



Viscosity measurements of epoxy resin filled with ferrite powders

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ABSTRACT

Purpose: The goal of this work was to determine influence of fillers on viscosity, especially of six mixtures that contain different amount of ferrite powder. It was made in order to find out an effect of introduced ferrite powder on epoxy resin processing conditions and parameters. Additionally viscosity of pure epoxy resin was determined for reference purposes. The influence of temperature on composites viscosity was also examined.

Design/methodology/approach: Viscosity of mixtures based on epoxy resin that contain ferrite powders and pure epoxy resin using Hoeppler viscometer was measured. Procedures of viscosity measurements were performed for three temperatures and for three filler contents.

Findings: Higher temperature of measurement resulted in lower values of viscosity while higher quantity of ferrite powder increased viscosity of mixtures. There was no difference between results of viscosity that were obtained for barium ferrite and strontium ferrite.

Research limitations/implications: The main problem of this work was limitations of research method. Mixtures before measurement had to be put to the vacuum venting in order to remove air bubbles that were introduced through mixing. Also an amount of powder introduced into the matrix was limited because for higher contents it was not possible to pour mixtures into glass pipe of measurement device.

Practical implications: Applied method allowed to determine the influence of temperature, kind and quantity of filler on viscosity. Viscosity is the main factor defining processing parameters in many processing technologies.

Originality/value: Results of viscosity for searched composites are not known up till now. Achieved results are planned in order to use them in future works of authors on polymeric magnetic composites.

Keywords: Polymers; Viscosity; Hoeppler viscometer

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MATERIALS

1. Introduction

Addition of fillers into polymer materials is a common industrial practice. Fillers can change properties of composites and create new materials. Filler materials, filler volume fraction, filler size and shape, size distribution and interactions between

matrix and filler, and finally interactions between solid particles affect mechanical and rheological properties of filled polymer composite [1-5].

An important rheological property of fluids is viscosity. Physical system and application as diverse as fluid flow in pipes, lubrication of engine parts, volcanic eruptions, planetary and

stellar magnetic field generation, all involve fluid flow and are controlled to some degree by fluid viscosity [6].

Viscosity is a fundamentally rheological parameter of macromolecular compounds (polymer) properties that defines resistance to flow and is related to the characteristics of composite materials widely used in many field of industry. The knowledge of viscosity can help to characterize polymers and to determine indirectly molecular mass. Liquid viscosity is important for calculation of the power requirements for the basic operations such as mixing, pipeline design, pump characteristics, storage, injection moulding, and transportation [7]. In processing technologies of polymeric materials viscosity is the most important technological characteristic.

The term of viscosity is defined as the measure of internal friction of a liquid. That property, related to molecular structure of a fluid, enables it to support tangential stresses for a finite time and thus to resist deformation. Viscosity is defined as the ratio of shear stress divided by velocity gradient (shear rate). In other words viscosity is a measure of the internal friction within a fluid. The time required for a liquid to drain out of a capillary tube is directly proportional to its viscosity. This resistance acts against the motion of any solid object through the fluid. In practice the viscosity of a fluid usually manifests itself as a resistance to flow, both in liquids and gases but at a much lower level in gases. The SI unit of viscosity is the Pascal times second [Pa s] but also in poise [P]. Ten poise equal one Pascal times second [1,7,8].

There are known two kinds of viscosity: dynamic viscosity and kinematic viscosity. Dynamic viscosity is used to characterize liquid products for example molten polymers (1).

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (1)$$

where: η – dynamic viscosity, $\dot{\gamma}$ – shear rate, τ – shear stress.

While kinematic viscosity is a measure of the resistance to flow of a fluid under the influence of gravity. The SI unit of kinematic viscosity (2) is the square meter per second [m²/s]. A more common unit of kinematic viscosity is the square centimetre per second [cm²/s], which is given the name stokes [St] after the Irish mathematician and physicist George Gabriel Stokes (1819-1903). Even this unit is also a bit too large and so the most common unit is probably the square millimetre per second [mm²/s] or centistokes [cSt].

$$\nu = \frac{\eta}{\rho} \quad (2)$$

where: ν – kinematic viscosity [m²s⁻¹], η – dynamic viscosity [Nsm⁻²], ρ – density [kgm⁻³].

