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ORIGINAL CONTRIBUTION

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Electrorheological properties of hydrolyzed poly(glycidyl methacrylate) suspensions

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Abstract Electrorheological behavior of silicone oil suspensions of macroporous poly[(glycidyl methacrylate)-*co*-(ethylene dimethacrylate)]) (0.60 : 0.40 w) hydrolyzed to various degrees was investigated. Polarizability of particles expressed by the particle dipole coefficient and, consequently, pseudoplasticity of the system at low shear rates after application of an external electric field steeply increased with the hydrolysis degree of the copolymer. As the size and shape of particles remain unchanged during hydrolysis, a series of model suspensions with the same hydrodynamic properties (Newtonian or slightly pseudoplastic when no electric field was applied) but with different intensity of the electrorheological effect could be prepared. Under these conditions, the use of Mason number failed to correlate the apparent viscosity of suspensions of particles with different polarizability in the electric field. On the other hand, when polarizability of particles of a suspension system changes due to a higher temperature, a single curve in the plot of apparent viscosity vs. the Mason number could be obtained.

Key words Electrorheology – polymer suspensions – hydrolyzed poly(glycidyl methacrylate)

Introduction

A large increase in the apparent viscosity of suspensions of solid particles in insulating fluids on application of an external electric field, described in the pioneer work of Winslow [1] as the electrorheological (ER) effect, has been the subject of many studies. The well-arranged information about this subject can be found in reviews [2–4]. The ER effect is caused by dielectric polarization of suspension particles leading to their strong electrostatic interactions, while an initially random distribution of particles changes into organized superstructure of particle chains spanning the gap between electrodes. Consequently, especially at low shear rates, pseudoplasticity of the system increases and, in some cases, even a yield stress appears due to a high stiffness of the ER structure. At higher shear rates, when the particle arrangement is destroyed, the apparent viscosity approaches to the value for the field-off state.

Many materials including polymers have been proposed as the active powder phase. A strong ER effect has been described in suspensions of semiconducting polymers [5–8]. On the other hand, to excite the ER effect in suspensions of many other particles, an activator such as water, adsorbed on the particle surface is necessary [3, 9–12]. It is assumed that in this case, an electric field externally applied to such activated suspensions causes polarization of the diffuse part of the counter ion cloud of the activator, distorting the electric double layer of particles and overlapping the clouds of neighbouring particles. Understandably, these systems are very sensitive to higher temperatures – at a moderately increasing temperature, desorption of the activator occurs and the ER effect diminishes.

So far, no systematic analysis of the dependence of ER effect on the polarizability of the suspension particle has been performed. Using suspensions of polyaniline with different doping levels, Gow and Zukoski [13] only concluded that the yield stress in general increases with particle permittivity. Thus, a systematic analysis of this problem is still lacking.

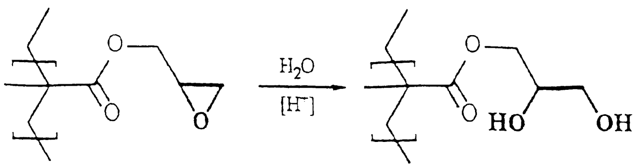
We found that in suspensions of particles of non-activated copolymer of hydrolyzed macroporous poly-[(glycidyl methacrylate)-*co*-(ethylene dimethacrylate)], a strong ER effect arises, the intensity of which depends on the degree of hydrolysis of the starting non-hydrolyzed material. In the temperature range 25–85 °C, intensity of the ER effect increased and the change was reversible. Accordingly, both hydrolysis degree and temperature control polarizability of particles. As the size and the shape of particles remain unchanged during the hydrolysis, it was possible to prepare a series of suspensions of particles with the same hydrodynamic properties for a study of relation between ER viscosity and particle polarizability, which is the object of this paper.

Experimental

Material

Macroporous poly(glycidyl methacrylate)-*co*-(ethylene dimethacrylate)] (0.60 : 0.40 w) was prepared by suspension polymerization of a monomer solution in a porogenic solvent and in an aqueous continuous phase [14], while particles of a perfect spherical shape were obtained. A fraction having particle size 10–15 μm was used for further investigation.

