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Viscoelastic behaviour of butyl acrylate/styrene/2-hydroxyethyl methacrylate/acrylic acid latices thickened with associative thickeners

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Abstract

The rheological behaviour of butyl acrylate/styrene/acrylic acid latices thickened with a hydrophobically modified ethoxylated polyurethane (HEUR) or hydrophobically modified alkali-soluble polyacrylate emulsion (HASE) was investigated. While the pseudoplastic character of frequency dependence of complex viscosity was similar for both thickeners, viscoelastic behaviour, expressed as the ratio of loss and storage moduli, significantly differed, indicating that the HEUR molecules, unlike swollen HASE particles, create a viscoelastic space structure. The increase in hydrophilicity of the particle surface, achieved by incorporation of 2-hydroxyethyl methacrylate (HEMA) monomer into the latex copolymer reduced the viscoelasticity of latices thickened with HEUR, but not of those thickened with HASE. This confirms that adsorption of hydrophobic end-groups on particle surface is important for thickening of latices with HEUR and that a physical network of latex particles interconnected by the thickener macromolecules is formed. *To cite this article: O. Quadrat et al., C. R. Chimie 6 (2003).*

Résumé

On a étudié le comportement rhéologique de latexes de copolymères styrène/acrylate de butyle/acide acrylique, épaissis par un polyuréthane éthoxylé hydrophobiquement modifié (HEUR) ou une émulsion de polyacrylate soluble dans l'alcali, également hydrophobiquement modifié (HASE). Alors que le caractère pseudo-plastique de la dépendance en fréquence de la viscosité complexe était similaire dans les deux cas, le comportement viscoélastique, exprimé comme le rapport des modules de perte et de conservation, diffère de manière significative, indiquant que les molécules de HEUR, à l'inverse des particules de HASE, qui sont gonflées, créent un espace structuré. L'augmentation de l'hydrophilie superficielle des particules de latex copolymère, due à l'introduction du monomère 2-hydroxyethyl méthacrylate (HEMA), induit une diminution de la viscoélasticité dans le cas de

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HEUR, mais pas dans le cas de HASE. Ceci confirme que l'adsorption de groupements terminaux hydrophobes sur la surface des particules joue un rôle important dans le phénomène d'épaississement dans le cas des HEUR, où un réseau physique de particules de latex est formé par les macromolécules d'épaississant. ***Pour citer cet article: O. Quadrat et al., C. R. Chimie 6 (2003).***

1. Introduction

Rheological characterisation is one of the most important methods providing information on suitability of latex materials for practical use. Reliable knowledge of flow parameters is especially required to set the optimum flow properties of thickened latices [1]. At present, excellent results in latex thickening are obtained with associative thickeners based on hydrophobically modified ethylene oxide urethane block copolymers (hydrophobic ethoxylated urethanes, HEUR) or hydrophobically modified alkali-soluble emulsion (HASE) [2,3]. It is assumed that hydrophobic segments of those materials adsorb on the latex and pigment particle surface [4–11]. Consequently, the particles are bridged by thickener macromolecules and the system forms a physical network, which is gradually destroyed after a shear field is applied. Due to the network structure, elasticity of a thickened latex may be expected, which may significantly influence application of this material.

Latices of acrylic copolymers carrying hydrophilic reactive groups are increasingly important as promising materials in the painting industry. Even a small amount of these groups may significantly improve properties of coating films if additional crosslinking with various resins or polyisocyanate proceeds after application. Incorporation of a hydrophilic monomer into the latex copolymer may change adsorption activity of associative thickener and, consequently, the flow or elastic behaviour of the thickened material. In this study, viscoelastic properties of model acrylic latices of copolymers, both with and without 2-hydroxyethyl methacrylate (HEMA), thickened with commercial associative thickeners (HEUR and HASE) produced by Rohm & Haas, are investigated.