Viscosity is the only parameter used to reological characterization for some class of materials that are named Newtonian liquids.

Authors measured the viscosity of compounds with different content of fillers in order to design and control technological process and properties of composites in the future works with functionally gradient materials. The knowledge about viscosity results is important for melts and solutions used for many advanced application by appropriate connection two or more materials in order to obtain better properties [9].

An important problem in creating polymer composites, especially Functionally Graded Materials (FGMs), is production of filled materials based on polymeric resins [10-12]. Epoxy

resins characterize by rather high viscosity that makes problems with introduction of filler in high quantity. For that reason the influence of filler on viscosity is important.

There are known many theories that concentrate on this problem. First conception is known as Einstein theory and concern fluid viscosity with spherical form of particles [1,14] (3):

$$\eta_r = \frac{\eta_s}{\eta_0} = 1 + 2.5\varphi \quad (3)$$

where: η_r – relative viscosity, η_s – dispersion viscosity, η_0 – fluid viscosity without filler, φ – volume content of filler.

This formula is used only for dispersions with low quantity of filler, which are non-interacting. Additionally Einstein assumed that solid particles are mono-dispersed buoyant spheres dispersed in Newtonian fluid.

Later some authors proposed different values of proportionality coefficient, other than 2.5. Depending on particles concentration, particles shape and size, depending on fluid rheological nature, proportionality coefficient differs in range from 1.5 to 5.5. In addition many formulas based on Einstein formula were arisen [5,13].

Generalization of all formulas in polynomial form that concern dispersion viscosity as a function of concentration $\eta(\varphi)$ proposed Thomas [13,14] (4):

$$\eta = \sum_{n=0} a_n \varphi^n \quad (4)$$

where: a_n – series coefficients.

The first term of the series a_0 (for $\varphi = 0$) equals the viscosity of the dispersion liquid $a_0 = \eta_0$. More comfortable in this case is formula for relative viscosity [13,14] (5):

$$\eta_{sp} = \frac{\eta_s - \eta_0}{\eta_0} = \sum_{n=1} b_n \varphi^n \quad (5)$$

The value of b_1 is equal 2.5 and is known from Einstein equation. While rest of coefficients are determined by experience. Thus, for $\varphi < 1$ $\eta_{sp} = 2.5\varphi$, i.e. the viscosity grows linearly with and increase in concentration, irrespective of a size of particles [13,14].

Another group of models based on idea of maximum quantity of filler. Maximum degree of filler loading (φ_m) depends on:

- shape and diameter of particles,
- scatter of diameter of particles,
- interaction between polymer – filler, and filler particles,
- flow conditions.

Value of maximum amount is from 0.52 to 0.74. The most of models for this group can be generalized by (6):

$$\eta_r = \frac{f(\varphi)}{(1 - \varphi_r)^p} \quad (6)$$

where: p – is a models parameter, while (7)

$$\varphi_r = \frac{\varphi}{\varphi_m} \quad (7)$$

Generalized concentration dependence of the viscosity, applying maximum concentration concept, can be written in the form (8):

$$\eta_{wz} = \sum c_n \varphi_r^n \quad (8)$$

where: c_n – parameter of models.

Maron and Pierce [15] proposed widely used formula for filled polymers melts (9):

$$\eta_r = \left(1 - \frac{\varphi}{A}\right)^{-2} \quad (9)$$

where: A – empirical constant.

Model of viscosity for filled polymers presents Steller [16] for any temperature, T , shear rate, $\dot{\gamma}$, and volumetric filler content, φ . His consideration starts from Doolittle equation [14] (10):

$$\ln \eta = A + B \frac{V_0}{V_f} = A + \theta \quad (10)$$

where: V_0 – occupied volume, V_f – free volume, A and B are material constants (independent of temperature, shear rate and volumetric filler content).

