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THE EFFECT OF FILLER CONTENT ON THE VISCOSITY OF POLYMER COMPOSITES

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Abstract: Currently, research on materials containing magnetic magnetic particles give opportunity to the prepare and study of composites with interesting magnetic features. One possibility for producing such materials is the use of fillers with magnetic properties. The final properties of such composites depend mainly on characteristic polymer matrix. However, the addition of magnetic materials arose use of new technologies. Such builders include the magnetic ferrites. Metal hexaferrites represent well researched group of magnetic materials (Mallick, 1993). Their high values of magnetocrystalline anisotropy and saturation magnetization enable widespread application of these materials as permanent magnets. Low price and excellent chemical stability with suitable magnetic characteristics classified ferrites to one of the most important magnetic materials (Rigbi, 1988).
The experimental material used was a composite formed by combining a polymer matrix (linear polyethylene HDPE), and the hard-magnetic strontium ferrite labeled FD 160S as a filler. Composites with different filler contents were prepared from the starting materials. The dependence of viscosity on the content of ferrite filler was determined by rheological measurements.
Keywords: ferrite filler, polymer matrix, composites, polyethylene, rheology

1. INTRODUCTION

Composites typically have a fiber or particle phase that is stiffer and stronger than the continuous matrix phase. Many types of reinforcements also often have good thermal and electrical conductivity, a coefficient of thermal expansion that is less than the matrix, and good wear resistance. One of the exception of these rules are rubber-modified polymers, where the discontinuous phase is more compliant and more ductile than the polymer, resulting in improved toughness (Mleziva, 2000).
First and foremost, composites are engineering materials that have been designed to provide significantly higher specific stiffness and specific strength (stiffness or strength divided by material density) – that is, higher structural efficiency – relative to previously available structural materials. In composite materials, strength and stiffness are provided by the high-strength, high-modulus reinforcements. The actual magnitude in

composite strength and stiffness can be controlled over a significant range by controlling the volume fraction of reinforcements and by selecting reinforcements with the desired levels of strength and stiffness. In fiber-reinforced composites, the strength and stiffness may be further controlled by specifying the fiber orientation (Bunsell, 1998). At present, the method of processing composite magnets based on thermoplastic is being promoted, mainly by injection molding technology. Depending on the binder, this technology requires cold or hot mixing of the magnetic powder with the binder in mixers, mixing extruders, or kneaders (Polak, 2018) (Chval, 2020). The most important raw materials used as polymer matrices for injection molding technology are thermoplastic, especially polyamide (PA) and polyethylene (PE). The technological requirements of the material indicate that the sample should meet the function of polymeric binder as a good connection of magnetic particles, enabling a high degree of filling and trouble – free processing of the material (Valášek, 2012) (Lokander, 2004).

2. EXPERIMENTAL MATERIAL AND METHODS

For preparation of composite materials the linear matrix of polyethylene (LITEN MB 71) was used. Liten MB 71 (HDPE) is a homopolymer with narrow molecular weight distribution, suitable for injection molding. A typical application is the production of parts that require good stiffness and impact resistance.

As a filler the hard-magnetic strontium ferrite labeled FD 160S was used. The composition of strontium ferrite corresponds to the general formula $SrFe_{12}O_{19}$. Sr ferrite with PVAL surface treatment was used for the preparation of composites.

Thermoplastic composites with different filler content in the polymer matrix – from 60 to 80% - were used as experimental material. Sample marked Z1 represents a mesh polyethylene matrix and sample Z2 – Z4 represents composites. The conditions of its composite preparation were as follows: temperature ranges from 137 to 182 °C (temperature of processing zones), screw speed 140 min^{-1}, torque 49%. The composition of the composites is given in Table 1 (percentage by volume).

Table 1

Composition of polyethylene – ferrite composites

Z1	100% HDPE
Z2	40% HDPE + 60% Ferrite
Z3	30% HDPE + 70% Ferrite
Z4	20% HDPE + 80% Ferrite

Rheology is the science of flow behavior of liquids and the deformation behavior of solids, as well. Plastics are considered to be viscoelastic materials, exhibiting both viscous and elastic properties, which are changing with temperature and time. These changes can be measured as a response of the material to deformation by periodic forces (during the forced vibration or small-amplitude oscillatory shear). Stress and strain are not in phase, the strain delays behind the stress by a phase angle. If the oscillatory shear is sinusoidal, then the **shear stress** is equal to

$$\tau(t) = \tau_0 . e^{i\omega} = \tau_0(\cos\omega t + i . \sin\omega t) \quad (1)$$

where τ_0 - stress amplitude, ω - angular frequency, t - time and i = $\sqrt{-1}$.