2. Experimental

2.1. latices

Two model latices of copolymers of butyl acrylate/styrene/acrylic acid with 0 and 25 wt % of 2-hydroxyethyl methacrylate denoted L0 and L25 with a fraction of solids of ca 50 wt % were prepared by a non-seeded semicontinuous emulsion copolymerisation with a monomer emulsion feed. The polymer recipe and the composition of the monomer feed are given in Tables 1 and 2. Technical-grade monomers butyl acrylate (Rohm, Darmstadt, Germany), styrene (Kaučuk Kralupy, Czech Republic), 2-hydroxyethyl methacrylate (Rohm, Darmstadt, Germany) and acrylic acid (Eastman Sokolov, Czech Republic) were used. Polymerisations were carried out in a glass reactor under nitrogen atmosphere using an ammonium peroxydisulphate–sodium disulphite initiator system and Disponil AES 60 (sodium polyglycol alkylaryl

Table 1
Polymerisation recipe for latices (in grams)

Reactor charge	
Water	200
Sodium disulphite	4
Monomer emulsion feed	
Water	200
Disponil AES 60	52
Ammonium peroxydisulphate	8
Monomers	800

Table 2
Composition of monomer feed (wt %)

Latex	Butyl acrylate	Styrène	HEMA	Acrylic acid
L0	49	49	0	2
L25	36.5	36.5	25	2

ether sulphate, Henkel, Germany) in an amount of 2 wt% of the active component (relative to the monomers) as an emulsifier. Such process guarantees statistical composition of the dispersed copolymer particles [12–14].

Low-molecular-weight salts were removed from latex samples by dialysis (Dialysierschlauch Kalle AG, Wiesbaden, Germany) against ultra-filtrated water (Milli Q) carried out until a constant conductivity was attained.

2.2. Thickeners

The effect of two commercial associative thickeners from Rohm & Haas (Germany), RM 12 W (HEUR) and TT 615 (HASE) has been investigated. No other information was provided by the manufacturer, except the expected rheological properties of the resulting thickened systems given in Table 3.

Capillary viscometry of dilute alkalinized thickeners (Fig. 1) revealed a great difference in intrinsic viscosity $[\eta]$ of these materials (Table 3). The relatively low value of this quantity for HEUR indicates well-dissolved HEUR macromolecules, possibly assembled in flower-like micelles [15]. In contrast, a high intrinsic viscosity of HASE is a result of highly swollen particles. A higher value of the Huggins constant k_H predicts a steeper increase in viscosity with the HASE concentration and the difference between the two thickeners becomes even more pronounced after alkalinization (Fig. 2).

2.3. Latex particle characterisation

The effective hydrodynamic volume of latex particles alkalinized with ammonium hydroxide to pH 8.5–8.8 at infinite dilution (intrinsic viscosity $[\eta]$, Table 4) was obtained by linear extrapolation of $\Phi/\ln \eta_r$ to the zero volume fraction Φ of the latex (Fig. 3) according to the Mooney equation [16]:

$$(1) \quad \eta_r = \exp\{[\eta]\Phi/(1 - \Phi/\Phi_c)\}$$

where Φ_c is the volume fraction of particles at which viscosity reaches the infinite value (the volume fraction at maximum packing of particles). The relative viscosity $\eta_r = \eta/\eta_s$, the ratio of the viscosity of latex η and that of the dispersion medium η_s, was measured with an Ostwald capillary viscometer at a constant low-shear stress $\tau \cong 0.8$ Pa.

Table 3
Characteristics of Rohm & Haas thickeners

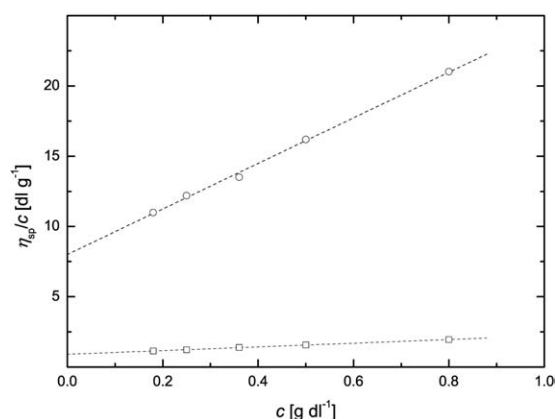| Type	Product	Producer's description	$[\eta]$ (dl g^{-1})	k_H
HEUR	RM-12 W	The most pseudoplastic of the HEUR's, provides excellent low shear thickening efficiency	0.9	1.2
HASE	TT 615	Very efficient at low shear but very thinning at high shear	8.0	2.5

