1}\) are attributed to an epoxy group. A hydroxyl group is indicated by a broad band at 4000 cm\(^{-1}\).

![Figure 1. Fourier transform infrared spectroscopy spectra of resin DGEBA.](image)

We use in our study the Algerian slag of the metallurgical plant of El Hadjar, Annaba. Currently the two blast furnaces of the plant produce 400 000 t/year of slag of which 20 % is crushed the rest is granulated. Blast furnace slag, or ground slag as he would like to call it, is a by-product of the manufacture of cast iron that has been cooled down by sprinkling with water, and is a hydraulic material when it is activated. It is in the form of nodules whose chemical composition includes calcium oxide in proportions of the order of 35 to 50%, silica, between 25 to 40% of lime and magnesia and up to 12% of other oxides in very small quantities (Table1).

| Components  | SiO\(_2\) | CaO | MgO | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | MgO | SO\(_3\) | Na\(_2\)O |
|-------------|----------|-----|-----|----------------|----------------|-----|--------|---------|
| Content (%) | 51.69    | 28.77 | 4.7 | 7.0            | 1.41           | 5.93 | 0.15   | 0.1     |
The particle size distribution shown in Fig. 2 shows that a large part of the particles has a diameter between 5 μm is between 4 μm and 5 μm as well as two other peaks, one at 0.5 μm and the other at 11 μm. This is due to the humidity and the strong reactivity with the slag during sieving caused by the presence of CaO in large quantities. The Scanning Electron Microscope (SEM) photograph and particle size analysis shown that the filler of BFS present nodules with a porous aspect due to the water vapor trapped during the quenching, we will take into account its influence on the workability, with the high specific surface area, determined using the BET method, value of 24.1 m².g⁻¹.

![Figure 2. Particles size distribution of blast furnace slag](image)

![Figure 3. SEM micrographs of blast furnace slag](image)

2.2. Methods
The rheological behavior was studied on the Haake VT500 viscometer, which allowed us to impose a shear rate of 0 to 550 s⁻¹ with a test temperature of 23 °C. The results of this study show the evolution of shear stress (τ) and apparent viscosity (η) as a function of shear rate.

2.3. Sample preparation
To study the rheological behavior of the elaborated matrices we used a total mass of 30 g composed of 2% by weight of diluent. The different percentages of the fillers are presented in table 2.

| Diluent | 2% Diluent =0.6g |
|---------|------------------|
| Control | 0.6g Diluant     |
| Rate    | %                |
|         | 10               |
|         | 20               |
|         | 30               |
|         | 40               |
|         | 50               |
| DGEBA/ %wt BFS | 2.94 | 5.88 | 8.82 | 11.76 | 14.7 |

3. Results and discussions

3.1. Chemical composition
Infrared spectroscopy has been widely used for the characterization of organic compounds and many reference libraries of spectra can be found easily. Qualitative and quantitative information can be obtained by this technique, although its use in epoxy systems is rather limited due to the location and intensity of oxirane ring absorptions. Two characteristic oxirane ring absorptions are observed in the range between 4000 cm⁻¹ and 400 cm⁻¹. The first, at 915 cm⁻¹, is attributed to CO deformation of the oxirane group, although work by Dannenberg et al (1956) [13] has shown that this band does not correspond exclusively to this deformation, but also to another unknown process. The second band is located at about 3050 cm⁻¹ and is attributed to the tension of the methylene group of the CH epoxy ring. This band is not very useful, because its intensity is low and it is also very close to strong OH absorptions, but in weak polymerization of epoxy monomers can be used as a qualitative indicator of the presence of epoxy groups.
Figure 4. FTIR spectrum of the composite DGEBA/ %wt BFS

In the case of the composite with DGEBA / 35 wt% HF slag, the difference between the front view and the surface view is very visible where we find in Fig. 5.a, b. a very homogeneous morphology, the particles of the slag are surrounded by the epoxy matrix and do not separate as in the case of pozzolan.

Figure 5. SEM micrographs of the composite DGEBA/ %wt BFS
The surface of the sample shows more agglomeration of particles, the presence of moisture generated by the gypsum favors this type of phenomenon. These can influence the material characteristics and form microscopic defects in the form of nodules of (30μm).

According to some authors [14], the presence of water can be explained by the two-phase morphology of the epoxy networks (Figure 5): a dense, highly cross-linked phase (or micro-gel) is embedded in an inter-nodular matrix of lower cross-linking density. Steric hindrance in the highly cross-linked areas would be responsible for the inaccessibility of some sorption sites.

As in the case of the first composite, an identification of the two phases visible in fig. 5.b showed the presence of the small nodules of the mineral load rich in (Si and Ca with traces of Fe). The matrix and represented as the majority phase and given by the element C. The two phases presented are crystalline in their majority, the slag used in this study presents crystalline phases.

