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ORIGINAL CONTRIBUTION

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Thickening effect of dispersions of ethyl acrylate-methacrylic acid copolymer prepared by different polymerization routes

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Abstract Thickening of latices (particle diameters 105, 157 and 221 nm) by model dispersions of ethyl acrylate-methacrylic acid copolymer (15 wt.% of the acid) prepared by both non-seeded and seeded semicontinuous emulsion copolymerizations was investigated. Using viscometry and dynamic and steady shear measurements, we found that the thickening effect of the dispersions strongly depends on their particle structure and the intensity of interactions between the components in the system. In weakly interacting systems (lower latex concentrations, large latex particles) the thickening effect of the dispersions is controlled by effective volume fraction of swollen particles. This leads to a higher viscosity of systems thickened by more swollen (less crosslinked) particles obtained by the non-seeded process. On the other hand, in strongly interacting systems (high latex concentrations, small latex particles) lower deformability of more crosslinked particles prepared by the seeded process causes a higher flow resistance of the systems thickened by this dispersion.

Key words Latices – dispersions – ethyl acrylate-methacrylic acid copolymers – thickening – rheology

Introduction

Dispersions of ethyl acrylate-methacrylic acid copolymers are often used to control rheological properties of various latex systems. It is well known that even a small amount of such materials increases the viscosity of a latex by several orders of magnitude. At the same time, a strong pseudoplasticity, yield stress and thixotropy were also observed [1, 2]. This effect is supposed to result from changes in structure of the dispersion particles of the thickening agent on neutralization. Due to electrostatic repulsions between ionized carboxylic groups attached to polymer chains, particles of original acid dispersions swell or, if the acid content is higher, dissolve.

The thickening mechanism of these materials has not been fully understood yet. It is supposed that at relatively low acid content swollen particles significantly increase the volume occupied by dispersion phase which enhances interactions between components of the system [1]. In the case of a higher acid content when the copolymers molecularly dissolve, bridging flocculation or mechanism resembling volume restriction flocculation has been proposed to explain experimental results [1, 3].

When investigating the thickening effect of dispersion of the copolymer containing 15 wt. % of methacrylic acid, prepared by semicontinuous emulsion polymerization, it was assumed that the structure of the particles is homogeneous and that they swell as a whole on alkali addition [3]. Further research on this material, however, indicated that the structure of the particles is more complicated: they were found to be heterogeneous, consisting of agglomerates of chemically crosslinked subparticles [4, 5].

Crosslinking of the constituent copolymer is obviously caused by chain transfer reactions occurring in radical copolymerization of ethyl acrylate [6]. Hence, one could expect that swelling of the particles or subparticles which plays an important role in thickening mechanism of the material would depend on polymerization route. A study of the influence of this factor on the thickening effect of model ethyl acrylate–methacrylic acid copolymers was the object of this work.

Experimental

Materials and methods

Both dispersions of ethyl acrylate – 15 wt. % methacrylic acid copolymers (EM dispersions) and electrostatically stabilized latices of ethyl acrylate – 1 wt. % acrylic acid copolymers were prepared by semicontinuous emulsion copolymerizations with a monomer emulsion feed. Polymerizations were carried out in a 3-l stainless steel reactor under nitrogen atmosphere at 80 °C using the ammonium peroxodisulfate-sodium disulfite initiator system and Disponil AES 60 (Na alkylaryl polyglycol ether sulfate, Henkel) as an emulsifier. Emulsions of technical grade ethyl acrylate (Chemical Works, Sokolov, Czech Republic) with methacrylic acid (Roehm, Darmstadt, FRG) or acrylic acid (Chemical Works, Sokolov, Czech Republic) were fed into the reactor at a constant rate during 3h. After polymerization, the solid content in the EM dispersions and latices was 25 and 50 wt. %; pH was 1–2.

