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Effect of ceramic nanopowders on rheology of thermoplastic suspensions

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Abstract

Rheological behaviour of thermoplastic polymer melts containing 20–50 vol.% of ceramic nanopowders was studied. For the preparation of thermoplastic polymer suspensions three ZrO_2 powders with specific surface areas from 6.5 to 123 $m^2 g^{-1}$ were used. Using a capillary rheometer, viscous behaviour was examined in the temperature range from 100 to 150 °C and in the shear rate range from 100 to 1000 s^{-1}. The viscosity of suspensions increased with increasing specific surface area of ceramic powder. The suspensions were of pseudoplastic nature, which was described by the power law. The power law exponent and the activation energy of viscous flow of suspensions decreased almost linearly with increasing specific surface area of the powder. The maximum volume fraction of the powder in the suspension also decreased with increasing specific surface area of the powder. The causes of the changes in viscous behaviour of the suspensions in dependence on the specific surface area of powders were discussed.

Keywords: A. Mixing; D. ZrO_2; Thermoplastic suspension; Rheology

1. Introduction

Polymers are filled with micrometre sized particle fillers in order to increase their mechanical, electrical and thermal-degradation properties or to decrease their price [1]. The content of filler usually ranges between 20 and 40 vol.%. Higher contents of micrometre and sub-micrometre sized ceramic particles (50–60 vol.%) are applied in ceramic technologies, where the polymer serves as a temporary binder [2]. The rheological behaviour of filled polymer melts has extensively been examined and properly described [1]. In ceramic technology, the common applications of thermoplastic polymer suspensions are limited to particles above 100 nm. One of the reasons is the low degree of loading that can be achieved in nanoparticle thermoplastic suspensions. The causes can in general be sought in the interaction of particles in the suspension [3], adsorption of organic molecules on the surface area of particles [4], and heavy agglomeration of nanopowders [5,6].

The present work is aimed at the study of steady shear viscosity functions of thermoplastic suspensions prepared with ceramic powders whose primary particles are of nanometre size.

2. Experimental

Three ZrO_2 powders stabilized with 3 mol% Y_2O_3 were used for the preparation of ceramic suspensions. The properties of the powders are given in Table 1. The thermoplastic polymer binder (organic component of the suspension) contained copolymer ethylene-vinyl acetate (Elvax 250, Du Pont de Nemours, USA), paraffin (54/56, Slovnaft, Slovakia) and stearic acid (1.0067, Merck, Germany) in a weight ratio of 2.4:1.6:1. The ceramic suspension was prepared by mixing the binder and powder in a heated two-blade kneader (HKD 2,5, IKA-Werke, Germany) at a temperature of 120 °C for 1.5 h. Ceramic suspensions contained 20 vol.% of ceramic powder. Suspensions with powder Z2 were also prepared with 25, 30 and 37 vol.% of solid phase, and suspensions with powder Z3 with 37 and 50.5 vol.% of solid phase.

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Table 1
Properties of ZrO_2 powders

Sample	Grade	Producer	Specific surface area ($m^2\ g^{-1}$)	Particle size	
				D_{SSA}[a] (nm)	D_{DIF}[b] (nm)
Z1	B223	VUT Brno, Czech Republic	123	8.3	252
Z2	ZrO_2	Nanoproducts, USA	43	25.1	312
Z3	TZ 3YS-E	Tosoh, Japan	6.5	154	113

[a] Calculated from specific surface area.

[b] Determined by laser diffraction.

Rheological measurement was performed on a capillary rheometer (Galaxy V, Kayeness, USA) with 30-mm nozzle of 1 or 0.75 mm in diameter, in the shear rate range from 100 to 1000 s^{-1} and at temperatures of 100 to 150 °C. The shear rate was corrected to the non-Newtonian behaviour of suspensions using the Weissenberg–Rabinowitsch method [1]. Selected experiments were multiply repeated to assess the measurement scatter.