Fig. 1. The dependences of reduced specific viscosity η_{sp}/c on the thickener concentration c. (□) HEUR, (○) HASE.
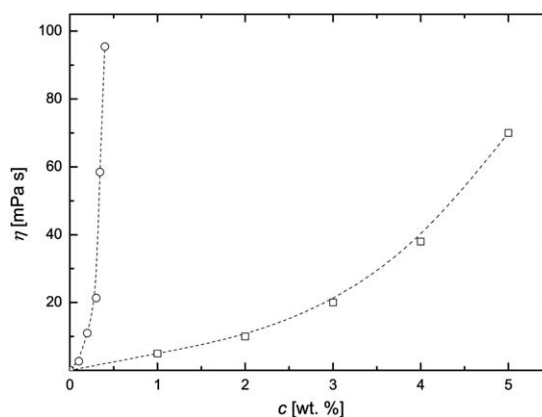

Fig. 2. The dependence of viscosity η of thickener solutions on the concentration c. Points denoted as in Fig. 1.

Table 4
Characteristics of latex particles. Particle diameter of acid latices (d_a) and intrinsic viscosity $[\eta]$, maximum packing volume concentration Φ_c and particle diameter of alkalinized latices (d_b)

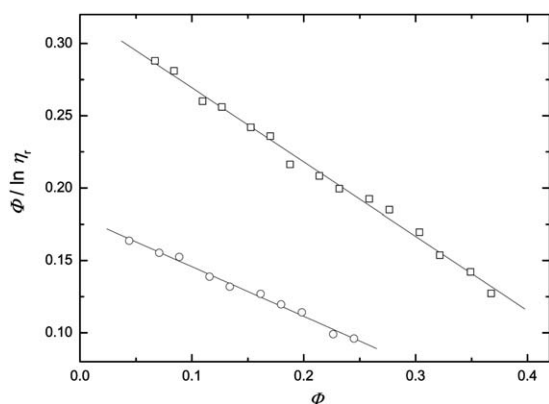| Latex	d_a (nm)	$[\eta]$	Φ_c	d_b (nm)
L0	124	3.14	0.63	124
L25	128	5.58	0.52	134

Fig. 3. The Mooney plot of $\Phi/\ln \eta_r$ vs. Φ, for alkalinized latices L0 (□) and L25 (○).

Hydrodynamic diameters of particles of original acid and alkalinized latices were measured by dynamic light scattering (Auto-Sizer LoC, Malvern Instruments, UK); the difference between L0 and L25 was less than 10 % in both cases (Table 4).

2.4. Sample preparation

We investigated latices of a medium concentration (30 wt % of solids), similar to the particle concentration in a water-borne painting material, thickened with 0.5 wt % of the thickener. The pH of the samples was adjusted by adding dilute aqueous ammonia to a mixture of dialysed latex with the thickener until pH reached the required value (8.5–8.8).

pH measurements were carried out using a digital pH-meter (Radiometer Copenhagen) with a combined electrode GK 2321 C. All measurements, including latex characterisation, were performed at 25 °C, with samples aged one day after pH adjustment.

2.5. Rheological measurement

Dynamic oscillatory experiments were performed on a rheometer ARES (Rheometrix Scientific, USA) equipped with a cone-plate geometry of 50 mm diameter and 0.02 rad cone angle. Measurements were carried out at room temperature in the region of linear viscoelasticity.

3. Results and discussion

The latex characteristics showed (Table 4) that the HEMA presence in the latex copolymer significantly

increases the effective hydrodynamic volume of alkalinized latex particles due to increased swelling and extension of ionic atmosphere [17]. Consequently, both complex viscosity η^* and the storage and loss moduli, G' and G'', of 30 wt % latex L25 also exceed those of L0 (Fig. 4). In both cases, the loss modulus is much higher than the storage modulus, which reflects low elasticity of latices. The decrease in complex viscosity η^* with frequency indicates a slight pseudoplastic character of both latices.