EM-N and EM-S dispersions were prepared by non-seeded and seeded processes, respectively, which provide particles of different structure. In the former case, the emulsifier was used in the polymerization (Table 1). In the latter case, a small amount of the EM-N dispersion particles without any emulsifier was used (Table 1). The z-average of hydrodynamic diameters of dispersion particles measured by autocorrelation spectroscopy of scattered light (Nano-Sizer, Coulter Electronics, Ltd., England) were 103 nm (EM-N) and 230 nm (EM-S dispersion), respectively (Table 2). Using scanning electron microscopy it was found that EM-N dispersions contained particles of a relatively narrow distribution of particle size while the EM-S particle distribution was slightly bimodal [5]. On alkali addition, the particles swelled and partly disintegrated; as inferred from changes in particle size of dispersions obtained after alkali addition and recovery of their latex character by careful acidification (with acetic acid to pH = 3.6–3.8, see [5] for details), the extents of particle disintegration of both EM dispersion did not differ significantly.

The lattice denoted as L 100, L 160, and L 220 were polymerized according to recipes leading to different particle size (Tables 1 and 2). In their preparation, concentration of low-molecular-weight substances were controlled to reduce differences in ionic strength of dispersion medium between individual materials.

Standard samples of EM dispersions were obtained by removing low-molecular-weight salts by dialysis (Dialysierschlauch Kalle AG, Wiesbaden, FRG) against twice distilled water until constant conductivity was attained. The content of acid groups in the copolymers was determined by conductometric titration with NaOH (OK 104

Table 2 z-Average particle diameters $\bar{d}$ of EM dispersions and latices. $[\eta]_L$ is intrinsic viscocity of L 100, L 160 and L 220 latices after alkali addition

	EM-N	EM-S	L 100	L 160	L 220
$\bar{d}$, nm	103	230	105	157	221
$[\eta]_L$	—	—	8.51	7.35	6.25

Table 1 Polymerization recipes (in g) for ethyl acrylate-methacrylic acid copolymer dispersions prepared by non-seeded (EM-N) and seeded (EM-S) polymerizations and ethyl acrylate-acrylic acid latices L 100, L 160 and L 220 of different particle size

	EM-N	EM-S	L 100	L 160	L 220
Reactor charge					
Water	400	400	400	200	200
Disponil AES 60	2.6	0	26	13	0
ammonium peroxodisulfate	2.0	0	0	0	0
sodium disulfite	0	0	1.0	1.0	1.0
seed latex	0	40*	0	0	0
Monomer emulsion feed					
water	800	800	360	560	560
Disponil AES 60	26	26	26	39	52
ammonium peroxodisulfate	2.0	4.0	6.0	6.0	6.0
ethyl acrylate	340	340	792	792	792
methacrylic acid	60	60	0	0	0
acrylic acid	0	0	8.0	8.0	8.0

* EM-N

conductoscope, Radelkis, Hungary). The amount of soluble polymer material in EM dispersions, determined by static light scattering analysis of the supernatant obtained after neutralization of the copolymers and sedimentation of swollen particles (Ultracentrifuge Beckmann L8-55, 1500 rpm, 2 h), was less than 1% of the total polymer material. Its influence on the behavior of the systems was neglected.

Samples for measurements were prepared by addition of a calculated amount of standard NH_4OH solution to originally acid materials. An excess amount of alkali was added so that the concentration ratio of NH_4OH to acid groups was 1.6. pH of the samples (PHM64 digital pH-meter, combined G 2321 electrode, Radiometer, Copenhagen) was 9.4–9.6. The mixtures were stable without any tendency to flocculation or phase separation in the period of several weeks. All the measurements were performed at 25°C, 24 h after sample preparation.

Viscometry

The hydrodynamic volume of swollen neutralized EM dispersion particles was characterized by intrinsic viscosity, $[\eta]$, obtained by extrapolation of η_{sp}/c values measured in a Ubbelohde dilution viscometer to zero concentration of dispersion particles ($c = 0$). The specific viscosity $\eta_{sp} = (\eta - \eta_o)/\eta_o$, where η is the viscosity of a dispersion system and η_o of continuous medium. Aqueous solutions of NH_4OH (pH = 9.5) were employed for dilution. The influence of electrostatic interactions between ionized carboxylic groups on the expansion of the particles was reduced by NaCl addition.