Five model samples of suspension particles were obtained by partial or complete hydrolysis of epoxide groups of primary non-hydrolyzed copolymer material [15]. While rather hydrophobic epoxide groups are relatively stable in water at neutral pH, strong acids and bases catalyze the ring cleavage with formation of hydrophilic and polar vicinal hydroxy groups:



The degree of hydrolysis was controlled by the reaction time and temperature in dilute (0.2 M) sulfuric acid. Afterwards, the resulting material was thoroughly washed with water and dried *in vacuo* over phosphorous pentoxide at 80 °C until a constant weight was attained. The microscopy confirmed that during this operation the size and spherical shape of the particles remained unchanged.

Table 1 Preparation and characterization of hydrolyzed poly(glycidyl methacrylate)

Polymer	Hydrolysis		Epoxide		Diol content
	Time [h]	Temperature [°C]	Content [mmol/g]	Conversion [%]	[mmol/g]
G-60	0.0	—	3.70	0.0	0.00
X-796	0.5	30	3.12	14.8	0.54
X-795	3.0	30	2.20	39.0	1.41
X-794	5.0	30	0.98	72.2	2.55
X-793	3.0	80	0.00	100.0	3.47

The mean concentration of non-hydrolyzed epoxide groups $\underline{c}$ was determined by IR spectrometry (Perkin-Elmer FT-IR spectrometer PARAGON 1000 PC) using a peak at 910 cm^{-1} [16]. Concentration of dihydroxypropyl groups (diols) was calculated from the difference between the starting amount of the monomer and the mean concentration $\underline{c}$ under the condition that no side reaction proceeds. The reaction conditions and product properties are given in Table 1.

Viscometry

Suspension of particles in silicone oil (LUKOOIL M, Chemical Works Kolín, Czech Republic, viscosity $\eta_c = 200$ mPa s) were mechanically stirred before each measurement. ER measurements of 5, 10 and 20 wt% suspensions of all samples of the copolymer were carried out in the range of shear rates 7.93–642.6 s^{-1} at 25 °C. Viscosity of a 5 wt% suspension of X-793 was also measured at elevated temperatures, 65 and 85 °C.

A coaxial cylinder rotational viscometer, Rheotest 2 (type RV, Prüfgeräte Werk Medingen, Dresden, Germany), was modified in the Institute for ER experiments. The rotating cylinder, 38.4 mm in diameter, and the outer cylinder separated by a gap of 0.8 mm were connected to a DC power supply, $E = 0.4$–2.0 kV (high-voltage source NB 411, Tesla, Czech Republic), which corresponded to the electric field strength 0.5–2.5 kV mm^{-1}.

Permittivity measurement

The permittivity of suspension particles, ε_p, was estimated from the permittivity of 20 wt% suspension, ε_s, and permittivity of the oil, ε_c, measured at 10^2 Hz with a RLCG

METER, BM 595 TESLA, using a volume-average relation [12]

$$\varepsilon_p = \varepsilon_c + (\varepsilon_s - \varepsilon_c)/\phi \ , \tag{1}$$

where ϕ is the volume fraction of the suspension.

Results

The measurement of apparent viscosity at constant temperature (25 °C) without using an electric field showed no influence of the hydrolysis degree of epoxy groups on the shape of slightly pseudoplastic flow curves of the suspensions. Practically, identical flow curves of suspensions of all samples suggest that the hydrolysis does not influence hydrodynamic properties of particles. On the other hand, under the influence of electric field, a significant dependence of low-shear viscosity on the diol content in the copolymer appeared. Whereas only a negligible change in the ratio of the apparent viscosity in the presence of electric field, η, to the viscosity in its absence, η_0, for non-hydrolyzed (G-60) and low-hydrolyzed sample (X-796) set in, in suspensions of other samples, a strong increase in η/η_0 with the degree of hydrolysis of epoxy groups in copolymer was found (Fig. 1). In the case of a 5 wt% suspension of fully hydrolyzed sample (X-793) at the highest applied field strength (2.5 kV mm^{-1}), the apparent viscosity at the lowest shear rate used (7.93 s^{-1}) increased more than twenty times with respect to the value η_0. At high shear rates, when the ER suspension structure was destroyed, the effect of electric field practically disappeared and apparent viscosity η_∞ became quite independent of the hydrolysis degree of epoxy groups. The convergence of the shear stress to a limit constant value indicates a yield stress about 44 Pa (Fig. 2e). At higher particle concentrations in the suspensions (10 and 20 wt%), an enhancement of the ER effect with the diol content in the copolymer was considerably stronger (Fig. 3).