Steller received model that described viscosity in dependence on amount of filler, temperature and share rate (11):

$$\frac{\eta(\dot{\gamma}, T, \varphi)}{\eta_0} = \left[\frac{\eta(\dot{\gamma}, T_0, 0)}{\eta_0} \right]^{\alpha\beta} e^{[\theta_0(\alpha\beta-1)]} \quad (11)$$

where: T – temperature, T_0 – reference temperature, α and β are function of free volume in unfilled and filled polymer.

The quantities η_0 and θ_0 relate to the flow of the pure polymer at the temperature T_0 in the Newtonian flow region.

Until now the universal quotation do not exist despite the fact there are many formulas. Moreover to fully describe viscosity of filled polymeric melts there should be considered at least six conditions [14]:

- real fillers characterize scatter of particles diameter,
- particles shapes are other than spherical,
- molten polymers are Non-Newtonian liquids,
- molten polymers have flow limit (yield stress),
- during the flow of polymers slippage on the channel walls can appear,
- between polymer and filler surface occur mutual interactions.

2. Methods of viscosity measurements

Polymeric solutions, polymeric dispersions and polymer melts are rheologically characterized mainly by rheometry methods. Two basic rheometry techniques are used: capillary rheometry and rotational rheometry. Different methods of viscosity evaluation are used for paints, varnishes, dilute polymeric solutions and casting compounds. In the present research casting compounds were tested. Because of this viscosity measurement methods used for this class of fluids are shortly characterized. For these fluids viscosity measuring methods are called viscosimetry and used devices are called viscometers. There are known few different methods of viscosity measurements. The most often used are: Ford viscosity cup, Falling Ball Method (Hoeppler viscometer), Capillary Flow Method (Ostwald or Ubbelohde viscometer), Rotational Viscometer, Brookfield viscometer etc. [8,17-19].

Ford viscosity cup is a simple and quick but not precise gravity method, allowing to evaluate kinematic viscosity, used for characterization of liquid polymers (solutions), enamel products, Newtonian paints, lacquers etc. The results in this method are expressed in seconds of flow time. The cup method uses nozzles 3, 4, and 6 mm in diameter. The flow time for the liquid flow through opening is measured until the first stream cutting/break of liquid occur. Nozzle should be well matched to follow the

condition that the flow time should fall between 30 seconds to 100 seconds. It is possible to convert time of flow, t , into kinematic viscosity using the following formula (12):

$$\nu_i = At - B \quad (12)$$

where: i refers to the number of the cup, A and B are constants to be determined from viscosity measurements of the standard oil.

Zahn viscosity cup is used to determine viscosity of liquids like in earlier mentioned method. This method is similar to the Ford cup but with one difference, namely Zahn cup can be used to measure viscosity directly in tanks or containers, and for liquids that have viscosity from 20 to 1600 cSt in the range. Results of measurements are approximate.

Shell viscosity cup is measured like in previous methods but there are 8 size of cup.

Falling Ball Method makes use of the Stokes formula for the determination of viscosity of liquids by measuring the rate (time) of fall of a spherical body through the liquid. The frictional force T resisting the motion of a ball moving under the influence of gravitational force in a viscous medium is given by the Stokes equation of hydrodynamics as (13):

$$T = 6 \cdot \pi \cdot \mu \cdot v \cdot R \quad (13)$$

where: π – the coefficient of viscosity of the medium, μ – dynamic coefficient of viscosity, v – the velocity of a ball, R – the radius of the ball.

One of apparatuses applying falling ball method is Hoeppler Viscometer. Empirical equation relating viscosity and time of ball falling and passing defined distance is given by the following formula (14):

$$\eta = K_H \cdot (\rho_K - \rho_F) \cdot t \quad (14)$$

Where: η – absolute viscosity in centipoises, K_H – constant of Hoeppler Viscometer, ρ_K – density of ball, ρ_F – density of liquid, t – arithmetic average of five measured flow times.