Viscosity of less concentrated mixtures was measured using an Ostwald capillary viscometer. The hydrodynamic volume of latex particles was characterized by their intrinsic viscosities $[\eta]_L$ obtained by linear extrapolation of $\phi/\ln \eta_r$ to zero volume fraction ϕ of the latices according to the Mooney equation [7]

$$\eta_r = \exp\{[\eta]_L \cdot \phi/(1 - \phi/\phi_C)\} , \tag{1}$$

where η_c is the volume fraction at which viscosity reaches an infinite value (the volume fraction at maximum packing). Relative viscosity $\eta_r = \eta/\eta_o$ was measured at volume fractions in the range 0.03–0.30. The densities of dispersions were determined pycnometrically.

Rheological measurements

Rheological experiments were performed using a cone-plate rotational rheometer Haake CV 20 N (Haake, FRG). The diameters of the cone and plate were 19.6 mm, the gap angle was 4°. Dynamic measurements were carried out in the linear viscoelastic region (shear strain 0.03–0.08, amplitude 0.3°). Flow curves were measured at a continuously increasing shear rate up to $200\,s^{-1}$ during 2 minutes followed by its decrease to zero in the same time interval. The corresponding flow curves were practically the same, indicating only a small influence of time effects on the flow behavior. The yield stress τ_o was obtained by the best fit of the experimental data using the Herschel-Bulkley equation [8],

$$\tau = \tau_o + \eta_a \cdot \dot{\gamma}^n , \tag{2}$$

where τ is the shear stress, η_a is the apparent viscosity, and n characterizes pseudoplastic decrease in viscosity of the system. The measurements were performed after stabilization of the samples for 5 min in the viscometer.

Results and discussion

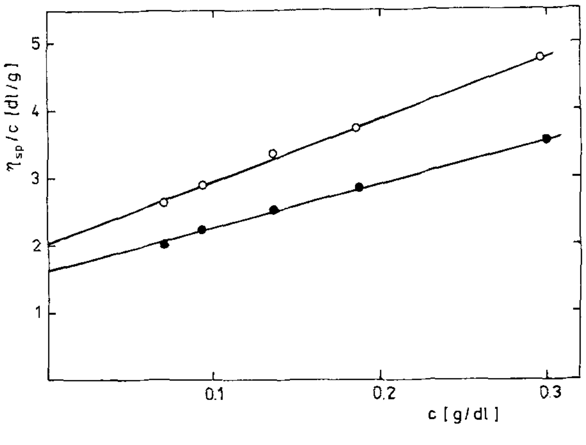
Characterization of swollen EM dispersion particles

Swelling of EM dispersion particles on alkali addition was sensitively reflected in their hydrodynamic volume and the volume swelling ratio ϕ_s/ϕ_o. Considering swollen particles as rigid non-draining spheres (hard spheres) the following equation holds [9]

$$\phi_s/\phi_o = \rho[\eta]/2.5 , \tag{3}$$

where η_s is the volume fraction of swollen particles, ϕ_o is the volume fraction of original (acid) particles of density ρ (1.15 g/cm^3), $[\eta]$ is the intrinsic viscosity of swollen EM dispersion particles and 2.5 is Einstein's theoretical value.

Fig. 1 Plot of the reduced viscosity η_{sp}/c vs concentration c of the EM-N (○) and EM-S dispersions (●) at 0.01 M NaCl. pH = 9.4–9.6



Experimental plots of η_{sp}/c vs c were linear even at the lowest NaCl concentration (0.01 M) used (Fig. 1), indicating that determinations of $[\eta]$ were not influenced by the polyelectrolyte effect. The high values of intrinsic viscosities and volume swelling ratios (Table 3) show significant swelling of particles after alkali addition. Due to the polyelectrolyte character of the material, however, swelling of particles rapidly decreased with NaCl concentration (Table 3).