Unlike suspensions of water-doped particles [5, 9], where desorption of water at about 40 °C causes that the viscosity-temperature plot passes through a maximum and, at a higher temperature, intensity of the ER effect decreases, a continuous increase in the ER viscosity with temperature of suspensions of hydrolyzed poly(glycidyl methacrylate) particles in the range 25–85 °C has been found. While the viscosity η_0 of all samples at low shear rates in the absence of electric field slightly decreased with the temperature or remained nearly constant, in the presence of electric field, it increased several times. At high shear rates, however, viscosity behaved in the same way as in the case, when no voltage was applied. The dependence of viscosity ratio η/η_0 on shear rate γ for X-793 at different temperatures is shown in Fig. 4.

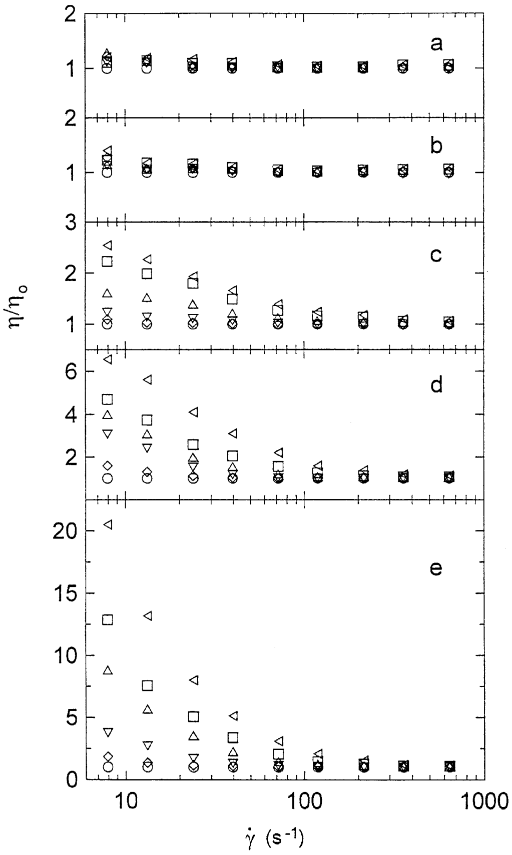


Fig. 1 Dependence of the viscosity ratio η/η_0 of the 5 wt% suspensions of the polymers on the shear rate γ at 25 °C. Polymers: (a) G-60, (b) X-796, (c) X-795, (d) X-794, (e) X-793. Field strength (kV mm^{-1}): (○) 0, (◇) 0.5, (▽) 1, (△) 1.5, (□) 2, (◁) 2.5

The plots of η/η_0 vs. E^2 at a low shear rate for 5 wt% suspensions are linear, with the slope s_E (Fig. 5), in agreement with the theory [17]. On the other hand, for higher particle concentrations (10 and 20 wt%), the plots are rather curved. This anomalous behaviour may be caused by some specific particle interactions due to percolation. For that reason, only results for 5 wt% suspensions were evaluated in the following study.

Discussion

Formation of organized structure of particles after application of an external electric field could be observed in an optical microscope. Micrographs of a 10 wt% suspension X-794 before and after application of a 1 kV mm^{-1} electric field strength confirm that particles form chains under the influence of the electric field (Fig. 6). It can be assumed that when sheared in the flow field, the chains

