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Rheological Behavior of the Epoxy Resin Loaded with the Pozzolan

Irekti Amar[1], Hami Brahim, Aribi Chouaib, Bezzazi Boudjema[1] and Briki Ibtissem[2]

1. Research Unit: Materials, Processes and Environment, University M'Hamed Bougara, Frantz Fanon City, 35000 Boumerdes Algeria

2. Institute of Electrical and Electronic Engineering, University M'Hamed Bougara, Frantz Fanon City, 35000 Boumerdes Algeria

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Abstract: The study is to synthesize composite materials with news formulations of thermosetting matrices by the incorporation of 40% of mineral fillers to reduce the cost of composite materials and to improve implementation by increasing the viscosity and reducing the withdrawal to its minimum value. The mineral filler increases significantly in rheological parameters, whatever it nature of the mineral filler. Compared to the control without charges, an increase of 60% of the shear stress and that of plastic viscosity were recorded for the epoxy resin. The software Rheowine viscometer enabled us to model and identified the rheological behavior of these mixtures with resin. The results obtained in this modeling, confirmed that the resin mixtures have shear-thinning rheological behavior, this last allows the model of the Ostwald de Waele.

Key words: Composite materials, mineral fillers, rheology, shear rate, shear stress.

1. Introduction

In the development of composites materials, the matrix acts as a binder of different reinforcements can distribute the stress, provide good resistance to chemical structure and the desired shape to the final product. But there are still some drawbacks that arise in the physicochemical and mechanical properties of thermosetting matrices.

The thermosetting matrix materials are most common in composite applications [1]. In this type of polymers, the molecules are chemically linked, forming a three-dimensional network. Treatment can be done by applying heat or a chemical reaction [2].

The loads are used in polymers for a variety of reasons, to reduce cost, improve processing, density control, thermal conductivity, thermal expansion, electrical and magnetic properties, flame retardancy and to improve the mechanical properties [3].

Corresponding author: Irekti Amar, PhD student, research field: materials science. E-mail: irekti@live.fr.

Each type of charge has different properties depending on particle size, shape and surface chemistry [4-6]. The most charges used in thermosetting resins are calcium carbonate; kaolin and alumina hydrate [7].

The other commonly used fillers include clay, carbon black, and the microspheres of mica, silica, and glass [8].

In general, fillers can change the performance of polymer compounds by changing the color, viscosity, barrier properties, processing rate, the electrical and thermal properties, surface finish, shrinkage [9- 15].

According to the work of Thai-Hung LE [16] we classify the means for measuring the viscosity into two categories:

The first category present the conditions close to the industrial process injection. They are made with capillary rheometers or nozzles rheological; they can also be made by trying the ‘squeeze flow’ with a lesser extent.

In the second category, we can find other mechanical testing used to characterize the filled resins; these tests are used on cone-plate rheometer or simple compression tests.

They are homogeneous tests that do not require prior knowledge of the law of flow of the material tested.

Rheological testing of mixtures prepared is made on the cone-plate viscometer or the sample undergoes a shear in the conical space between the plane and the cone. The geometry of the cone, package-ensures constant velocity gradient throughout the volume.

The rheograms obtained, represents the evolution of the shear stress as a function of shear rate of resin mixtures containing 40% of mineral filler (pozzolan).

2. Materials and Methods

2.1 Materials Used

2.1.1 Epoxy Resin

In the work, the MEDAPOXY STR of the company Granitex was used: They are known for their high performance and best qualities.

2.1.2 Calcium Carbonate

For this study, the calcite accelerated a rhombohedral crystal lattice which was used with a weight of 5%, in order to ease implementation and increase flexural modulus. The characteristics of the calcite used are presented in Table 1.

2.1.3 Pozzolan

Algeria has a significant amount of pozzolanic material of volcanic origin, which stretches along 160 km between the Algerian-Moroccan border and the Sahel of Oran, this natural product, is a siliceous volcanic rock ranging from red to black, the studies and industrial tests have shown the importance and usefulness of this product in several areas.

2.2 Geometric Shape of Particles

The particles have different shapes: spherical, chipped and angular. Those different geometric shapes depend on the nature of the charges and their mode to obtain. As shown in Fig. 1. The pozzolan particles have spherical and less angular form.

The addition of the load increases the aesthetic properties of the resin matrix which appears transparent to light yellow tints with the addition of particles it is possible to change the color of the composite. The fillers can be transparent.

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2.3 Preparation of Material

The manufacturing protocol is identical to the one used for industrials. It is described by the supplier Granitex. To observe the effects of interfaces epoxy/fillers, the spiked samples are formulated.