It can be seen (Table 3) that swelling of EM-N dispersion particles prepared by non-seeded polymerization was higher than that of EM-S particles prepared by the seeded process. Practically the same differences, ca 25% in $[\eta]$ of both materials in the whole range of NaCl concentrations used, obviously indicated that swollen EM-N dispersion particles were less compact than the EM-S ones.

Thickening effect at latex concentration 5–25 wt. %

Viscosity of mixtures containing a fixed amount of the latices progressively increased with concentration of EM dispersions which indicated a pronounced thickening effect of these materials (Fig. 2). The intensity of the effect strongly depended on the latex concentration and latex particle size. At the concentration 5–15 wt. % of latices with small particles (L 100 and L 160), the viscosity of the mixtures with the EM-N dispersion was higher than if the EM-S dispersion was used (Figs. 2a, b). However, if the content of the latices was higher (20 and 25 wt. %), a different behavior occurred: viscosity of the mixtures containing the EM-N dispersion was lower (Fig. 2c). On the other hand, for latex with the largest particles (L 220), the viscosity of mixtures with the EM-N dispersion exceeded that with the EM-S for all latex concentrations.

The pronounced influence of the latex particle size on the thickening effect of the EM dispersions is apparent from Fig. 3. At 5 wt.% of latices only a slight decrease in viscosity with increasing latex particle size can be seen (Fig. 3a) while at higher latex concentrations (15 and 25 wt %) the viscosity of thickened latices initially decreased very rapidly and then leveled off (Figs. 3b, c). A higher thickening effect of the EM-N compared to the EM-S dispersion at latex concentrations 5–15 wt.% (Fig. 3a, b) and opposite behavior at 25 wt.% of L 100 and L 160 latices can be seen (Fig. 3c).

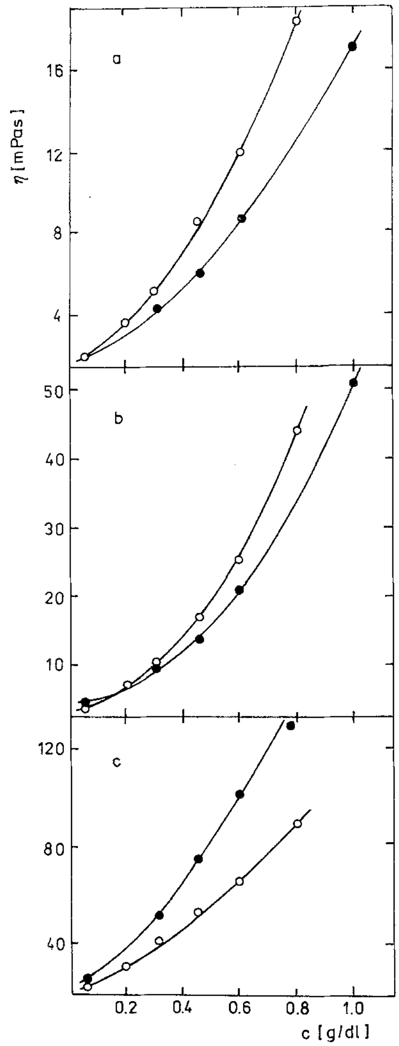


Fig. 2 Dependencies of viscosity η on concentration c of dispersions EM-N (○), EM-S (●): a) 5, b) 15 and c) 25 wt.% of latex L 160. pH = 9.4–9.6

The observed decrease in viscosity with latex particle size seems to result from a smaller specific surface area of

Table 3 Intrinsic viscosities $[\eta]$ and volume swelling ratios ϕ_s/ϕ_o of EM dispersions at various NaCl concentrations after alkali addition. (ϕ_s and ϕ_o are volume fractions of swollen and of original acid particles, resp.)