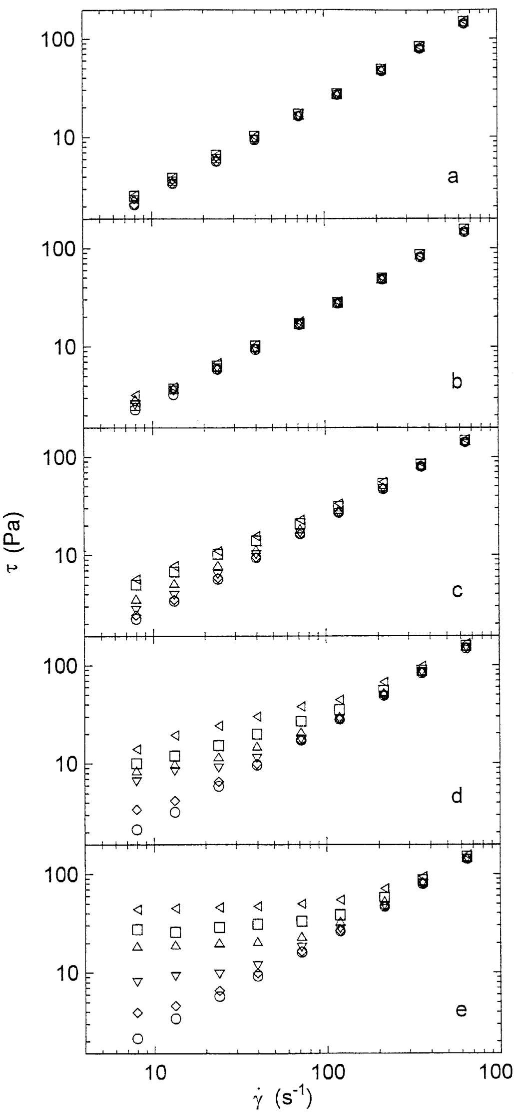


Fig. 2 Dependence of the shear stress τ of the 5 wt% suspensions of the polymers on the shear rate γ at 25 °C (for explanation of symbols, see Fig. 1)

subsequently rupture and new ones are formed, while the system displays a pseudoplastic character.

Change in particle polarizability with the hydrolysis degree of copolymer

The critical strain of a fully developed chain structure in the ER system can be estimated by the bulk polarization theory [12, 18]. Thus the relative viscosity, η/η_c, of particle suspension, where colloidal and thermal forces acting on particles are negligible in comparison with the polarization forces depends only on a volume fraction of the solids

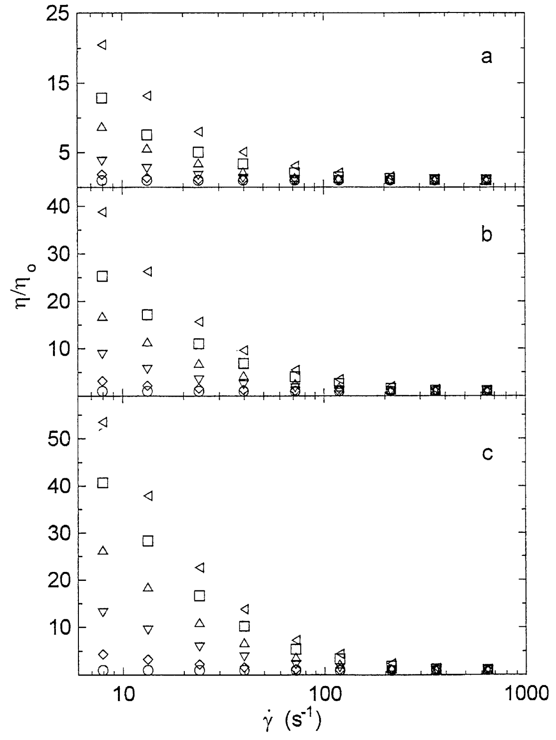


Fig. 3 Dependence of the viscosity ratio η/η_0 on the shear rate γ for the suspensions of the polymer X-793 at 25 °C. Concentration of the polymers (wt%): (a) 5, (b) 10, (c) 20 (for the explanation of symbols, see Fig. 1)