The **complex shear modulus G*** is defined as

$$G^* = \frac{\tau(t)}{\gamma(t)} \tag{2}$$

Equation (2) can be resolved into two parts

$$G^* = G' + i.G'' = \frac{\tau_0}{\gamma_0}(\cos\delta + i.\sin\delta) \tag{3}$$

The first, G′ is in phase with strain and the second G″ is out of phase with strain for angle δ. Therefore, the two dynamic moduli can be defined as

$$G' = \frac{\tau_0}{\gamma_0}\cos\delta \tag{4}$$

$$G'' = \frac{\tau_0}{\gamma_0}\sin\delta \tag{5}$$

The G′ is called the **storage modulus** and G″ is called the **loss modulus**. The G′ value is a measure of the deformation energy stored by the sample during the shear process. Thus, it represents the elastic behavior. The G″ value is a measure of the deformation energy used up by the sample during the shear process and therefore it represents the viscous behavior of a material. The **complex viscosity η*** is defined by the equation

$$\eta^* = \frac{\tau(t)}{\dot{\gamma}(t)} \tag{6}$$

$\dot{\gamma}$ **-** is the **shear rate**.

The described parameters very sensitively react on the structural changes evoked by reactions with environment (Mezger, 2006) (Farrar, 2001). By the Frequency Sweep test (FS) – Two-plates- Viscoelastic properties were investigated for the composite HDPE – ferrite filler and the influence of filler content was evaluated. The measured characteristics were: Complex viscosity **η*** (Pa.s), storage modulus **G′** (Pa) and the loss modulus **G"** (Pa). The measurements were made by the Physica Rheometer MCR 301 with a convective thermal device CTD 450 by Frequency Sweep test to study changes of viscoelastic properties, changes of molecular mass and its distribution after various types and time of exposure. The principle of the mentioned evaluations is shown in Fig. 1, where, by drift of the intersection point of the modulus, a character of structural changes affected by environment exposure can be determined (Wollny, 2003) (Malkin, 2005) (Mark, 2007).

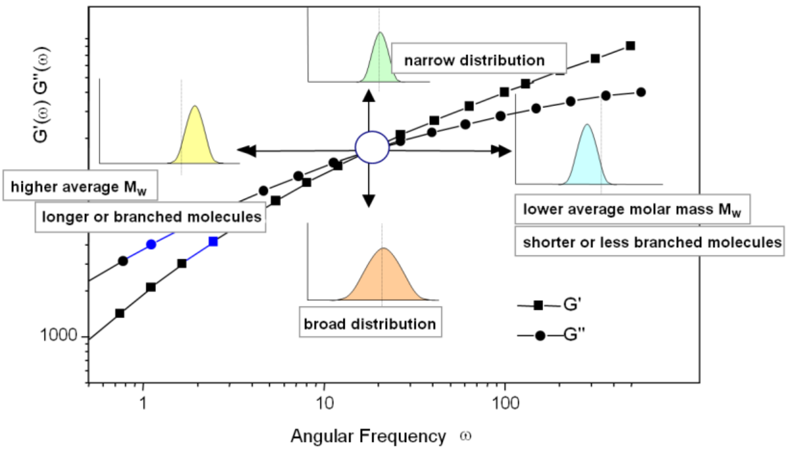

Fig. 1. Determination of selected material characteristics from the curves obtained by the FS test

3. RESULTS AND DISCUSSION

The ferrite powder Sr coated with PVAL, which provides spherical particles we can see on Fig. 2.

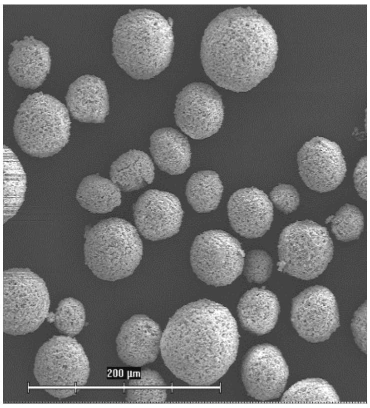

Fig. 2. Sr ferrite particles with PVAL

The spherical shape of Sr ferrite was formed by spraying the ferrite dust with polyinylacohol (PVAL) during production. The spherical particles do not fill the volume perfectly, as a result closed air remains in the pores between the particles and in the pores of the ferrite particles. This can cause adversely effect of the adhesion between the filler and the matrix. To improve the adhesion of the filler to the matrix, PVAL was removed from the surface of the filler particles by dissolving in hot water (70 °C). The regular spherical shape is lost and the particles disintegrate to the original grain size (Fig. 3).