Hoeppler viscosity method is based on the principle that viscosity may be measured by the time required for a standardized ball to roll down an inclined tube filled with the tested fluid e.g. melt or solution. The length of the measuring distance amounts to 100 mm. The ball size is selected according to the initial viscosity measurement results and to fulfil the requirement that time of ball passing between reference marks should fall in the range: no less than 60 and nor more than 300 seconds. If the flow time is less than 60 seconds or longer than 300 seconds then it is necessary to choose bigger or smaller ball, accordingly.

Examined liquid should be deaerate in order to avoid air bubbles that change results of viscosity value.

Moreover the advantage of this method is that it can be also use for different, but constant during tests, temperatures (in the range of -60°C to 150°C). Temperature constancy is assured by using circulating bath supplied by thermostat.

This method is useful for liquids with viscosities between 10^{-3} to 10^5 Pa s. Due to the simplicity of design, the falling sphere method is particularly well suited to high temperature viscosity studies. Hoeppler viscosity method was also utilized in the present research.

Falling Cylinder Method is similar to the previous method but solid cylinder freely falls vertically in the direction of its longitudinal axis through a liquid sample within a cylinder container. Physical basics are the same as in falling ball method. Falling cylinder method is used to determine relative viscosities

of different transparent fluids. It is possible to measure absolute viscosities between 10^{-3} to 10^7 Pa s.

Falling methods in opaque liquids are different from methods that are applied to transparent liquids where observation of falling body is possible. Techniques for opaque liquids have varied realizations but they all have in common the ability to detect the body as it moves past the sensor.

Capillary Flow Method (Ostwald or Ubbelohde viscometer), is the most common design of gravity type viscometer in the U-tube type with at least two reservoir bulbs connected to a capillary tube passage with inner diameter D . Capillary viscometer are characterized by capillary volume and diameter. Capillaries with 1-1.5 mm diameters and with length 50-150 mm are most commonly used. Viscometer is filled with the liquid until the liquid reaches level marked as "A". Next viscometer is placed into a constant temperature bath to equilibrate the temperature of the test liquid. The efflux time is measured for that volume flow through the capillary under gravity. There are known few methods that modified original Ostwald viscometer design in order to minimize certain undesirable effects, to increase the viscosity range, or to meet specific requirements of the tested fluids. Glass capillary viscometers are often used for low-viscosity fluids.

Modified Ostwald viscometers according to [18] are divided into two categories, namely:

1. Constant volume viscometer at filling temperatures:
 - Cannon-Fenske routine viscometer is used for measuring the kinematic viscosity of transparent Newtonian liquids in range of 0.5 to 20000 cSt. It can be used for the study of non-Newtonian liquids, wax crystallization, and oil flow characteristics at low temperatures
 - Cannon Manning semi-micro viscometer,
 - Pinkevitch viscometer, is used for determination kinematic viscosity of transparent Newtonian liquids in the range of 0.6 to 17.000cSt,
2. Constant volume at the test temperature:
 - Zeitfuchs viscometer can be used for determinate viscosity of Newtonian oils in range of 0.6 to 3.000 cSt at temperatures from 50 to 250°C,
 - SIL viscometer (0.6 to 10.000 cSt),
 - BS/U-tube viscometer (0.9 to 10.000 cSt),
 - BS/U-tube miniature viscometer (0.2 to 100 cSt).

Ubbelohde viscometer is useful for determination of the kinematic viscosity of transparent Newtonian liquids in the range of 0.3 to 100.000 cSt. This method can be used at all temperatures.

There are also methods applied for determination viscosity of opaque and non-transparent liquids:

- Cannon-Fenske Opaque (0.4 to 20.000 cSt),
- Zeitfuchs cross-arm (0.3 to 10.000 cSt),
- Lantz-Zeitfuchs (60 to 120.000 cSt, at temperatures 50-250°C),
- BS/IP/RF.