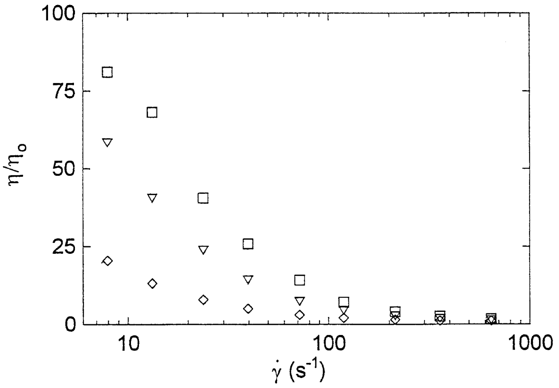


Fig. 4 Dependence of the viscosity ratio η/η_0 on the 5 wt% suspensions of the polymer X-973 at the field strength 2.5 kV mm^{-1} on the shear rate γ. Temperature (°C): (◇) 25, (▽) 65, (□) 85

and the dimensionless Mason number

$$Mn = \eta_c\gamma/2\varepsilon_0\varepsilon_c(\beta E)^2 \qquad (2)$$

characterizing the relation of viscous and polarization forces. Here, η_c is the continuous phase viscosity, ε_0 is the permittivity of the free space, ε_c is the permittivity of the

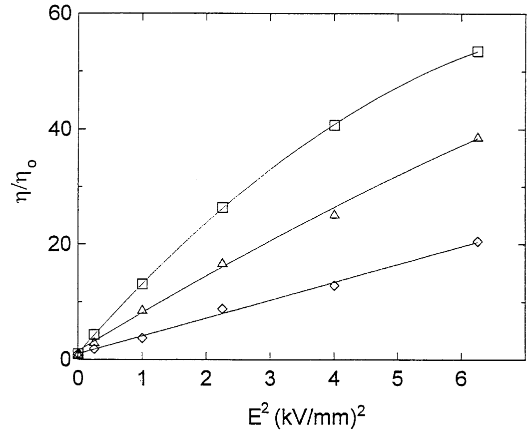


Fig. 5 Dependence of the viscosity ratio η/η_0 vs. E^2 of the polymer X-973 at the shear rate 7.93 s^{-1} at 25 °C. Concentration of the polymer (wt%): (◇) 5, (△) 10, (□) 20

continuous phase, γ is the shear rate and E is the applied electric field strength. The particle dipole coefficient $\beta = (\varepsilon_p - \varepsilon_c)/(\varepsilon_p + 2\varepsilon_c)$ is a measure of particle polarizability in the electric field relative to that of the continuous phase. The dependence of η/η_c on Mn was experimentally verified for a wide range of field strengths and shear rates [12].

We found that, similarly to the viscosity ratio η/η_0 at the lowest shear rate used, permittivity ε_p as well as the particle dipole coefficient β increased with the diol content in the samples (Table 2, Fig. 7), which indicated increasing polarizability of the particles. Using these data, the log–log plot of the relative viscosity, η/η_c, of 5 wt% suspensions as a function of the Mason number shows (Fig. 8) that the results obtained at different field strengths and shear rates can be reduced for each sample to a single descending straight line with slope s_{Mn} which, at some critical Mn^* value, takes a horizontal course at a constant viscosity η_∞.

The absolute magnitude of the slope $|s_{Mn}|$ of the linear region at $Mn < Mn^*$ increased with the diol content in the copolymer from 0.08 for a non-hydrolyzed sample (G-60) to 0.91 for a sample with the highest hydrolysis degree (X-793) (Table 2). It seems that $|s_{Mn}|$ converges to unity, a value reported for suspensions of hydrated

Fig. 6 Micrographs of 10 wt% suspension of the polymer X-794 at 25 °C: (a) before and (b) after application of electric field strength $E = 1$ kV mm^{-1}