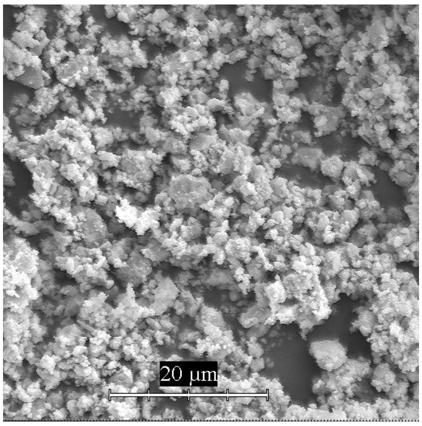

Fig. 3. Sr ferrite without PVAL surface treatment

Rheological measurements were used to evaluate the change in viscosity, loss and accumulation modulus. The change in the position of the intersection of both modules was observed, which indicates the transition from viscous and deformation behaviour to the elastic features and is a qualitative characteristic of the material. Rheological measurements were performed at 180 °C, the amplitude was 5% and the angular velocity was from 500 to 0.05 1/s.

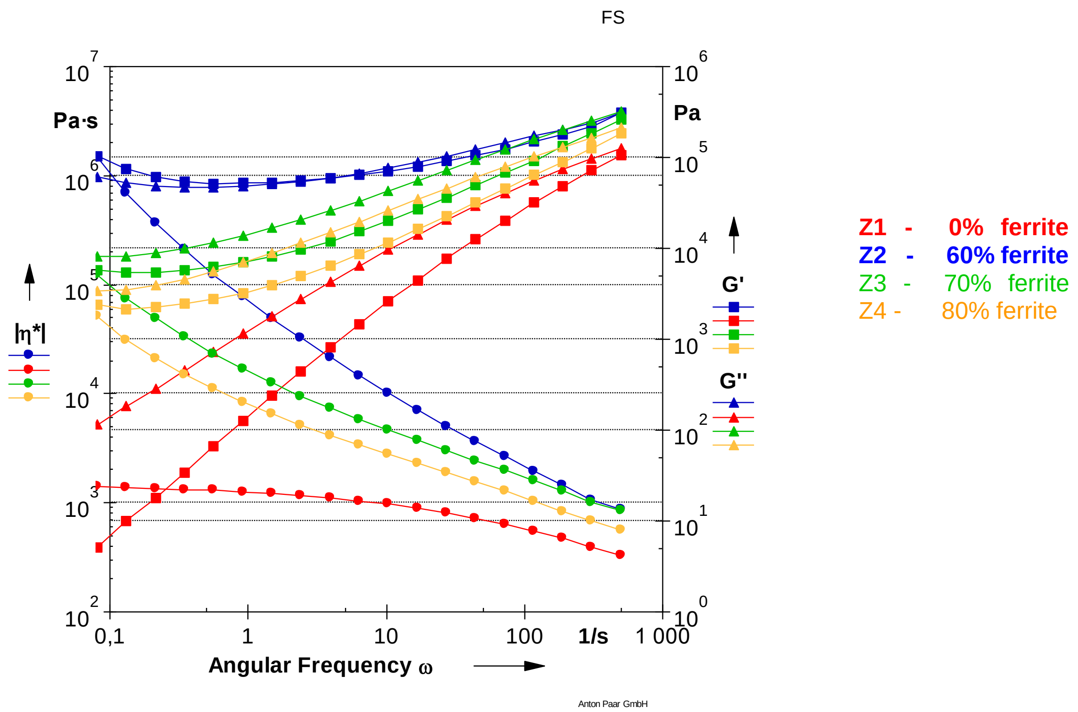

Fig. 4. The course of FS curves of HDPE composites - ferrite with different filler content

Figure 4 shows a graphical course of measured characteristics for HDPE-ferrite composite with different filler content. As can be seen from Figure 4, the viscosity values increase with increasing filler content, but the viscosity decreases with increasing frequency, resulting in a decrease in the creep resistance of the polymer, which is typical of polymeric pseudoplastic melts. The curves documenting the course of modules G 'and G "have the same tendency. The position of the intersection of the curves of these modules changes in composites with a filler content of 60, 70 and 80%.

4. CONCLUSION

The tested composites represent a thermoplastic-ferrite filler system. The properties of the final product depend on the properties of the thermoplastic polymer as well as on the properties of the filler and its content in the composite. The results of testing composites are as follows:

- Sr ferrite particles with PVAL form spherical porous particles. The spherical particles do not fill the volume perfectly, as a result of which closed air remains in the pores between the particles as well as in the pores of the ferrite particles, which can adversely affect the adhesion between the filler and the matrix and the mechanical properties of the composites,
- by removing the PVAL from the surface of the ferrite particles, their spherical shape is lost and the particles disintegrate to their original grain size,
- the FS test confirmed the increase in complex viscosity depending on filler content. as well as a change in the position of the intersection of the G' and G "modules, which signals changes in molecular weight. All composites demonstrate a change in the position of the intersection of the modules in the horizontal direction, signaling a narrowing of the molecular weight distribution.

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