This viscometers have general name Reverse Flow Viscometers.

Rotational Viscometers, measure torque needed to rotate measurement instrument (cylinder or roller), which is immersed in researched liquid. The torque at constant rotational velocity is a measure of fluid viscosity. Depending on viscosity, there are known various rotating parts (Fig. 1):

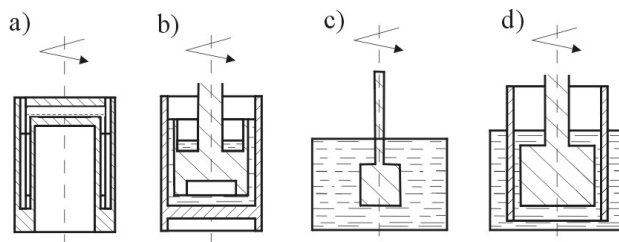


Fig. 1. Rotating parts used in rotational viscometers: a – cylinder turned in cylinder, b – roller turned in cylinder, c – stirrer free turned, d – roller turned in motionless/immobile pipe [17]

Brookfield viscometer is a rotational apparatus which measures the torque required to rotate a spindle at constant speed immersed in oil of a given temperature. It is used for measuring low temperature viscosity of lubricants, for instance it is applied for characterize viscosity of phenolic resins, epoxy resins, polyester resins and glues.

Ultrasonic methods are more technically complicated than conventional viscosity measurement techniques. It is possible to relate some ultrasonic wave characteristics with tested liquid viscosity. Ultrasonic methods most often apply an energy of an acoustic wave travelling through a liquid as a viscosity measure.

Many researchers use viscosity measurements as a crucial part useful for research, design and control the processes, and effects of processing, moreover it is important in many engineering applications in industries. In the present research viscosity was tested as a property needed to fully characterize compounds for future programme concerning FGM production with casting and rotational moulding. Viscosity is one of properties allowing to control solid particles motion in polymeric matrix and in this way to control content and properties gradients.

3. Experimental

3.1. Materials and methods of research

Materials

The following materials were used in research programme: epoxy resin Epidian 6, purchased from Nowa Organika-Sarzyna (Poland) as matrix; barium ferrite and strontium ferrite powders as fillers were used, they were obtained from ZAM Trzebinia (Poland). Characteristics of used materials are presented in Table 1 to Table 3.

Table 1. Characteristics of epoxy resin Epidian 6

Density (20°C)	1,17g/cm ³
Viscosity (25°C)	10000-15000 mPa·s
Boiling point	> 200°C
Melting point	-
Ignition temperature	> 200°C
Autoignition point	> 300°C

Table 2.
Characteristics of barium ferrite

Component %					Humidity % max	Fe ₂ O ₃ [mol] BaO [mol]
Fe	Ba	Mn max	BaSO ₄ max	SiO ₂		
58.6-59.6	12.7-13.7	0.5	1.0	0.3-0.6	0.5	5.6-6.2

Table 3.
Characteristic of strontium ferrite

Component %					Humidity % max	Fe ₂ O ₃ [mol] SrO [mol]
Fe	Sr	Mn max	SrSO ₄ max	SiO ₂		
61.4-62.4	8.6-9.6	0.5	1.0	0.3-0.6	0.5	5.6-6.2

Viscosity measurement

In this experimental procedure ferrites as fillers with epoxy resin were mixed. For each filler type three mixtures were prepared: containing 3%vol., 6%vol. and 10%vol. of filler in epoxy matrix. Mixtures were subjected to deaeration in vacuum drier SPT 200 HORIZONT before viscosity examination in order to avoid air bubbles that strongly affect the results of viscosity. Deaeration was made at the vacuum under-pressure of 95 kPa for one hour at the temperature of 80°C. Subsequently mixtures were poured into glass cylinder of viscometer. Measurements on Hoespler viscometer (Fig. 2) in three temperatures (70°C, 80°C and 90°C) were made. Temperatures constancy during measurement process was obtained by using ultra-thermostat. Silicon oil heated in thermostat was used to control temperature in bath.

