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FTIR Analysis and Rheological Behavior of Bisphenol: A Diglycidyl Ether Resin Filled Fume-Silica

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Abstract: Silica-fume as fillers into polymers materials affect significantly the physical, mechanical and the electrical properties of the polymers. The polymer that we studied here is an epoxy based resin (STR) and silica fume (FS). This paper presents the dependency of the rheological behavior of the STR epoxy resin on the FS content within a temperature at which the reaction thermoset is neglected. We used a cone-plate viscometer for the study of the rheological behavior, and a scanning electron microscope is used for the analysis of the dispersion state of the FS in STR epoxy resin. Compared to the control without loads, an increase of 50% of the shear stress and the plastic viscosity were recorded for the composite. 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 give us the model of Ostwald de Waele.

Key words: FTIR, rheology, fume silica, STR Epoxy resin, shear rate, shear stress.

1. Introduction

As a filler for polymer nanocomposites, nanofillers rich in SiO_2, which have small dimensions and high aspect ratios, have received much attention as materials with potential for use in many applications due to their remarkable physical, chemical, and electrical properties [1, 2]. Nanocomposites and reinforced polymer nanocomposites have been shown to improve their rheological, electrical and thermal properties [3-5].

Epoxy resins are very convenient polymer materials because of their good mechanical, thermal, and electrical properties [1]. Due to their high performance the epoxy resins are widely used in the composite and coating industries [2].

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

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 [9-14].

According to the study of Thai-Hung Le [15], we classify the means for measuring the viscosity into two categories: the first category presents, the conditions close to industrial process injection. They are made with capillary rheometers or nozzles rheological or even, to a lesser extent, trying the "squeeze flow". In the second category one can find other mechanical testing used to characterize the filled

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resins, these are tests 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 4% to 24% of mineral filler (silica fume).

2. Experiments

2.1 Materials and Methods

2.1 Materials

2.1.1 Epoxy Resin

The STR Epoxy resin provided by Granitex company, whose basic components toichiometric mixture of epoxides and amines) are first mixed and degassed.

2.1.2 Fume Silica

In this study, we used silica fume as mineral filler in the resin to improve its rheological behavior.

Silica fume is a by-product from the manufacture of silicon, ferrosilicon alloys different or zirconia. From a chemical standpoint, the fume silica is mainly composed of silicon oxide (Table 1).

Silica fume is composed primarily of pure silica in non-crystalline form. X-ray diffraction analysis of silica fumes reveals that material is essentially vitreous silica, mainly of cristobalite form. Silica fume has a very high content of amorphous silicon dioxide and consists of very fine spherical particles. Silica fume generally contains more than 92% SiO_2 (Table. 1).

The very particular characteristics of fume silica make a highly reactive powder due to its high silica content of the amorphous state and its extreme thinness. The beneficial effects of silica fume on the microstructure and mechanical properties of the resin are mainly due to the ability to react with the polymer chains and particular the physical effect of silica fume such as filler effect. Both effects lead to both a significant increase in density and improved mechanical strength. The density of silica fume is usually 2.2, but also a little higher when the silica content is lower. It is more dense than the density of the resin (1.15).

This product is present in the form of an ultra-fine powder or light gray. When considering the properties of the epoxy resin to silica fume, it is important to keep in minds that using these two ways:

- As substituted resin, to reduce the amount of resin used, usually for reasons of economy;
- As addition, to improve the rheological properties of the resin.

Fig. 1 shows the distribution of grain sizes after sifting.

The morphology of the FS is shown in Fig. 2 the fumed silica particles are in the form of spheres having diameters of between 0.03 μm and 25 μm (average diameter of the usual lying below 0.1 μm).

2.1.3 Formulations and Load Distribution in Matrix

Distributions and orientations of loads in epoxy resin strongly influence the size and structure of the final network samples. Control and understanding are key issues for improving the properties of this type of epoxy resins and may also cause deformation of the surface and thus affect the final quality of the samples.

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

Table 1 Chemical composition of fume silica.