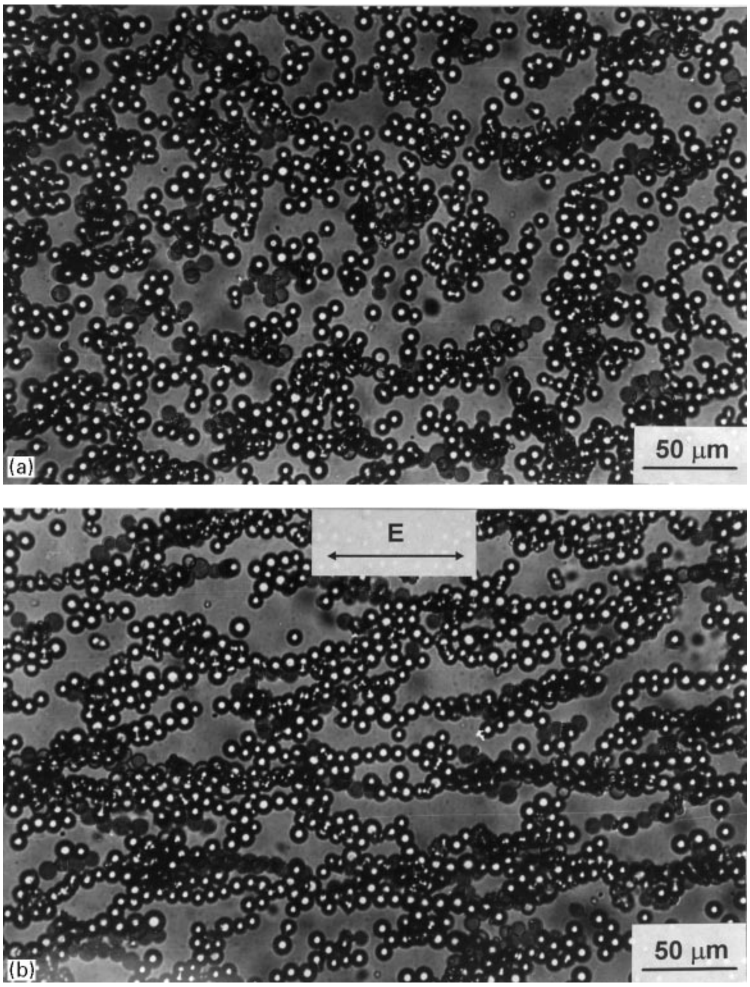


Table 2 Permitivity ε_p, particle dipole coefficient β of the polymers and the slope of curves $|s_{Mn}|$ in Fig. 8 for polymer particle at 25 °C

Polymer	ε_p	β	$\lvert s_{Mn}\rvert$
G-60	4.3	0.18	0.08
X-796	4.4	0.19	0.11
X-795	5.2	0.25	0.32
X-794	7.1	0.37	0.56
X-793	10.4	0.50	0.91

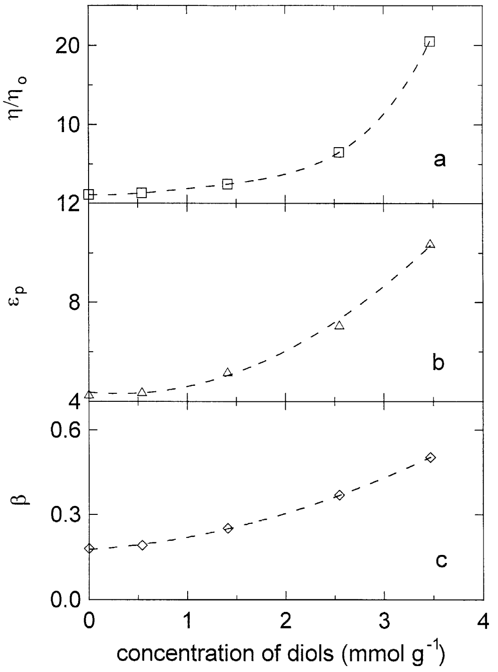


Fig. 7 Dependence of (a) viscosity ratio η/η_0, (b) particle permitivity ε_p, and (c) particle dipole coefficient β on the diol content at $\gamma = 7.93\ s^{-1}$ for 5 wt% suspension of the polymer X-793 at 25 °C

poly(methacrylate) particles in chlorinated hydrocarbon oil [12].

From Eq. (2), critical shear rate γ_{cr} as a function of Mn^* and particle dipole coefficient at a constant electric field strength can be expressed as

$$\gamma_{cr} = K\,Mn^*\,\beta^2 \tag{3}$$

where $K = 2\ \varepsilon_0\varepsilon_c E^2/\eta_c$. A slight decrease in Mn^* from about 3 to 2 upon increasing the hydrolysis degree of the particles (Fig. 8) corresponds to the much higher increase in β^2 (Table 2). As a result, the critical shear rate with the hydrolysis degree of the particles increases, which suggests that when the particle polarizability is higher, a more stiff ER structure arises resistant against disintegration in the flow field.