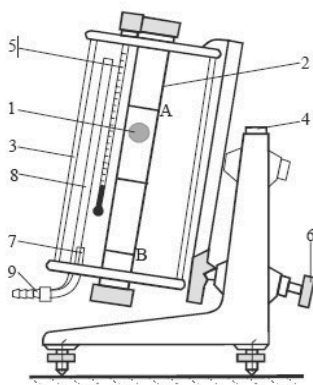


Fig. 2. Hoespler viscometer: 1 – standardized falling ball (glass or steel); 2 – glass cylinder with examined liquid; 3 – jacket for filling with thermostatic liquid; 4 – level; 5 – thermometer; 6 – spring bolt; 7,8,9 – connections to thermostat; A,B – marks to measure the falling time relating to the constant K_H (eq. (14))

Each point of result presented hereafter was obtained as an average value calculated from five measurements, according to standards requirements.

3.2. Results and discussion

Results of viscosity measurements for epoxy-barium ferrite compounds as a function of temperature are shown in Fig. 3.

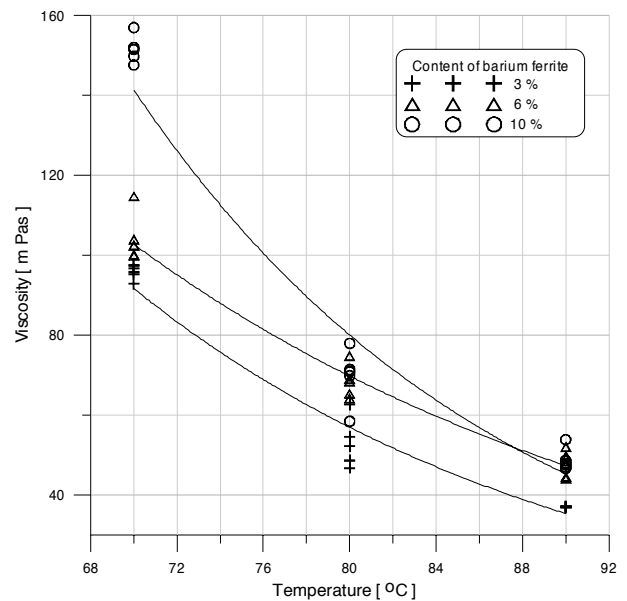


Fig. 3. Viscosity for compositions with barium ferrite

There are presented five values for each filler content and temperature point. Fig. 4 present dependence of viscosity on filler content. The same dependences for strontium ferrite filled compounds are shown in Fig. 5 and Fig. 6. As can be seen in Figures 3 and 5, for both fillers, mean values of viscosity decreased markedly with increasing investigation temperature. It is the result of generally observed polymers viscosity decrease with temperature increase. Very known is Arrhenius law for temperature dependence of viscosity (15):

$$\eta(T) = \eta_r \left[\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right] \quad (15)$$

where: η_r – viscosity in reference temperature, E – activation temperature, R – gaseous constant, T_r – reference temperature.

For composite with the highest content of barium ferrite substantial results scatter was observed. Probably it is the result of composite heterogeneity. Whereas results of viscosity that were obtained for different contents of filler showed inverse relationship. That is, higher values of viscosity were achieved for higher content of filler as it is presented in Figures 4 and 6. It is in consistency with theoretical considerations presented earlier. Furthermore, dependences of viscosity on filler content for higher testing temperature and dependences of viscosity on temperature for higher fillers content are characterized by greater approximation line inclination. It can be explained by the following consideration. Solid particles form spatial network that highly increase resistance to flow. The lower is viscosity of matrix (in higher temperatures) the greater is its influence on

formed network. Low viscosity fluid is able to destroy formed network and in this way lower the viscosity.

a little bit higher viscosity. Additional research concerning solid particles geometry is needed to explain observed differences.

