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SYNTHESIS AND RELEVANT RHEOLOGICAL PROPERTIES OF LATEXES

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Dedicated to the memory of Professor Anton Šebenik

ABSTRACT

The emulsion polymerisation of styrene/2-ethylhexylacrilate/acrylic acid polymer particles with narrow particle size distribution is described. By syntheses, the weight ratio between styrene and 2-ethylhexylacrilate was varied in order to obtain particles with different viscous and viscoelastic properties. These parameters were measured with Carry - med S.L.C. rheometer 500. The results show that particles containing more 2-ethylhexylacrilate exhibit a higher viscosity level and higher storage and loss moduli than particles containing more styrene.

INTRODUCTION

Emulsion polymerisation is a technologically and commercially important reaction used to produce synthetic polymers and latexes for a wide range of applications including water-borne coatings, adhesives, sealants, synthetic rubbers and many others [1]. Emulsion polymerisation is a method of producing latexes with desired particle size and its distribution, molecular weight and its distribution, composition, morphology, film-forming properties etc. [2]. One of the most important characteristics of latexes from the theoretical and practical point of view are their rheological properties. Rheological measurements often give important information about the structure of latexes. By rheological measurements the sample is subjected to shear stress which causes deformation of polymer particles. The extent of deformation depends on the stress and chemical structure of particles. In our case, particles containing more 2-ethylhexylacrilate (2-EHA) are softer and consequently more deformable than particles containing more styrene (S). That is the reason why latexes exhibit viscoelastic properties. This term is used to define the liquids that behave as ideal liquids but under low stress conditions they behave like solids exhibiting elastic recovery. Given sufficient stress, the sample undergoes irreversible deformation and flows. Our work was focused on the rheological behaviour of latexes as a function of their chemical composition, reflected by oscillation measurements.

EXPERIMENTAL

1. Synthesis of latex

A 1.5-litre, 3-neck glass reactor with condenser, peristaltic pump and flow-variable pump was used. The reactor was dipped into a temperature controlled water bath at 80^0C. The procedure used for the “in situ” seeded emulsion was as follows: 2 g of emulsifier was dissolved in 260 g of water at 60^0C. Then 0.4 g ammonium persulfate (APS) was added and the reactor was heated to 80^0C. 20 g of preemulsion was added with the composition shown in Table 1. After 10 minutes of reaction at 80^0C the remaining preemulsion and 100 g of 1-% solution of APS were simultaneously and continuously pumped for 4 hours. After that the latex was neutralised with a 25 % solution of ammonia to achieve pH 8.0 ± 0.1 and then cooled down to room temperature.

The variable in our experiments was the weight ratio between styrene and 2-EHA. The measured characteristics are presented in Table 2.

Table 1. Composition of preemulsion.

Component	Mass (g)
Water	200
Emulsifier	20
Acrylic acid	15
Styrene	242, 297, 352, 407
2-EHA	308, 253, 198, 143

Figure available in printed version only

Figure 1. Scanning electron micrograph of latex particles 4.

2. Properties of latexes

a. Particle size

The particle size was measured using the Malvern Autosizer IIC. The size range of the apparatus is in a region from 3 nm to 3 μm. The instrument produces a He-Ne laser wave of wavelength 633 nm. The scattering angle is fixed at 90^0. The pictures of samples were made by electronic microscope Jeol 300.

b. Glass transition temperature (T_g)

The values of glass transition temperature were obtained using Perkin Elmer DCS 7. The heating rate was 20 ^{0}C/min and second heating was considered. The weight of samples was 20 mg. Before measurement samples were dried at 1 hour 105 ^{0}C.

Table 2. Properties of latexes.

	Latex			
Characteristic	1	2	3	4
Weight ratio S/2-EHA	44/56	54/46	64/36	74/26
Particle size (μm)	0.22	0.22	0.23	0.23
Glass transition temperature(^{0}C)	-3	11	33.7	52.8
Polydispersity	1.06	1.05	1.03	1.04
Storage modulus, G' (Pa)	240	162	122	73
Loss modulus, G'' (Pa)	28	20	15	8
Phase angle (^{0})	7	7	7	6

b. Rheological properties

Latexes exhibit various degrees of elasticity and viscosity [3-6]. Viscoelasticity is used to describe the rheological properties expressing characteristics from viscous fluids to elastic solids. For a viscoelastic material, shear stress and shear strain are not in phase, but, rather, displaced by a certain phase angle δ. From the knowledge of shear stress τ, deformation γ and phase angle δ, it is possible to completely describe the viscoelastic behaviour of a material by the two mechanical dynamic functions, the storage shear modulus, G', and the loss shear modulus, G''.