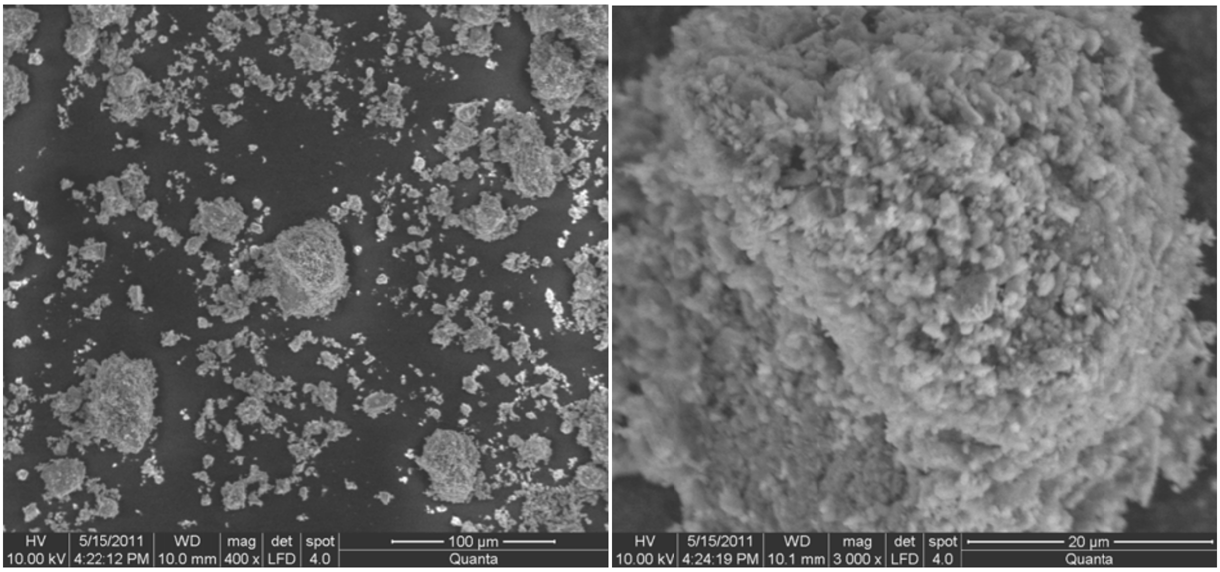
One day before the casting, the amount of charge needed to charge the samples was weighed and placed in an oven at 80 °C in order to dry. Two hours before, the resin and hardener were weighed and placed in an oven at 80 °C in order to precondition the material. The two quantities are mixed for 15 minutes in a mixer preheated to 60 °C under vacuum for degassing of the material and the elimination of bubbles formed during the mixing phase. The charge is incorporated in the mixture according to the compositions shown in Table 3.

Table 1 The calcite characteristics.

Purity (%)	99.9
Density (kg/m^3)	2,710
Melting temperature (°C)	1,339
Hardness on the Mohs scale	3
Refractive index	1.48-1.65

Table 2 Chemical analysis of natural pozzolan.

Components	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3	Total
Rate (%)	45.67	8.98	3.45	15.10	10.14	0.50	0.68	0.19	84.73



(a) (b)

Fig. 1 SEM images of pozzolan particles.

Table 3 Formulations of the composites.

Components		Size	Formulations MPC (Matrice, Pozzolan, $CaCO_3$)
			Rate %
	Resin	-	40
	hardener	-	20
Matrice	Pozzolana	< 100 µm	35
	$CaCO_3$	< 20 µm	5

2.4 Equipment

The rheology is important for better development of composite parts [11, 14]. In this work, the mixture prepared based on the inorganic filler are tested to see the influence of pozzolan on the rheological behavior of the mixture which compare well with the pure resin, the shear stress and viscosity are parameters studied under conditions of normal temperature and pressure.

For testing, we used the device viscometer Haake VT500 cone shown in the Fig. 2.

The sample undergoes a shear in the space between the plane and the cone. The geometry of the plane-cone ensures constant velocity gradient over the entire space provided it is in contact. In addition, it should use only cones whose angle is between 0.5° and 4°.

A high velocity gradient on a small sample volume leads inevitably frictional heating, causing in turn a lowering the viscosity. If this phenomenon occurs in an exaggerated way, it is recommended to capture the flow curve point by point. This procedure is to remain at a constant speed for brief periods. The stops between the measuring points can each return to the right temperature.

3. Results and Discussion

The Fig. 3 shows the evolution of the main rheological parameters such as the plastic viscosity and shear stress as a function of shear rate of the unfilled resin and loaded with 40% of pozzolanic powder.

Clearly from these results, the inorganic filler increases the rheological parameters considerably. Compared to the control without mineral powder (Resin without load), an increase of 10% of the shear stress and of the plastic viscosity were recorded for the composite (MPC). This is explained in first part by the physical role provoked by the fill pozzolan.