NaCl	$[\eta]$, dl/g		ϕ_s/ϕ_o		$[\eta]_{EM-N}/[\eta]_{EM-S}$
concentration	EM-N	EM-S	EM-N	EM-S	
0.01 M	2.05	1.65	94.3	75.9	1.24
0.04 M	1.20	0.96	55.2	44.2	1.25
0.20 M	0.90	0.77	41.4	35.4	1.17
0.80 M	0.39	0.31	17.9	14.3	1.26

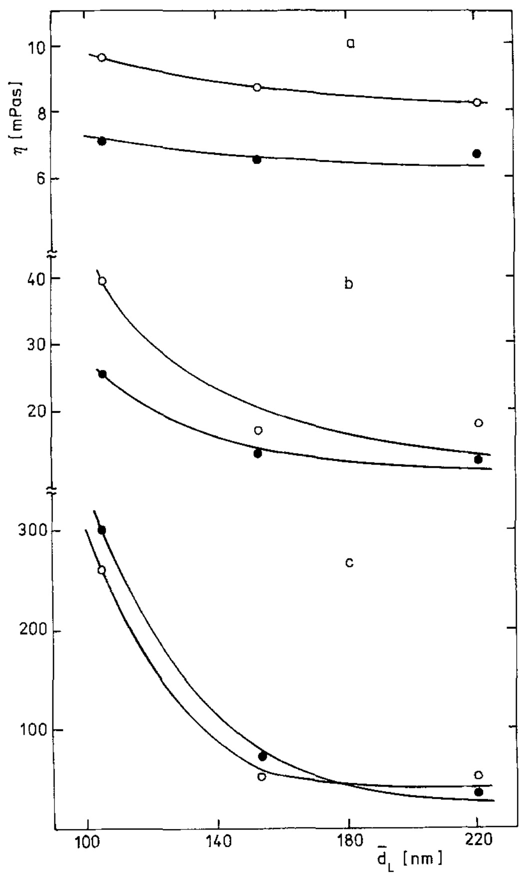


Fig. 3 Dependences of viscosity η on the latex particle diameter $\bar{d}_L$ 0.45 wt.% of EM-N (○) and EM-S (●) dispersions, concentrations of latices: a) 5, b) 15 and c) 25 wt.%. pH = 9.4–9.6

large particles. This lowers the contribution of electrical double layer to hydrodynamic volume of particles, as reflected in a decrease in $[\eta]_L$ with particle size (Table 2), and reduces interactions between particles in the system. Consequently, the high viscosity of the thickened latices and its rapid decrease with particle size (Fig. 3b, c) indicate strong interparticle interactions and low viscosity and its leveling at the highest particle size corresponds to weaker interactions between particles. Hence, a more pronounced thickening effect of the EM-N dispersions seems to occur in weakly interacting systems while the EM-S dispersion is a more efficient thickening agent in strongly interacting systems.

Swollen particles of EM dispersion resemble chemically crosslinked microgels [3]. Taylor et al. [10, 11] and Carnali et al. [12] investigating aqueous dispersions of modified starch, cellulose and crosslinked poly (acrylic acid) and Wolfe et al. [9, 13] in his study of dispersions of crosslinked poly (methyl methacrylate) found that flow properties of these systems at low concentrations are controlled by effective volume fraction of swollen particles ϕ_{eff}. Considering microgel particles as hard spheres, ϕ_{eff} was expressed as [12, 13]