The storage modulus G' is given as

$$G' = \frac{\tau_0}{\gamma_0}\cos\delta \qquad (1)$$

where τ_0 and γ_0 are shear stress strain amplitudes, respectively. This quantity represents a measure for the strain energy recoverably stored in the substance. Thus it characterizes the elastic behaviour of the sample.

The loss modulus G'' is given as

$$G'' = \frac{\tau_0}{\gamma_0}\sin\delta \qquad (2)$$

This quantity represents a measure for the energy dissipated as heat and thus lost. It therefore characterises the viscous behaviour of the viscoelastic material.

The loss factor is defined as:

$$\tan\delta = \frac{G''}{G'} \qquad (3)$$

The quantity is proportional to the ratio between the amount of the dissipated and stored energy and hence also between the viscous and the elastic portion of the sample.

From these measurements the dynamic viscosity, η', can be determined in the following manner:

$$\eta' = \frac{G''}{\omega} \qquad (4)$$

Where $\omega = 2\pi\nu$ and ν is the frequency.

The strain amplitudes must be low enough in order not to destroy the structure of the examined sample. To determine the linear viscoelastic region, stress sweep tests are used. The strain amplitudes to which G' and G'' are constant are the maximum permissible amplitudes for the structure to remain undamaged. After that the frequency sweep test is carried out in the region of linear viscoelasticity.

RESULTS AND DISCUSSION

Flow curves, stress sweep and frequency sweep measurements were carried out by Carri - med S.L.C. rheometer 500, using cone and plate geometry (6 cm/2^0) at 20^{0}C. The flow curves of all latexes show slightly pseudoplastic behaviour and latex 1 also shows the slightly thixotropic behaviour. Latexes containing more 2-EHA exhibit a higher yield value. The flow curves are shown in Figure 1.

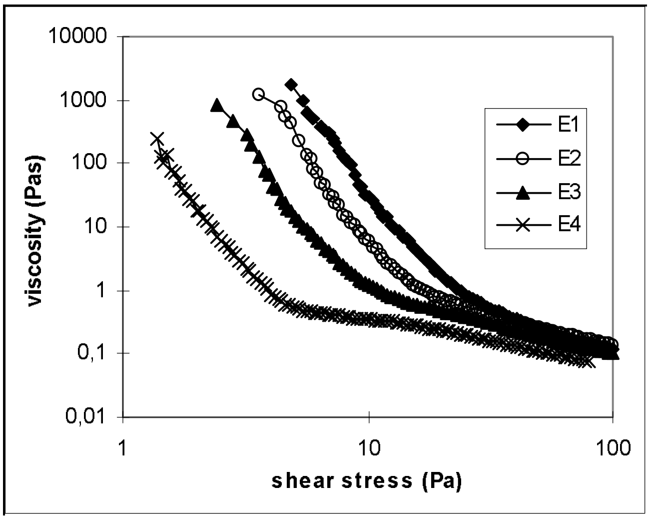

Figure 1. Flow curves of latexes.

Stress sweep measurements

Stress sweep tests were carried out at a constant frequency of 1 Hz. From Figures 2 and 3 it can be seen that the linear viscoelastic region extends from the stress of 2 Pa to the stress of 3 Pa (in this region G', G'' and phase angle δ are constant). The phase angle value in this region is for all samples about 7^0. The latex particles 1 and 2 are soft and elastic (T_g is -3^{0}C and +11^{0}C, respectively) and latex particles 3 and 4 are hard and stiff (T_g is +33.7^{0}C and +52.8^{0}C, respectively). Shear stress deforms polymer particles so that they take the shape of an ellipsoid. The deformation depends on the chemical composition: the more 2-EHA the particles contain, the greater is their deformation. This structure change is reflected in the storage modulus, G', which increases with increasing amount of 2-EHA in the particles. The particles of latex 1, containing 56% of 2-EHA, have G' of 240 Pa in the linear viscoelastic region, but the particles containing 26% of 2-EHA. On the other hand, exhibit in the linear viscoelastic region G' only of 73 Pa.