Components	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	PF
Rate (%)	92.3	0.10	0.20	1.0	2.90	1.30	0.90	1.20

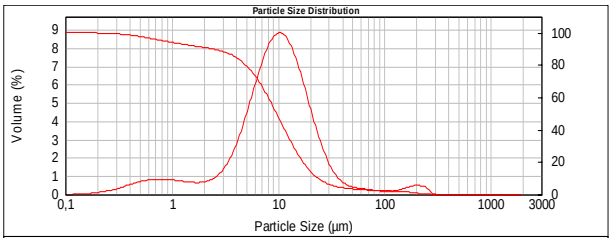


Fig. 1 Distribution of grain sizes of fume silica.

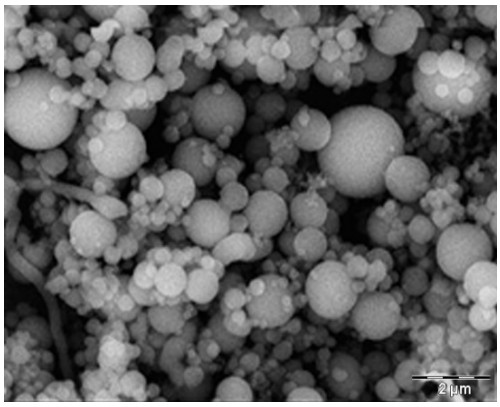


Fig. 2 SEM EDXS Photography fume silica at 2 µm.

One day before the casting, the Amount of charge needed to load 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 two quantities are mixed for 15 min in a mixer preheated to 60 °C under vacuum for degassing of the material and the elimination of bubbles formed falling on the mixing phase. The load is incorporated in the mixture According to the compositions shown in Table 2.

The morphology of the developed matrices we see that the particles are spherical and form a cluster for the weight percentage of 3% of the load (Fig. 3) and has an approximation due to the grain in the percentage compact structure weight of 0.5% silica fume, an average load distribution is observed by cons there is a good load distribution for 6% silica fume.

It follows that the higher the percentage of the load increases over the distribution of the grains is improved.

The Infrared Spectroscopic (FTIR) analysis (Fig. 4) was performed in order to identify new groups, new chemical bonds formed during the reaction of nano-matrices with their reinforcements. The results are shown in Table 3.

We observed the appearance of new groups due to the attraction between molecules of the resin and particulate fillers, which have had their specific surface area increase after fine grinding, which facilitates impregnation of nano-reinforcement in the organic matrix, there are a few peaks with remarkable intensity.

The characteristic absorptions of the different existing between the anions and cations of the mixture are, for example strips nanocomposites; C-Cl, Fe^{3+}-OH-Mg, Al-Mg-OH.

The spectra of pure resin has 3 remarkable absorption bands on the elongation of O-linked H bond located to 3,432.15 cm^{-1}, a C-O elongation ether to 1,240 cm^{-1} and to the last 1,511 cm^{-1} for the links = CH and C = C.

2.2 Measurement and Characterization of Composites

2.2.1 Rheological Properties

We have seen in this work, the mixtures selected in order to discern the influence of different loads with their size on the rheological behavior of the mixture and to compare to that of the pure resin. The shear stress and viscosity are parameters studied at normal temperature and pressure conditions.

Table 2 Formulation of samples tested.

Components		Formulations						
		Resin	Rfs1	Rfs2	Rfs3	Rfs4	Rfs5	Rfs6
		Rate %						
Matrix	Resin	33.33	67 .76	64.13	60.87	56.90	53.34	49.80
	Hardener	66.67	28.23	27.86	27.12	27.09	26.64	26.18
Laod	Fume silica (FS)	00	4	8	12	16	20	24