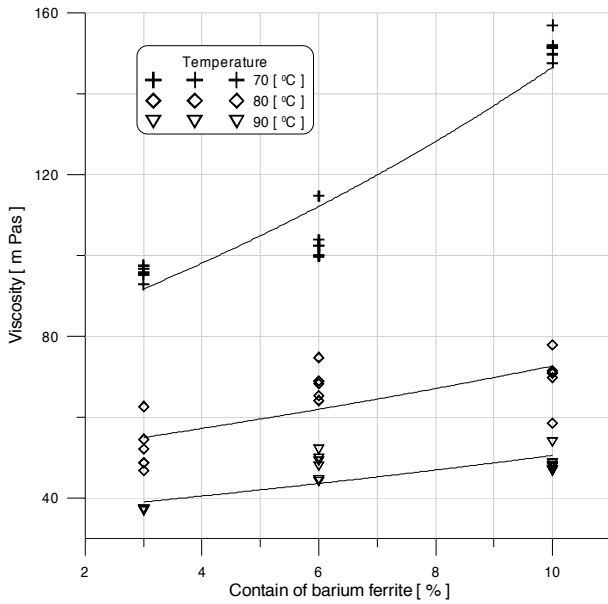


Fig. 4 Viscosity for different temperatures of composition with barium ferrite

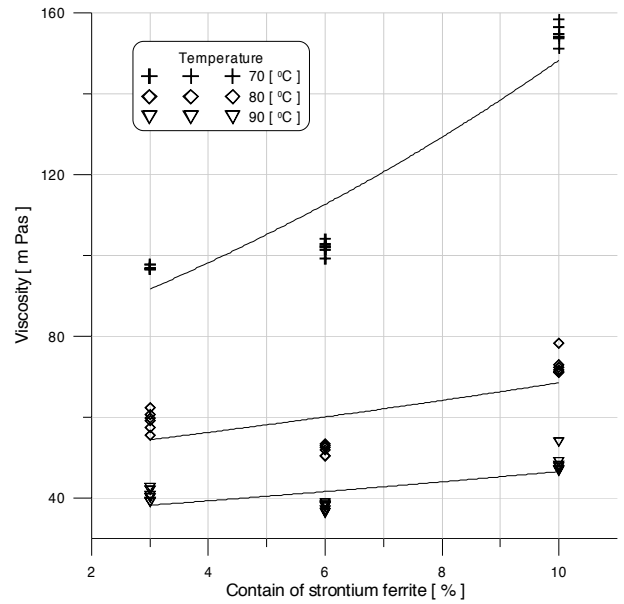


Fig. 6 Viscosity for different temperatures of composition with strontium ferrite

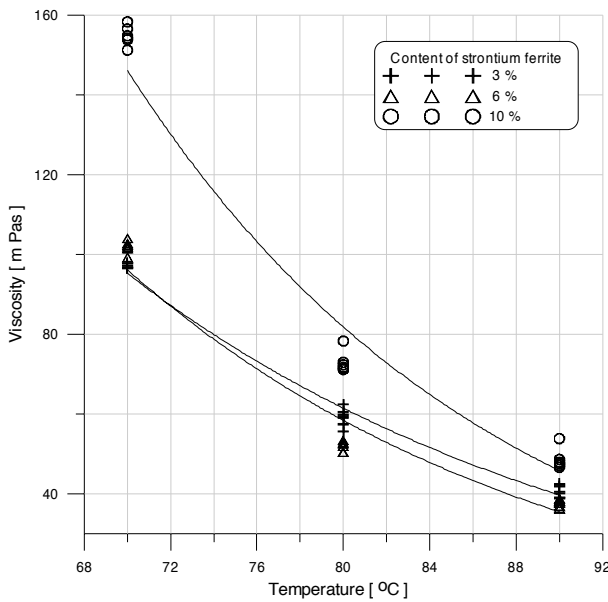


Fig. 5 Viscosity for composition with strontium ferrite

Figure 7 presents results comparison of viscosity measured in 70°C for two mixtures: epoxy-barium ferrite and epoxy-strontium ferrite. As can be seen viscosity is very similar for both fillers. Compounds that contain strontium ferrite as a filler exhibited

