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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

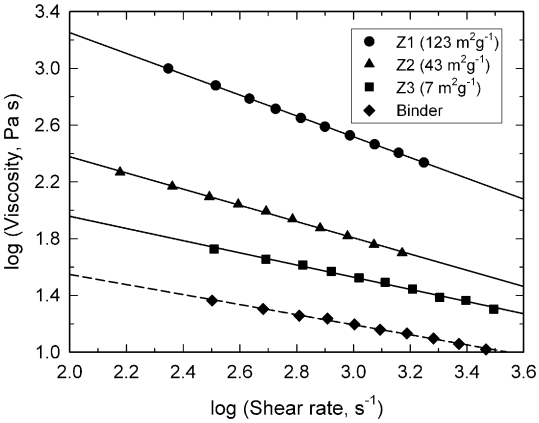

Fig. 1. Viscosity of binder and ceramic suspensions of powder volume fraction $V = 0.2$ as a function of shear rate at a temperature of 100 °C.

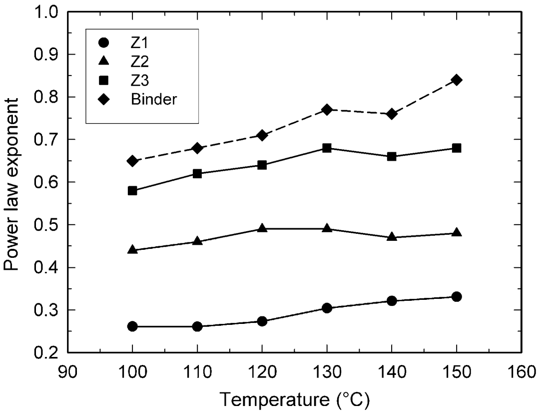

Fig. 2. Temperature dependence of power law exponent for binder and ceramic suspensions of powder volume fraction $V = 0.2$.

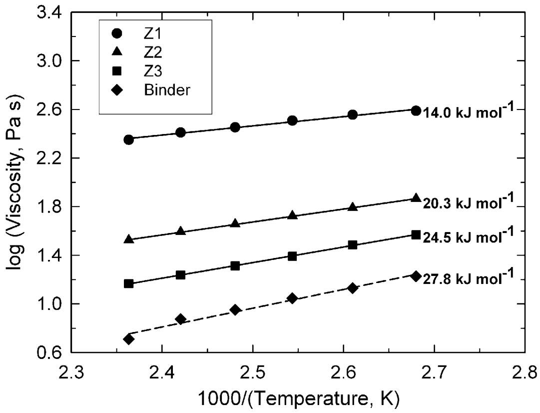

Fig. 3. Temperature dependence of viscosity of binder and ceramic suspensions ($V = 0.2$) at a shear rate of 800 s^{-1}. Calculated activation energies of viscous flow are given in the graph.

that the activation energy was dependent on the shear rate. The activation energies calculated for other shear rate values also decreased roughly linearly with increasing specific surface area of the ceramic powder.

To describe the dependence of viscosity on the volume fraction of ceramic powder in the suspension, several models have been proposed in the literature, from which the following simple empirical relation is often used with success [8]:

$$\eta_r = \frac{\eta}{\eta_0} = \left(1 - \frac{V}{V_m}\right)^{-2}, \tag{3}$$

where η_r is the relative viscosity, η_0 is the viscosity of binder, V is the volume fraction of powder, and V_m is the maximum volume fraction of powder. V_m represents an important parameter of ceramic suspension, primarily from the viewpoint of practical application of suspension. V_m gives the suspension loading at which, theoretically, viscosity increases to infinity. In practice this means that at this moment the mixture ceases to be plastic. The maximum volume fractions of individual powders were estimated from relation (3) on the assumption that this relation described the behaviour of examined suspensions with sufficient accuracy. The values of V_m for individual suspensions are given in Table 2. The relative viscosity of suspensions increased with temperature the more, the greater the difference between the activation energy of binder and that of the respective suspension. But the values of maximum volume fraction of ceramic powder in the suspension almost did not change with temperature. The plot in Fig. 5 gives the dependence of the relative viscosity of ceramic mixtures on the V/V_m ratio, inclusive of the model dependence according to relation (3).

Table 2
Maximum powder volume fraction in ceramic suspensions

Suspension	Maximum powder volume fraction		
	100 °C	120 °C	150 °C
Z1	0.25	0.25	0.24
Z2	0.45	0.44	0.42
Z3	0.61	0.61	0.60

It follows from the above results that from the standpoint of suspension rheology the most important parameter of fine ceramic powders was the value of specific surface area. Although the measured particle size of raw ceramic powders was similar (100–300 nm), it results from the size of the specific surface area of powders that the particles of materials Z1 and Z2 were formed by agglomerates of substantially finer primary particles (see Table 1). Stearic acid contained in organic binder could help to disperse and to sterically stabilize the nanoparticles, but even the most powerful mixing equipment is unable to break up existing nanoparticle agglomerates [5]. For bigger particles (dense agglomerates of nanoparticles) stearic acid does not provide true steric stabilization due to its short molecule chain. Only ‘‘semisteric’’ stabilization occurs, i.e. the attraction potential among the particles is not eliminated completely, it is only reduced [9,10]. So, the attractive London dispersion forces led to the appearance of flocs of particles or even to an appearance of the immobilized network of particles [3].