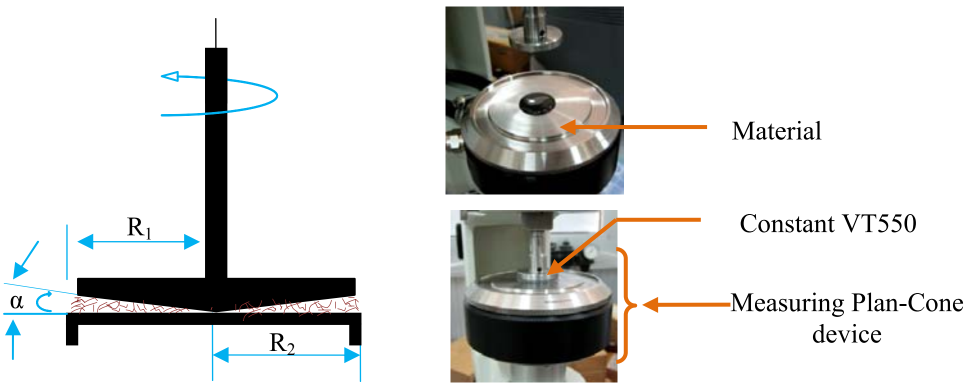


Fig. 2 Viscometer Haake VT500.

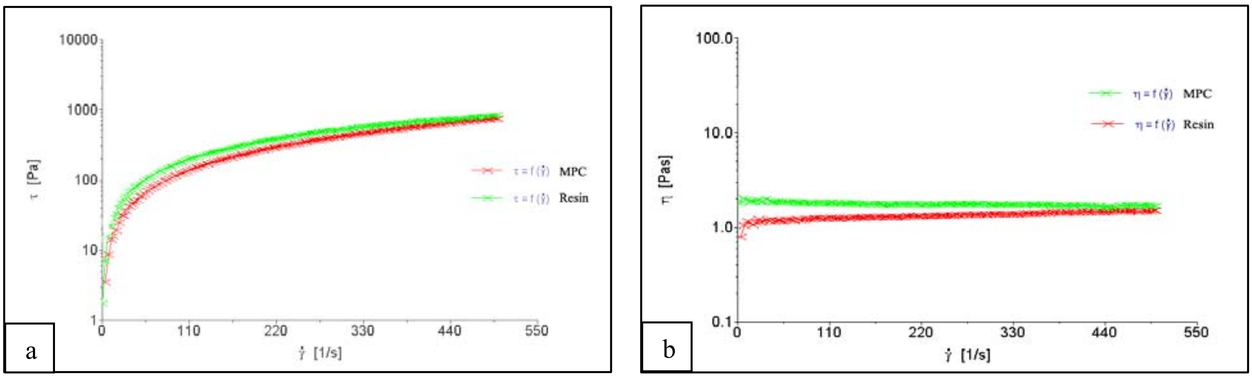


Fig. 3 Rheological behavior of matrices studied (a) evolution of shear stress as a function of shear rate, (b) evolution of the viscosity versus shear rate.

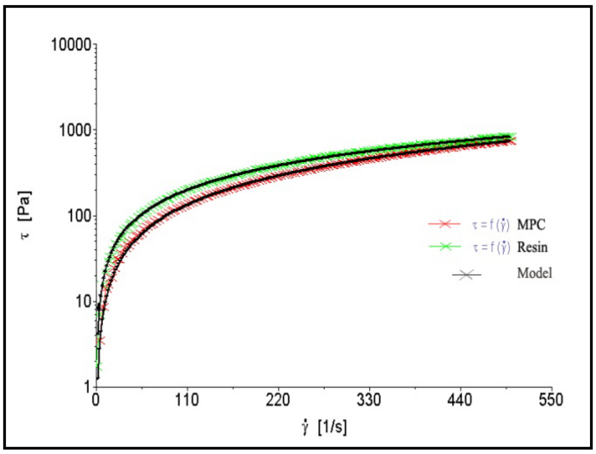


Fig. 4 Model of the evolution of shear stress as a function of shear rate.

In the second part, the finer mineral filler penetrates in the chains of the resin causing a densification of the network.

SEM images (Fig. 5) is taken on resins with/without 40% mineral. This shows the densification of the network of the resin and powder used and also shows an even distribution of load over the entire volume of the sample.