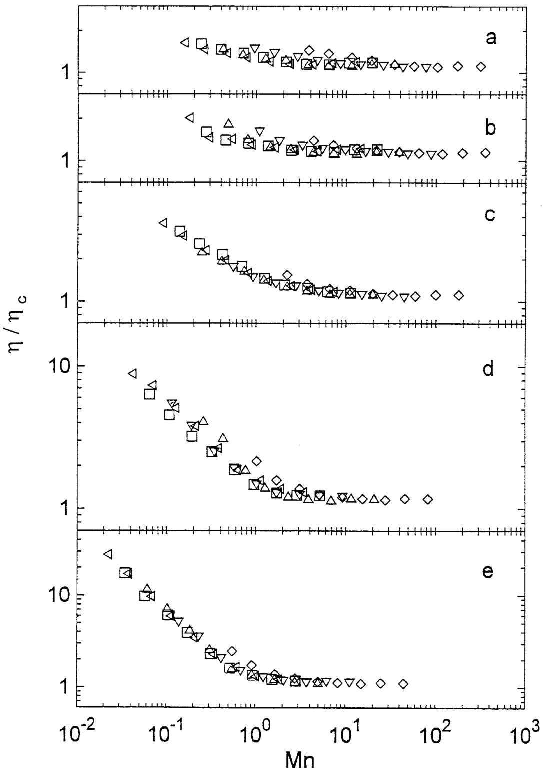


Fig. 8 Dependence of the relative viscosity η/η_c on the Mason number Mn for 5 wt% suspensions of the polymers at 25 °C (for explanation of symbols, see Fig. 1)

The results demonstrated that to obtain a general dependence of η/η_c on the Mason number for particle suspensions with similar hydrodynamic properties and polarizability increasing as a consequence of a change in the chemical structure fails. In view of the fact that the values of particle permittivity obtained by calculation using a linear dependence on the volume fraction need not be quite correct, the applicability of the Mason number as a universal parameter in electrorheology calls still for a further investigation.

Change in particle polarizability with temperature

Similarly to the diol content, also higher temperatures caused a considerable increase in particle polarizability and, on application of the electric field, an increase in the pseudoplastic behavior. Even if permittivity of the oil slightly decreased, permittivity of a fully hydrolyzed sample (X-793) rose more than three times and, as a result, dipole coefficient of particles also increased (Table 3). The plot of the relative viscosity vs. the Mason number suggests that for 5 wt% suspension of fully hydrolyzed

Table 3 Material properties of X-793 at various temperatures

Temperature [°C]	η_c [m Pa 5]	ε_c	ε_p	β
25	200	2.63	10.4	0.50
65	145	2.49	28.0	0.77
85	125	2.43	30.2	0.79

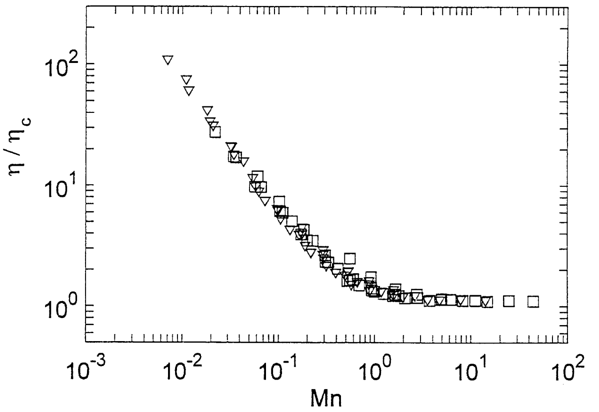


Fig. 9 Dependence of the relative viscosity η/η_c on the Mason number Mn for 5 wt% suspensions of X-793 at 25 °C (□) and 65 °C (▽)