![Figure 6. EDS composite DGEBA/ %wt BFS](image)

3.2. Rheological behaviour of composite DGEBA/ %wt BFS

Rheological characterization of thermoset polymers is of great importance in understanding the fundamental nature of complex suspensions. The effect of filler distribution and size on the shaping of new epoxy-based materials requires a thorough understanding of the rheological behavior. A number of studies
have reported the rheological behavior of filled thermoplastic polymers [15-17]. But rheological studies on bisphenol-A diglycidyl ether (DGEBA) are limited. The aim of this study is to investigate the rheological behavior of DGEBA filled with silica-rich mineral powders. The viscosity and shear stress as a function of temperature and filler rate were investigated.

In this study, formulations were developed to test the best compositions with favorable rheological behavior for better processing of these matrices. The evolution of viscosity and shear stress of DGEBA resin filled at rates (10 to 50% wt%) with slag is shown in Fig. 7.

Fig. 7. shows the increase in stress and viscosity with increasing percentages wt% of filler. At 50% slag the rheogram marked a very large increase in viscosity at a low shear rate.

![Figure 7. Rheological behavior composite DGEBA/ %wt BFS.](image)

(a) Evolution of viscosity (\(\eta\)) as a function of shear rate - (b) Evolution of stress (\(\tau\)) as a function of shear rate

### 3.2.1. Rheological model

The Rheowine software of the viscometer, allowed us to identify a model and a rheological behavior of these resin blends. The obtained result confirmed that all the resin mixtures have a rheological behavior rheofluidifying and that their behavior follows the model of Ostwald de Waele [18], [19] described in the following relation (1):

\[
\tau = k \gamma^n
\]

\(\tau\) : Shear stress;
\(k\) : Constant of consistency;
\(\gamma\) : Shear rate;
\(n\) : Flow index.

The principle of the model is to consider that the flow index \(n\) and consistency \(K\) are not constants but vary with the shear rate [20].

According to this model, the value of the flow index \(n\) confirms the rheofluidizing behavior of these formulations. The apparent dynamic viscosity is then given by relation (2):

\[
\eta_a = \frac{\tau}{\gamma} = k\gamma^{n-1}
\]

Thus, if:
7

- $0 < n < 1$, The fluid is rheofluidic or pseudoplastic;
- $n = 1$, it is Newtonian;
- $n > 1$, it is rheo-thickening or dilating.

The Ostwald-de Waele, Carreau-Yassuda and Cross models represent behavior without threshold stress. In the case of "threshold fluids" we add the threshold stress ($\tau_0$). If the applied stress remains below this critical value ($\tau_0$), the material behaves like a solid. Otherwise, the material returns to the behavior of a fluid. The two most widely used models for characterizing threshold fluids are, respectively, the Bingham (1922) model [21] and the Herschel-Bulkley (1926) model [22], where $\eta_p$ is the plastic viscosity, $k$ is the consistency of the fluid and $n$ is the flow index. Both of these models are able to represent the rheological behavior of many fluids above the threshold stress. We note that many other models with different fitting parameters can be found in the literature [23-24]. We ourselves have proposed a model derived from the Herschel-Bulkley model to better represent both small and large deformations for threshold fluids such as clay suspensions [25].

This model is approximate since it is only valid in a shear range whose interval depends on the fluid itself. It omits the two Newtonian plateaus ($\eta_0$ and $\eta_\infty$) which are well modeled by the Carreau-Yasuda law. However, it models the behavior of polymer melts well over a wide range of the shear rate corresponding to typical values for plastic injection molding and is therefore frequently used in this field. Moreover, this model allows to compare the rheological behaviors of different fluids based on the physical indices it provides, in particular the consistency K in [Pa.s] which could summarize the rheological results of the studied mixtures. The value of K, which represents the viscosity at low shears, more precisely at $\gamma=1$ s$^{-1}$, would give an indication of the cohesive state between the components of a structured fluid.

4. Conclusion

The rheological behavior study of the composite on the basis of the formulations mentioned above has highlighted the convergences of the tested mineral filler, in spite of the differences in composition and use. First, we marked the evolution of the main rheological parameters such as plastic viscosity and shear stress. It is clear from the results obtained that the mineral filler significantly increases these rheological parameters. Compared to the samples without mineral filler (DGEBA), a 50% increase in shear stress and plastic viscosity was recorded for the DGEBA/5%wt BFS composite. This can be explained by the physical filling role played by the fillers on the one hand, and on the other hand, the particle size distribution of the fillers as well as their geometrical shapes which help enormously to densify the network. The Ostwald de Waele model is repeated on all the tested compositions and confirms the rheological rheofluidifying behavior of this type of composite.

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