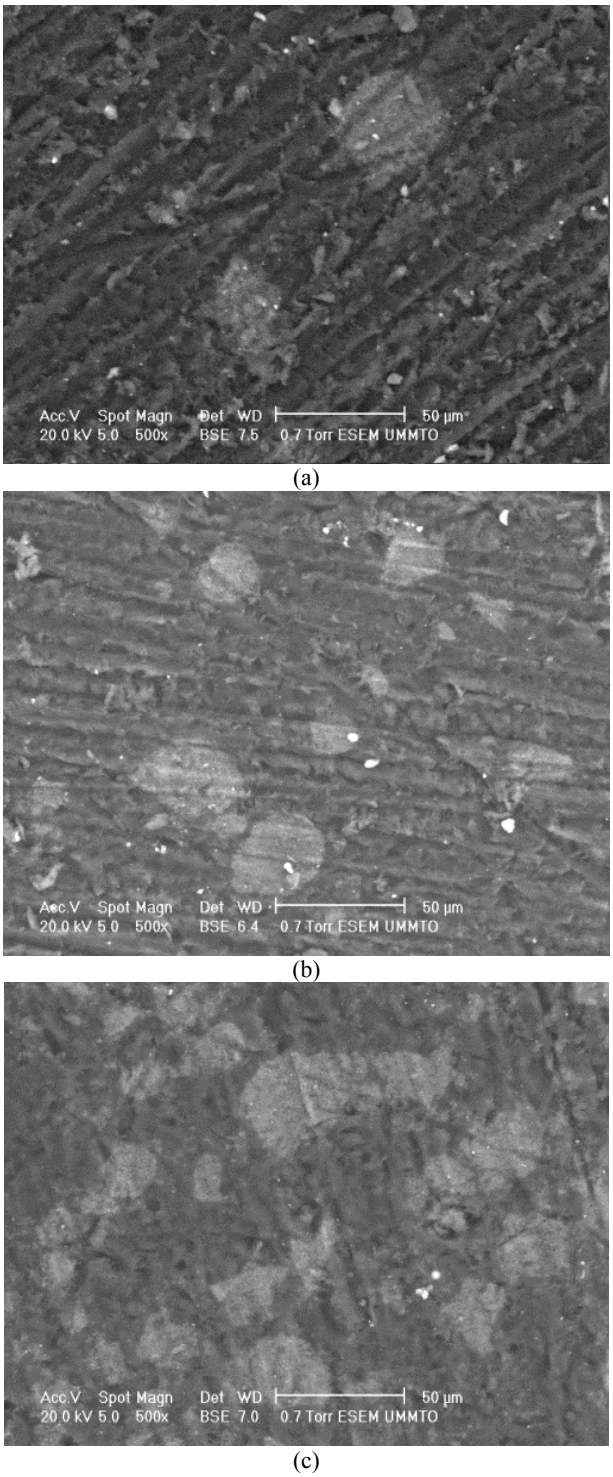


Fig. 3 SEM image of (50 µm) for wt % (a) Rfs1, (b) Rfs2 and (c) Rfs3.

2.2.2 Measuring Dispositive

The rheology is significant for better development of composite parts [16, 17]. In our work, the mixture prepared based on the inorganic filler are tested to see the effect of silica fume on the rheological behavior of the mixture All which compares well with the pure resin.

For testing, we used the device viscometer Haake VT500 shown in the Fig. 5.

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

A high velocity gradient in a small sample volume leads inevitably to frictional heating, causing has in turn lowering the viscosity. If this phenomenon occurs in an exaggerated way, it is recommended to capture the flow curve item by item. 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.

The hydrostatic pressure is neglected and the systemtemperature is not taken into account.

3. Results and Discussion

The study of the rheological behavior was performed on the viscometer Haake VT500, that allowed us to impose a shear rate from 0 to 550 s^{-1} with a test temperature of 23 °C. The results of this study show the evolution of the shear stress (τ) and apparent viscosity (η) as a function of shear rate.

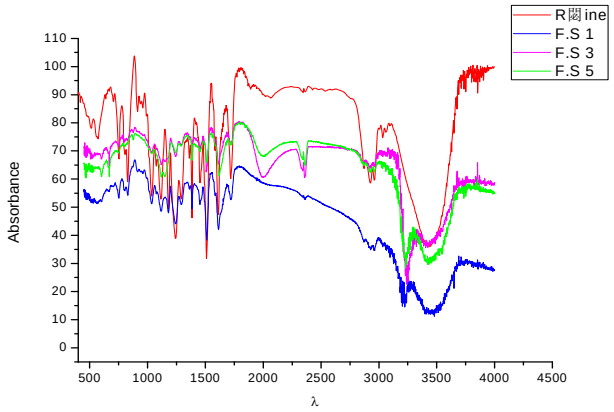


Fig. 4 FTIR spectra obtained over a wavenumber range between 500 and 4,000 cm^{-1} for the dry surfaces of the nanocomposite Rfs.

Table 3 FTIR Results of the pure resin, fumed silica and pure nanocomposites 0.5%, 3% and 6% of FS.