3.1 Identification of the Rheological Behavior

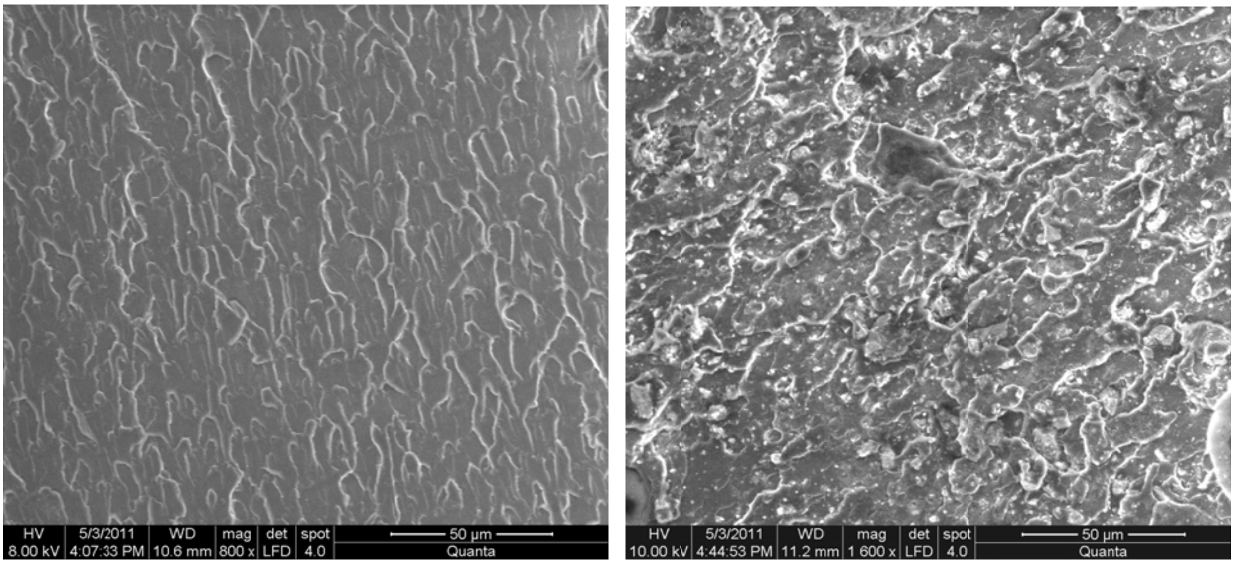
The Rheowine software of the viscometer, allowed us to identify a model and rheological behavior of these mixtures of resin.

The result of this modeling Fig. 4, confirmed that all resin mixtures have a shear thinning rheological behavior and this behavior follows the Ostwald-de Waele model described in Eq. (1) where the shear of stress (τ) is proportional to the constant consistency (k), shear rate (γ) and flow index (n).

$$\tau = \mathrm{K} \cdot \dot{\gamma}^{n} \quad (1)$$

The results were verified by the model given by Gibson and Williamson [17] and Gulino [18].

According to these results, the value of the flow index (n) obtained showed that these resins have shear thinning behavior.



(a) (b)

Fig. 5 SEM images of samples used (a) resin, (b) composite MPC.

4. Effect of Mineral Filler

The rheological test results obtained by the filled resin clearly show the effect of the nature of the powder on the rheological properties of the resin. The increase in shear stress and viscosity is about 10% compared to the control without mineral filler. This is partly due to the external morphology of the pozzolana grains. This difference lies in the grain outer shape that can be spherical Fig. 1 and else to the presence of some finer further increasing these properties.

The morphology of the epoxy resins was not yet fully understood but they are described in the literature as inhomogeneous [19]. This assertion is based on SEM observations of fracture surfaces of epoxy networks Fig. 5a.

They reveal the presence of a nodular morphology within a size range of 10 to 100 nm. The nodules are supposed to be sites of increased cross linking density.

The SEM image shown in Fig. 5b confirms the description of spherical nodules of pozzolana highly cross-linked of matrix in which the cross linking density is lower. It shows that this type of charge with the shear rate applied can cause a heterogeneous distribution of the cross linking density, this feature explains the role of this charge of a hydrophilic surface in the large increase in viscosity and decrease withdrawal. The inhomogeneities can also be formed by a possible phase separation during the conversion or when the monomers react together, there is a competition between the reactive groups and the formation of clusters by the hard charging and mixing of the resin with a high density [19, 20].

5. Conclusions

The results of our study showed convergence behavior of the load test. The rheological test results obtained by the filled resin clearly show the effect of the nature of the powder on these properties. The increase in shear stress and viscosity is about 10% compared to the control without mineral filler. This is partly due to the external morphology of the pozzolana grains (this difference lies in the grain outer shape that can be spherical) and partly to the presence of some finer which increasing further these properties.

With increasing of shear rate, a slight increase in temperature is noticed and reduced the viscosity depending on Ostwald-de Waele model, this property provides the structural and physical benefits for this material. Moreover, the resulting composite has the properties dielectric, thermal and mechanical remarkable [20]. The latter give the composite a large number of applications some of them are of a high technological level.

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