Dynamic properties of latex L0 thickened with HEUR differed markedly from those of latex L0 thickened with HASE. For both thickeners, the low-frequency dynamic moduli increased by more than one order of magnitude; however, the storage component was dominant in the whole frequency range of HEUR spectra (Fig. 5a) whereas it exceeded the loss component only slightly and only at the highest frequencies used with HASE (Fig. 5b). This behaviour may be ascribed to the adsorption activity of the hydrophobic segment of the thickeners on the latex particle surface. The HEUR thickener may be assumed to adsorb by hydrophobic ends to particles of latex L0 and forming
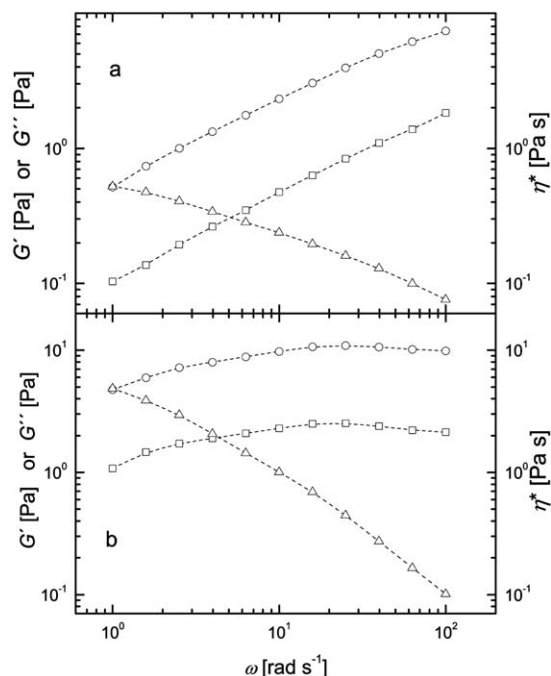

Fig. 4. The frequency dependence of the storage modulus G' (□), loss modulus G'' (○) and complex viscosity η^* (△) of latex L0 (**a**) and latex L25 (**b**).
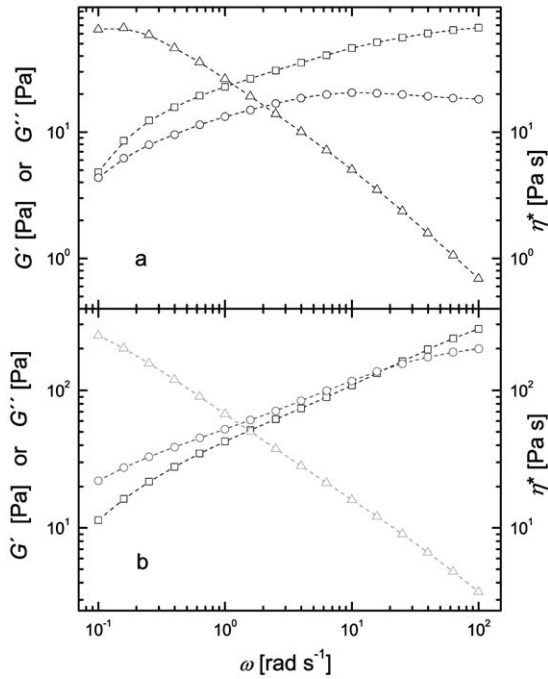
Fig. 5. The frequency dependence of the storage modulus G' (□), loss modulus G'' (○) and complex viscosity η^* (△) of latex L0 thickened with 0.5 wt % of HEUR (**a**) or HASE (**b**) thickener.

Fig. 6. The frequency dependence of the storage modulus G' (□), loss modulus G'' (○) and complex viscosity η^* (△) of latex L25 thickened with 0.5 wt % of HEUR (**a**) or HASE (**b**) thickener.

a relatively strong physically bonded highly elastic network of bridged latex particles. In contrast, bridging by HASE is weak, and the somewhat higher complex viscosity of L0 thickened with HASE is caused by excluded volume of swollen HASE dispersion particles.

Fig. 6 illustrates the effect of the HEMA inclusion in the latex copolymer on the viscoelasticity of thickened material. With both thickeners, storage and loss dynamic moduli were higher for L25 than for L0. In the case of HASE, the storage modulus at low frequencies was lower than the loss modulus; with increasing frequency, this difference diminishes similarly to thickened L0. This indicates that the viscous character dominates in both HASE-thickened latices and, therefore, is not influenced by the HEMA present in latex particles.