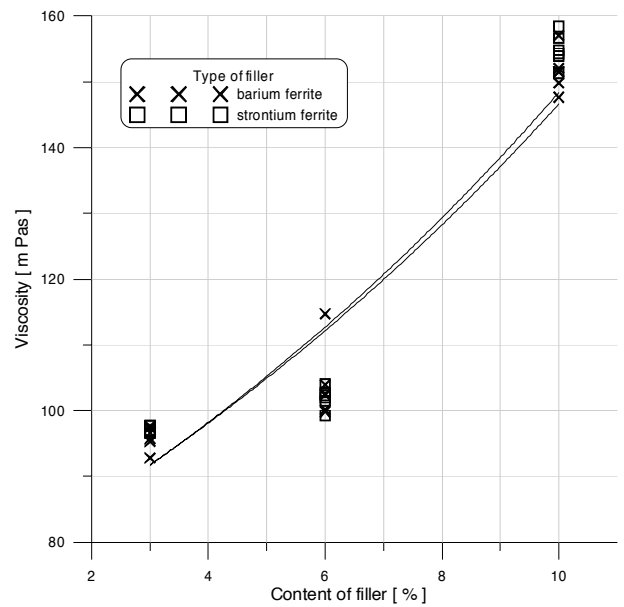


Fig. 7 Comparison viscosity for two kinds of filler in 70°C

Comparing relative viscosity of compositions for 70°C is presented in Fig. 8. It was observed that experimental viscosity results, which were obtained for filled epoxy resin are approximately to relative viscosity that was obtain according to Einstein's theory. Moreover as can be seen, results for 3%vol. and

6%vol. of fillers are a little bit less, while higher content of fillers (10% vol.) are higher than results calculated according to Einstein's theory.

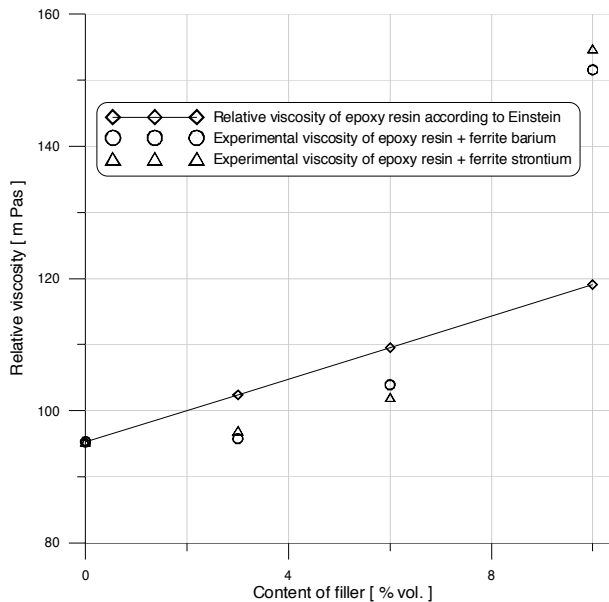


Fig. 8 Comparison of experimental and theoretical dependences of viscosity on filler content for two ferrites in 70°C

4. Conclusions

This study was carried out in order to determine the viscosity values of the filled compounds. Basing on the obtained results the following conclusions were drawn:

- lower values of viscosity for higher temperatures of measurement were obtained while higher quantity of ferrite powder increased viscosity of mixtures,
- results of viscosity that were obtained for barium ferrite and strontium ferrite presents very small difference between them,
- research method was used only for 3, 6 and 10%vol. of fillers because it was impossible to measure viscosity for higher amount of ferrites in mixtures, for that reason in future works it is planned to use another method of viscosity measurement.

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