	Band (cm^{-1})		
Assignment	F.S wt 0.5%	F.S wt 3%	F.S wt 6%
Stretching OH	3,332.56; 3,216.28	3,251.34	3,254.52
Stretching H_2O	3,332.56	3,480	-
Fe^{3+}- OH-Mg	747.832	831.331	746.073
Stretching C-H	1,714.94; 1,967.1	1,995.43; 1,726.54	1,998.71; 1,723.26
Stretching C=C	1,511.95; 1,614.94	1,513.39; 1,615	1,611.77; 1,513.39
Stretching C-O	1249.49	1,241.22	1,241.22
Si- O	1,036.87; 565.107	1,037.92	1,110.06
Al- OH-Mg	-	831.331	828.052
Stretching Si-O-Al	565.107	-	-

Measuring Plan-Cone device

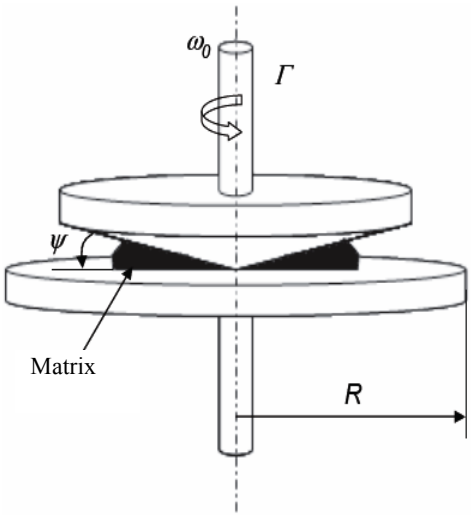


Fig. 5 Viscometer Haake VT500.

3.1 Influence of Silica Fume on the Rheological Behavior of Epoxy Resin

The Fig. 6 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 different rates of silica fume.

According the Fig. 1b, the mesh formed by the particles of silica fume gene the mobility of resin components in a single flow, thus increasing the strain with the filler content.

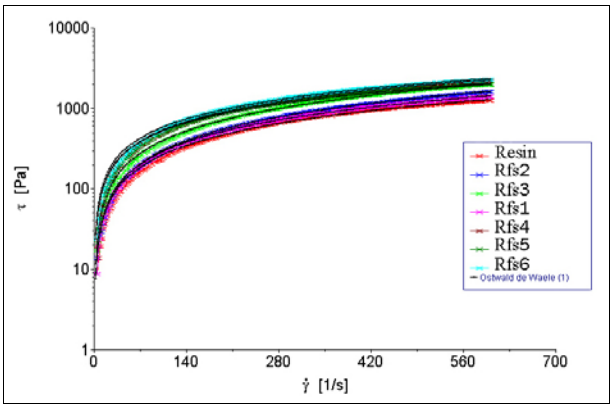
The viscosities at infinite shear rate for a resin mixture at a given temperature can be considered equal to the viscosity of the matrix and Rfs1 Rfs2 this test temperature. For above 23 °C the viscosity follows a behavior type Arrhenius. The viscosity η is shown in (Fig. 6b).

The curves in Fig. 7a show the evolution of the shear stress as a function of shear rate. It was found that the rate plays an important role in increasing the shear stress, and note that when the rate of silica fume increases the shear stress increases in parallel and has a better rheological behavior by contribution those other loads.

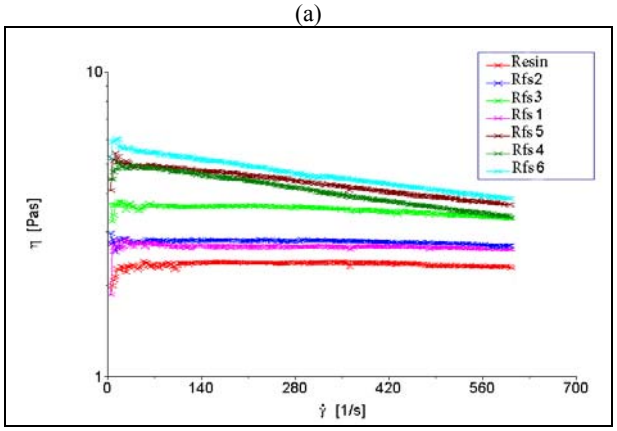
All that has been classified the matrix as such is an elastic Newtonian fluid, wherein the flow setting is delayed by elastic effects: in a first time, a portion of the applied mechanical energy is gradually stored in the fluid form elastic energy is what entails a stress relaxation to its equilibrium value.