On the other hand, if the latex L25 was thickened with HEUR thickener, the loss modulus at low frequencies increased more than the storage modulus and the viscous component prevailed. At medium frequencies, the moduli became identical and at higher frequencies, the loss modulus decreased and reached a
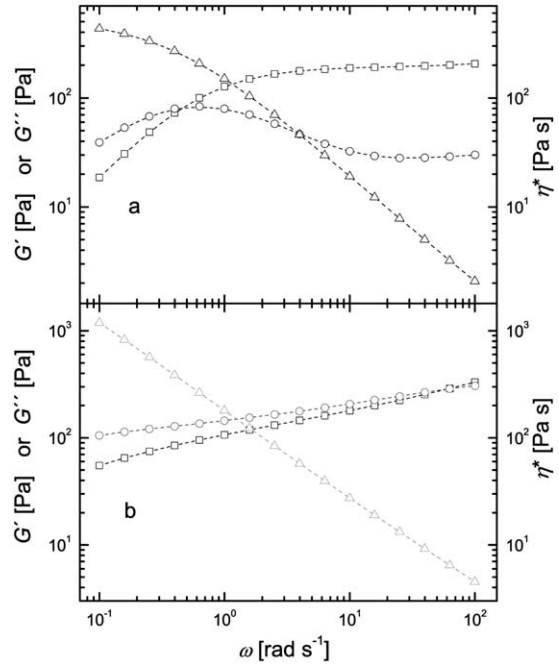
limit value. The different viscoelastic character of thickened latices is clearly characterised by the frequency dependence of the phase angle as the ratio of the loss and storage moduli (tan δ) in Fig. 7.

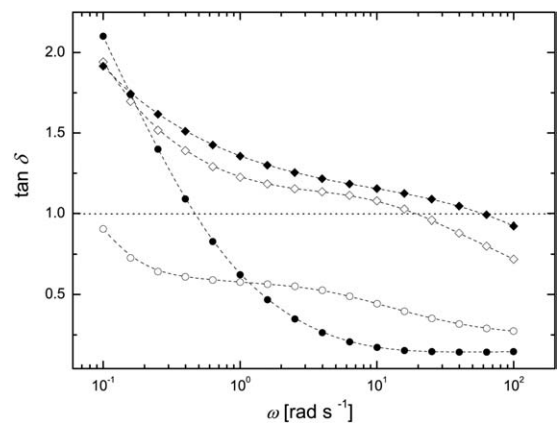If HEMA is incorporated in the latex copolymers, the particle surface becomes more hydrophilic and its

Fig. 7. Frequency dependence of tan δ. Latex L0 (○) and L25 (●) thickened with HEUR, latex L0 (◇) and L25 (◆) thickened with HASE.

association with the hydrophobic segments of the thickener is lower. Consequently in the case of HEUR, the latex–thickener network, responsible for the elasticity of the material, is weaker and the loss modulus prevails especially at low frequencies corresponding to high relaxation times. At higher frequencies, however, the response to the frequency is too low and the storage modulus becomes dominant.

In the latices thickened with HASE, the thickening due to hydrodynamic interaction of swollen latex and thickener particles is more important than the adsorption mechanism. The swollen physical network is loose and its elasticity is lower in comparison with HEUR-thickened system, which results in higher loss modulus. In this case, the HEMA on the surface of latex particles has a much lower effect on the structure of the thickened system. After thickening, the courses of the dependence of loss and storage moduli of latices L0 and L25 thickened with HASE on the frequency are similar.

It has to be stressed that the description of the HEMA effect on viscoelasticity applies to HEUR and HASE at concentrations used and generalization should by made with regard to the predominant thickening mechanism (particle bridging vs. excluded volume increase) rather than to the thickener type (HEUR vs. HASE), because it is possible that after equalizing, for example, the low frequency viscosity, either by increasing the HEUR concentration or by decreasing the HASE concentration, the thickening mechanism and therefore the HEMA effect will become similar.

4. Conclusion

The results demonstrated that the presence of hydrophilic comonomer, such as 2-hydroxyethyl methacrylate, in the copolymer of acrylic latices thickened with hydrophobically modified urethanes (HEUR) might significantly influence the elasticity of the product. In contrast, a much lower elasticity and higher viscosity of latices thickened with hydrophobically modified alkali-soluble emulsion (HASE) are not affected.

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