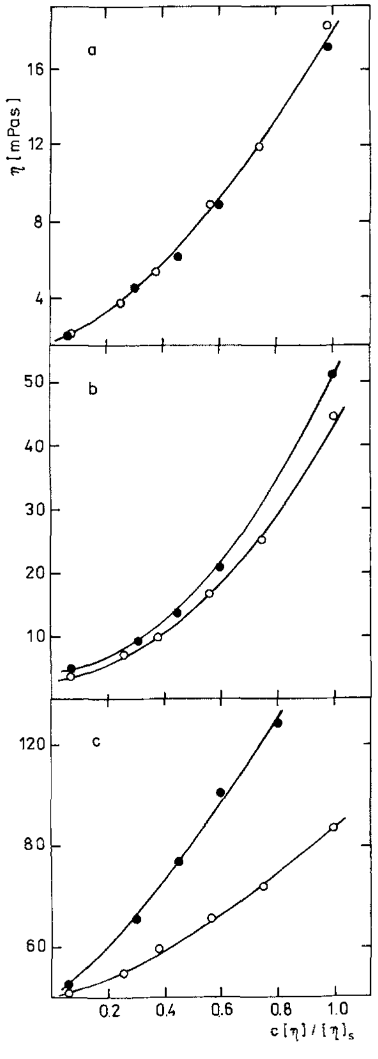
$$\phi_{eff} = c[\eta]/2.5 \tag{4}$$

Due to the fact that intrinsic viscosities of EM dispersions and viscosities of the mixtures were not measured at the same ionic strength, we did not relate our experimental results to the volume of hard spheres but, instead, to the volume of seeded particles proportional to $[\eta]_s$. Thus the reduced concentration of swollen particles was defined as

$$\phi_r = c[\eta]/[\eta]_s \,. \tag{4}$$

It was shown (Fig. 4a) that ϕ_r scales the viscosity data up

Fig. 4 Dependences of viscosity η on reduced concentration of swollen particles $\phi_r = c[\eta]/[\eta]_s$ of dispersions EM-N (○), EM-S (●): a) 5, b) 15 and c) 25 wt.% of latex L 160. pH = 9.4–9.6



to 10 wt. % of a latex L 100 and L 160 very well. The same behavior was found for latex L 220 but, in this case, in the whole range of its concentrations. The results suggest that under these conditions the thickening effect is controlled primarily by the volume occupied by swollen EM dispersion particles. Due to this fact, the high viscosity of the systems thickened with the EM-N dispersion (Fig. 2a, b) results from a higher volume of its swollen particles.

On the other hand, at 15 and more strongly at 20 and 25 wt.% of latices L 100 and L160, when the thickening effect of the EM-S dispersion exceeds that of EM-N, the effective volume fraction of swollen particles as a universal scaling parameter failed; using this variable even more pronounced differences between viscosities of the systems appeared (Fig. 4b, c).

Thickening effect at latex concentration 35 wt. %

A stronger thickening effect of the EM-S dispersion at higher latex concentrations was revealed by the dynamic and steady shear measurements on mixtures containing 35 wt.% of the latices. Figure 5 shows a typical dependence of elastic G′ and loss G″ moduli, and yield stress τ_0 of latex L 160 on concentration of the EM dispersion which exhibited a rapid growth. Higher thickening effect of the EM-S dispersion than that of the EM-N one is apparent in the whole range of their concentrations (Fig. 5). With increasing latex particles size the effect of EM dispersion weakened as in the case of less concentrated systems (Fig. 6); however, the EM-S dispersion exhibited a more pronounced thickening effect even for latex L 220 with the largest particles.

High values of viscosity, yield stress and dynamic moduli indicate a high filling up of space by the dispersion particles [14]. Under these conditions, strong interparticle interactions compress the electrical double layer surrounding latex particles and, simultaneously, compress swollen deformable particles of EM dispersions. We suppose that in this case the flow properties of the systems depend on the resistance of swollen EM dispersion particles to deformation in the shear field like in the case of concentrated microgel dispersions [9, 12, 13].

Fig. 5 Dependences of loss G″ modulus (○), storage G″ modulus (△) at angular frequency $\omega = 9.2\ \mathrm{s}^{-1}$, and yield stress τ_0 (□) on concentration c of EM-N (empty) and EM-S (full) dispersions. 35 wt.% of L 160 latex. k = 0 (G″), 0.3 (G″) and 0.9 (τ_0). pH = 9.4–9.6