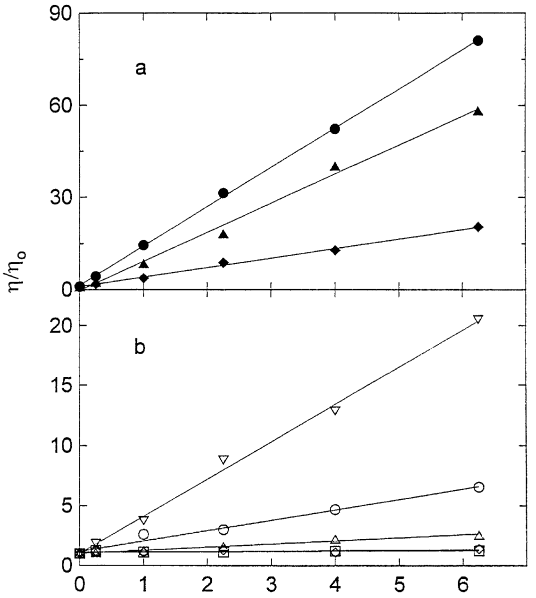


Fig. 10 Dependence of the viscosity ratio η/η_0 of the polymer suspensions on the squared field strength E^2 at the shear rate 7.93 s^{-1}: (a) increasing the polarizability of particles due to temperature (°C): (◆) 25, (▲) 65, (●) 85; (b) increasing the polarizability of particles at 25 °C due to various degrees of hydrolysis of the copolymer. Polymers: (□) G-60, (◇) X-796, (△) X-795, (○) X-794, (▽) X-793

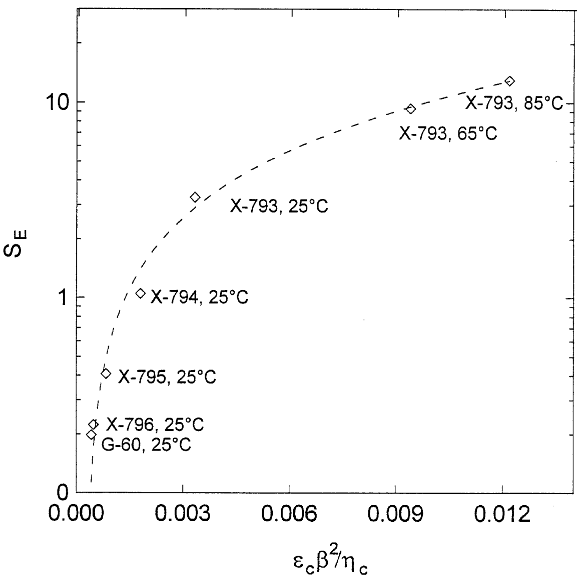


Fig. 11 Dependence of the slope s_E on $\varepsilon_c\beta^2/\eta_c$ for various polymers and temperatures

copolymer at 25 and 65 °C (Fig. 9) the ratio between viscous and polarization forces is the only quantity controlling the ER effect, independently of the temperature in this range.

The slope s_E of the plots of η/η_c vs. E^2 at a low shear rate increased with particle polarizability caused both by a higher hydrolysis degree and by higher temperature (Fig. 10). A convex dependence of s_E on the term $\varepsilon_c\beta^2/\eta_c$ proportional to the ratio of the polarization to the viscous forces made a common line for samples with different hydrolysis degrees and at different temperatures (Fig. 11) showing that with increasing polarization of particles an increase in the intensity of the ER effect diminishes.

Conclusion

It was shown that polarizability of suspension particles of macroporous poly[(glycidyl methacrylate)-*co*-(ethylene dimethacrylate)] increased both with hydrolysis (increasing the content of diol groups) of copolymer and with temperature while a change in hydrodynamic behavior of the suspensions under the influence of electric field significantly differed. In the former case, an increase in the $|s_{Mn}|$ in the range of $Mn < Mn^*$ characterizes increasing pseudoplasticity of the system. Under these circumstances, the Mason number could not reduce viscosities of suspension of particles with different dipole moments at different pseudoplasticity to a single curve. However, if polarizability of particles was enhanced by a higher temperature, the flow character of the suspension remained unchanged and the plots η/η_c vs. Mn at different dipole moment of particles provided a common line.

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