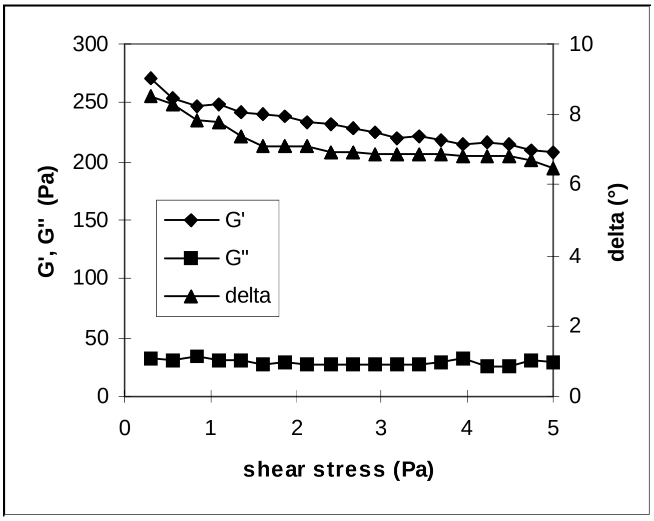

Figure 2. Stress sweep test for latex 1.

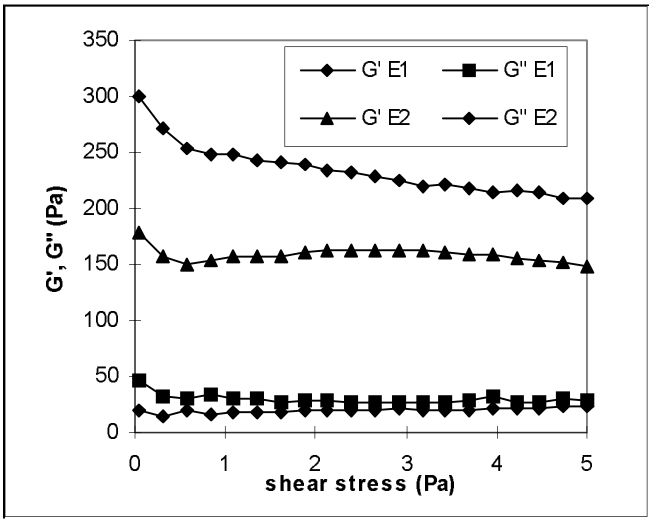

Figure 3. Storage modulus and loss modulus as a function of shear stress for latexes 1 and 2.

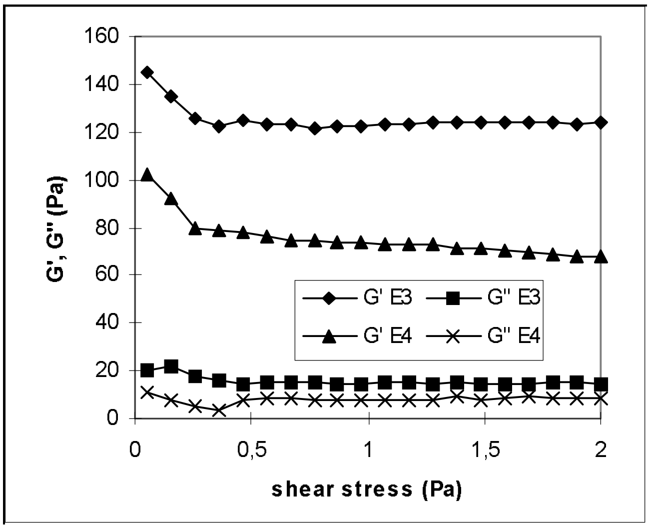

Figure 4. Storage modulus and loss modulus as a function of shear stress for latexes 3 and 4.

Latexes 2 and 3 have the storage moduli of 152 Pa and 120 Pa, respectively (see Figures 3 and 4 for this region). The loss modulus, G'' also increases with the increasing amount of 2-EHA in particles. These results show that the soft particles are able to convert more energy into heat than the hard ones. The phase angle of all latexes is in the range from 6^0 to 7^0.

Frequency sweep measurements

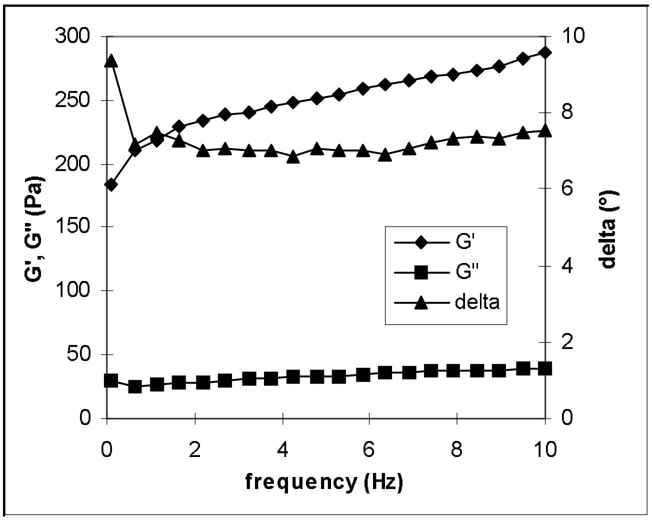

Figure 5. Frequency sweep test of latex 1.