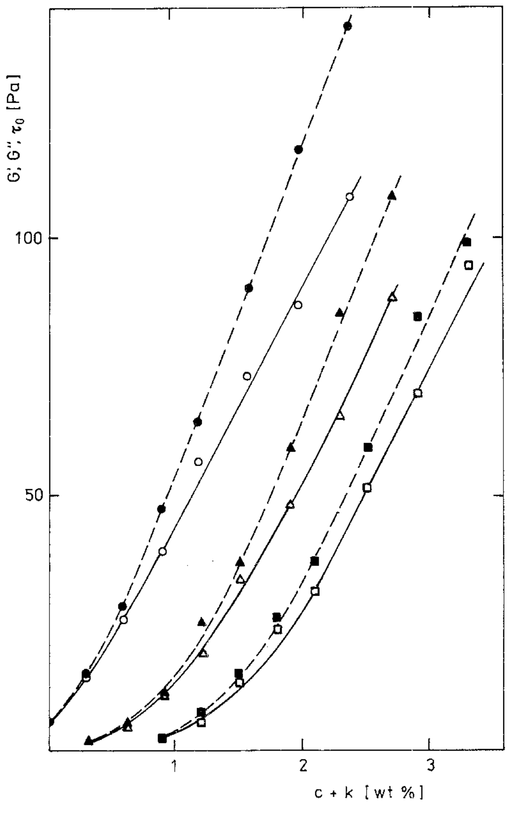
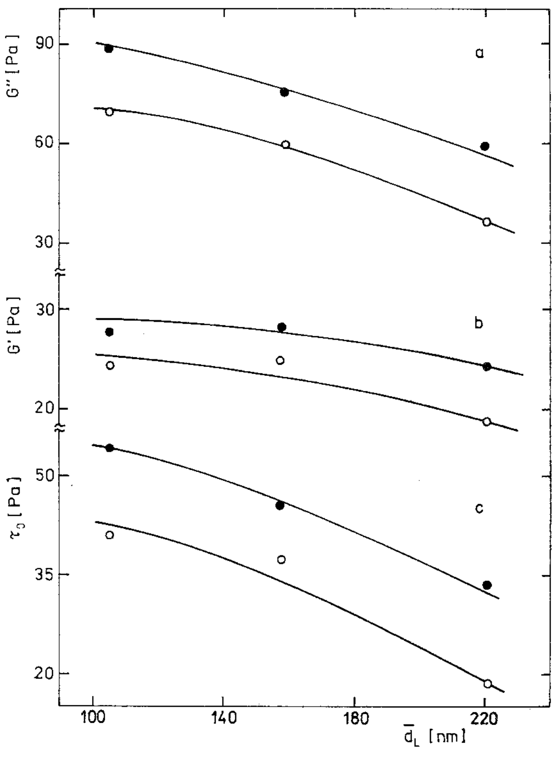


Fig. 6 Dependence of a) loss G″, b) storage modulus G′ (at $\omega = 9.2\ \mathrm{s}^{-1}$), and c) yield stress τ_0 on the latex particle diameter $\bar{d}_L$. 1.35 wt. % of EM-N (○) and EM-S (●) dispersions, latex concentration 35 wt. %. pH = 9.4–9.6



As both particle swelling and resistance of swollen particles to deformation depend on the degree of their crosslinking, our results suggest that during non-seeded and seeded polymerizations particles of different crosslinked structure arise. It could be assumed that in the case of EM-N dispersion, the non-seeded process provides less crosslinked particles. On the other hand, due to crosslinking reactions occurring concurrently with particle growth, seeded particles are more crosslinked. Hence, swollen particles of the EM-S dispersion should be more compact than non-seeded one which is reflected in their smaller hydrodynamic volume and lower thickening effect at lower latex concentrations. However, if the latex concentration is higher, a lower deformability of more crosslinked particles in the shear field enhances the flow resistance of the system.

Conclusion

We have demonstrated that thickening effect of dispersions of ethyl acrylate – methacrylic acid copolymers may be strongly affected by the particle structure obtained in given polymerization route and also influenced by the intensity of interactions in the thickened system. To confirm the decisive role of these factors experiments with particles of more defined crosslinked structure are in progress in our laboratory.

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