Whatever the filler concentration, the viscosity of the resin is lower than that of matrices. The difference in viscosity, insignificant for concentrations below 8%.

In Fig. 6b, we observe that the evolution of the viscosity of the resin according to different shear rates. At above 20% the viscosity decrease of load it is



(a)



(b)

Fig. 6 Rheological behavior of matrices studied. (a) Evolution of shear stress as a function of shear rate; (b) Evolution of the viscosity versus shear rate.

explained by the increase in temperature of the mixture due to friction between particles under the effect of shear rate.

3.2 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. 6a), 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 **(γ̇)** and flow index (n).

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

The results were verified by the model given by Gibson and Williamson [18] and Gulino [19].

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

3.3 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 silica fume. This difference lies in the grain outer shape that can be spherical Fig. 1b and else to the presence of some finer filler 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. 7.

They reveal the presence of a nodular morphology within a size range of 10 to 20 nm. The nodules are supposed to be sites of increased cross linking density.

The SEM image shown in Fig. 7 confirms the description of spherical nodules of fume silica 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

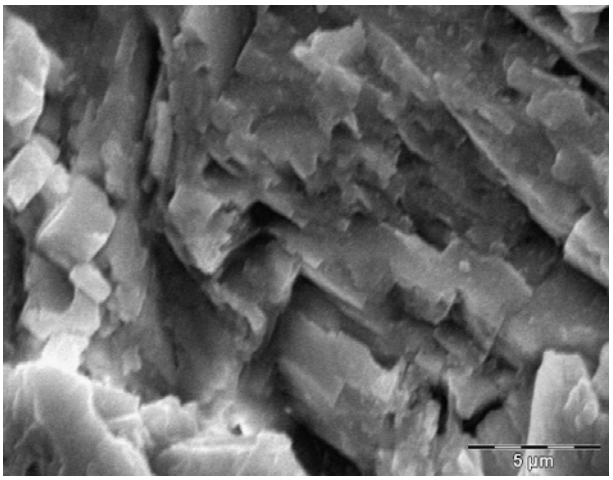


Fig. 7 SEM image of fracture surface of samples used Rfs5.

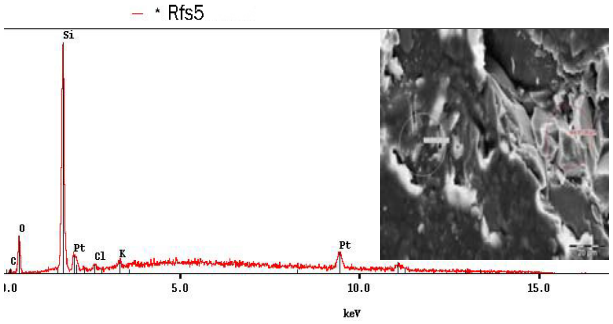


Fig. 8 EDS analysis of the composite Rfs5.

in the large increase in viscosity and decrease withdrawal. The inhomogeneity can also be formed by a possible phase separation during the conversion or when the monomers react together (Fig. 7), 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 [20, 21].

The Fig. 8 shown the EDS analysis of the composite Rfs5 showed that the number of the clippings bond is lower in the presence of silica in the curing of the resin. These observations are explained by a screening effect and interactions between chemical species formed and the reactive functions in silica surface.

4. Conclusions

The flow of the resin at ambient temperature 23 °C is significantly influenced by the concentration of silica fume. The mixtures are modeled with a law Ostwald-de Waele (Eq. (1)). The parameters are adjusted for each concentration of FS.

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 kind of the powder on properties thesis. 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 silica fume grains (this difference lies in the outer grain shape that can be spherical) and partly to the presence of some finer fillers all which Increasing further these properties.

With Increasing of shear rate, a slight Increase in temperature is noticed and Reduce 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 dielectric properties, thermal and mechanical remarkable [22, 23]. The lathing give for the composite a wide number of applications, some are of a high technological level.

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