The frequency sweep tests were made in the region of 0.1 to 10 Hz at constant shear strain amplitude of 0.015. G' and G" increase slightly with increasing frequency, but the phase angle remains constant in a wide range of frequencies. Its increase is observed only in latex 4, where the phase angle increases up to 14^0. The measurements are shown in Figures 5, 6 and 7.

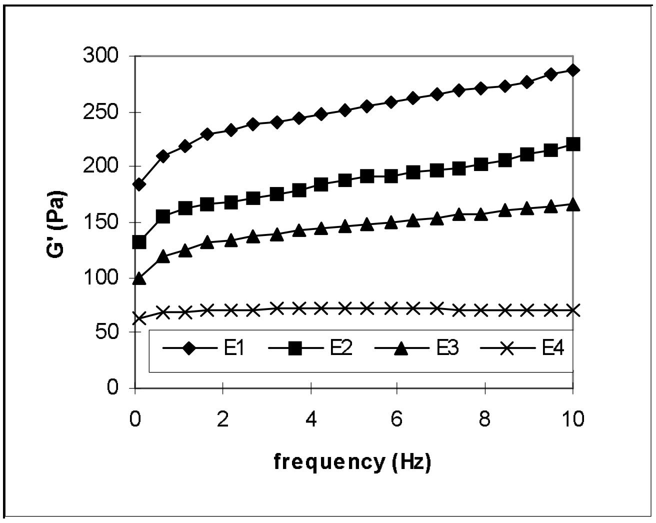

Figure 6. Storage modulus as a function of frequency.

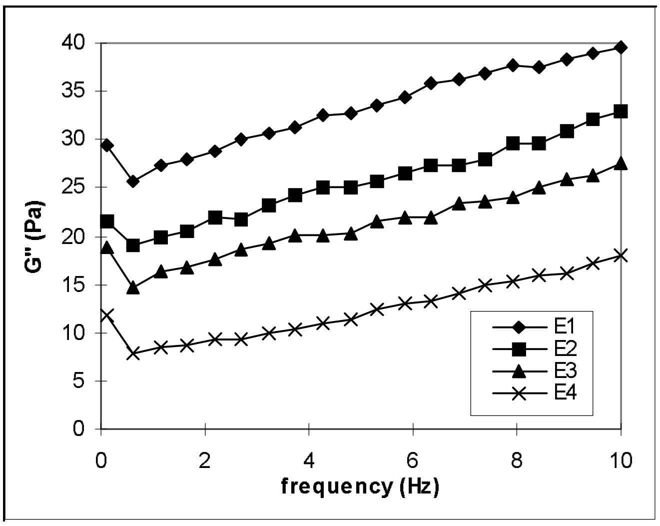

Figure 7. Loss modulus as a function of frequency.

CONCLUSION

Latexes are colloids of elastic polymer particles possessing a very complex structure especially under deformation by shear stresses. Under these conditions elastic particles are deformed and these deformations may be observed by rheological measurement. The rheological behaviour of latex particles strongly depends on their composition. Latex particles containing more styrene are harder and stiffer than particles containing more 2-ehtylhexylacrilate. With increasing stiffness of particles, the storage modulus G' as well as the loss modulus G" decrease, but their ratio remains constant between 8 and 9. These values might be acceptable for commercial latexes. The fraction of styrene in particles that is appropriate for application is up to 55-weight %. Above this concentration, the film-forming properties of films are poor unless coalescing aids are added.

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POVZETEK

Opisali smo postopek za polimerizacijo stirena in 2-etilheksilakrilata v emulziji. Pri polimerizaciji smo dobili delce z ozko porazdelitvijo delcev. Pri sintezah smo spreminjali razmerje stirena proti 2-etilheksilakrilatu. Na ta način smo dobili delce z različnimi viskoznimi in viskoelastičnimi lastnostmi. Te parametre smo izmerili z reometrom Carry - med S. L. C. 500. Rezultati so pokazali, da delci, ki vsebujejo več 2-etilheksilakrilata izkazujejo višjo viskoznost in tudi višjo vrednost akumulacijskega modula in modula izgub.