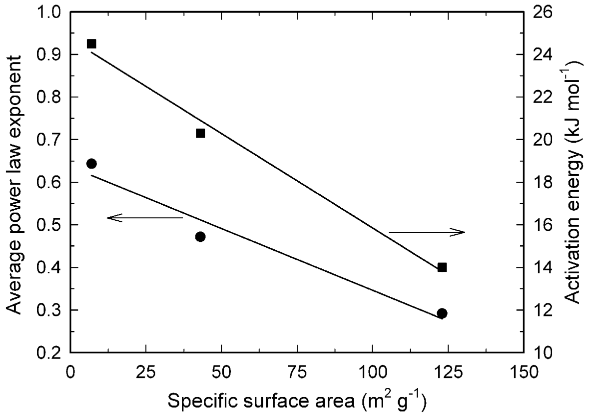

Fig. 4. Average power law exponent and activation energy of viscous flow of ceramic suspensions ($V = 0.2$) as a function of specific surface area of ceramic powders.

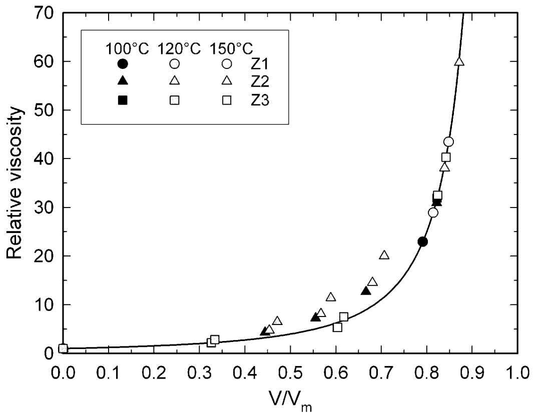

Fig. 5. Relative viscosity of ceramic suspensions as a function of V/V_m ratio. The model dependence according to relation (3) is also given in the graph.

With increasing shear rate the bond between particles got destroyed and the remaining agglomerates became oriented, which gave the mixture its pseudoplastic character. The results confirmed that for the powder with the highest specific surface area (in which the highest degree of agglomeration and the strongest particle interactions are assumed) the lowest value of power law exponent was established (i.e. the highest degree of pseudoplasticity). The reason for the increased viscosity of suspensions with a powder of high specific surface area was, in addition to the above interaction and agglomeration of primary particles, the adsorption of organic molecules on powder surface. This grafted and partially immobilized layer increased the effective volume fraction of the ceramic in the suspension according to the relation [4]:

$$V_{\mathrm{ef}} = V\left(1 + \frac{\delta}{r}\right)^3, \tag{4}$$

where V_{ef} is the effective volume fraction, δ is the thickness of adsorbed layer on the particle surface area, and r is the particle diameter. If we assume that a minimum immobilized layer of 2.4 nm in thickness (the thickness of monomolecular layer of stearic acid) was formed on the powder surface area, then in the case of spherical monodispersion particles, the effective volume fraction for ceramic powder Z3 would increase from $V = 0.2$ to $V_{\mathrm{ef}} = 0.22$, for powder Z2 the value V would increase to $V_{\mathrm{ef}} = 0.34$, and for powder Z1 it would increase to as much as $V_{\mathrm{ef}} = 0.79$. The value $V_{\mathrm{ef}} = 0.79$ is unrealistically high (random dense packing of spherical monodispersion particles is $V = 0.64$). This seems to suggest that for powders with a primary particle size of about 8 nm we cannot expect uniform adsorption of molecules of stearic acid on every particle, as in the case of larger particles. This means that the amount of stearic acid for the saturation of the surface area of nanopowders will be lower than the value 1.49 mg m^{-2} established for submicrometre sized particles [11]. The adsorbed layer of binder components on the surface of ceramic particles also affects the activation energy of viscous flow of suspensions. The change in activation energy in dependence on the specific surface area of powder in the suspension is the main finding of this work and up to now it has not been sufficiently described and explained in the literature. We assume that the binder components adsorbed on the particle surface as well as near to the surface as further layers [12] are partially aligned and have a smaller free volume (i.e. a limited amount of unoccupied places for their motion) compared with non-adsorbed molecules. This arrangement changes only a little with temperature. The greater the proportion of binder adsorbed to the surface, the smaller the suspension response to a temperature change, and the lower the activation energy. Cihlar and Racl [13] have shown that for a ceramic powder with a low specific surface area, in which the proportion of adsorbed binder is negligible, the activation energy of pure binder was comparable with that of the suspension.

All the phenomena discussed above, i.e. binder adsorption on the particle surface, increased interaction of particles and the presence of agglomerates in the suspension resulted in low maximum volume fractions of nanopowders in the suspension.

4. Conclusions

The viscosity of thermoplastic suspension increased with increasing specific surface area of ceramic powders. The pseudoplastic character of ceramic suspensions became more pronounced with increasing specific surface area of powders. The activation energy of the viscous flow of suspensions was lower than in the case of pure binder and it decreased with increasing specific surface area of powders. The specific surface area of powder also markedly affected the maximum volume fraction of powder in the suspension. The changes in the viscous behaviour of ceramic suspensions in dependence on the specific surface area of powders were explained by the growing proportion of adsorbed binder on the surface of particles and by the increased interaction and agglomeration of nanometre sized primary particles.

Acknowledgments

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