3. Results and discussion

Fig. 1 gives the dependence of viscosity on shear rate for pure binder and ceramic suspensions of ceramic powder volume fraction $V = 0.2$. It follows from the graph that adding ceramic powder to binder led to increased viscosity, which was the greater, the higher the specific surface area of powder. Ceramic suspensions exhibited similar behaviour at all the temperatures examined. Ceramic suspensions and pure binder behaved pseudoplastically, i.e. their viscosity decreased with increasing shear rate. The dependence of viscosity on shear rate could be described using the Oswald–de Waele power law [7]:

$$\eta = K\dot{\gamma}^{n-1}, \tag{1}$$

where η is the viscosity, K is the consistence coefficient, $\dot{\gamma}$ is the shear rate, and n is the power law exponent giving the deviation from the Newtonian behaviour (for $n = 1$ a Newtonian liquid is concerned). The plot in Fig. 2 shows the temperature dependence of the power law exponent for individual suspensions and pure binder. In the case of pure binder, exponent n increased slightly with temperature. Similar temperature dependence was also established for ceramic suspensions but at lower values of exponent n. The value of average power exponent ranged from 0.74 (for pure binder) to 0.29 (for ceramic suspension with the powder of the highest specific surface area).

The dependence of the viscosity of ceramic suspensions and binder on temperature is shown in Fig. 3. The temperature dependence could be described well by the Andrade–Eyring relation [7]:

$$\eta = A \exp\left(\frac{E}{RT}\right), \tag{2}$$

where A is the constant, R is the universal gas constant, T is the absolute temperature, and E is the activation energy of viscous flow. Viscosity decreased with increasing temperature. A measure of the temperature dependence of viscosity is the activation energy, which was calculated from the above relation. The activation energy of suspensions was lower than that of pure binder. For ceramic suspensions, the activation energy decreased with increasing specific surface area of powders.

It is obvious from Fig. 4 that with increasing value of the specific surface area of ceramic powders the value of power law exponent decreased almost linearly (i.e. the pseudoplasticity of suspensions increased) and so did the activation energy of the viscous flow of suspensions. It should be added

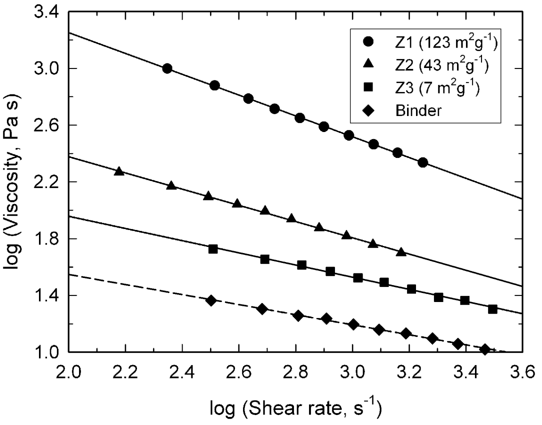

Fig. 1. Viscosity of binder and ceramic suspensions of powder volume fraction $V = 0.2$ as a function of shear rate at a temperature of 100 °C.

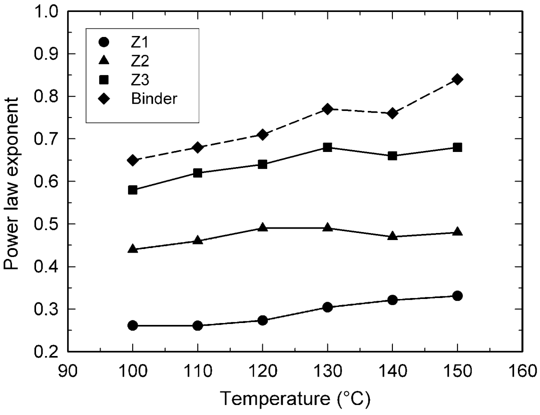

Fig. 2. Temperature dependence of power law exponent for binder and ceramic suspensions of powder volume fraction $V = 0.2$.