Colloid Polym Sci 277:276–281 (1999)

SHORT COMMUNICATION

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Stability of a model alkali-soluble associative polymer in the presence of a weak and a strong base

Received: 19 May 1998
Accepted in revised form: 26 October 1998

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Abstract Hydrophobically modified alkali-soluble emulsion (HASE) polymer is solubilized by the addition of a base. When the pH is increased to greater than 6.5, methacrylic acids on the polymer backbone are neutralized and the carboxylated latex polymer goes into solution causing a large increase in the viscosity due to inter-molecular associations of the hydrophobes. The stability of the viscosity of the polymer solution at pH in the range 9–10 was studied in the presence of a strong (NaOH) and a weak [1-amino-1-methylpropanol (AMP)] base. No change in the viscosity or the moduli was observed for the polymer in AMP. Reduction in the viscous and elastic properties of the polymer solution in NaOH was observed after 4 weeks. Such small changes are detectable using the superposition of oscillation on the steady shear technique. The decrease in the viscoelastic properties is attributed to the hydrolysis reaction of the urethane groups of the macromonomer, which resulted in a decrease in the number of hydrophobes per polymer chain. It is recommended that a weak base be used to neutralise the HASE polymer in order to avoid the possibility of compositional changes in the polymer after neutralisation for more than 6 weeks.

Key words Model associative polymers – Alkali – Neutralization – Rheology – Stability

Introduction

Polymers with hydrophobic groups attached to a hydrophilic backbone, such as the hydrophobically-modified hydroxyethyl cellulose and hydrophobically-modified ethylene oxide urethane polymer, are used as thickeners in a number of water-borne applications, particularly in paint formulations for coating industries [1–3]. These polymers provide a better balance of rheological properties in aqueous solutions, compared to their unmodified counterparts, due to association of the hydrophobic groups to form a network composed of temporary junctions or aggregates of several polymer chains.

A new class of associative polymers being increasingly used in a number of applications is the hydrophobically modified alkali-soluble emulsion (HASE) polymers [4–6]. These polymers have a comb-like structure with pendant hydrophobic groups randomly distributed along a polymethacrylic backbone. The HASE polymers have several advantages over other associative polymers in terms of cost as well as ease of dosing and wide formulation latitude. They are supplied as latex, typically at low pH between 3 and 4. The thickening characteristics occur upon neutralization of the emulsions to pH 7 and above. This solubilizes the backbone, thus facilitating intermolecular associations of hydrophobic groups, with a resultant increase in the solution viscosity. The role of the neutralizing base in the thickening efficiency of HASE polymers and the stability of the solution is thus of critical importance to their performance.

Our interest in the present study is the time stability of the solution viscosity of the HASE polymer neutralized with sodium hydroxide (NaOH) and 1-amino-1-methyl-propanol (AMP). As most of the applications in which the final products are kept on the shelf for up to 6 months to 1 year are coating-related, it is important to study if the viscosity changes with time upon neutralization to pH between 8 and 10. However, our immediate interest stems from the fact that it would be necessary to determine how stable the polymer solutions are once they are prepared for testing. From time to time, additional tests may need to be performed on the same sample and the stability of the solution viscosity is then an important issue.

The aspect concerning the performance of HASE polymers affected by the type of alkali used has not been addressed previously. This paper discusses the behavior of a model HASE polymer in aqueous solution at high pH neutralized with NaOH and compares the results with those of the solution neutralized using the organic base AMP over a period of 4–6 weeks. Although the shear viscosity of the solution is not affected significantly, the results obtained using the technique of superposition of oscillations onto steady shear flows clearly indicate that the presence of NaOH in solution has a detrimental role in reducing the elastic component of the polymer to a significant degree. The implications of these results are discussed.

Experimental section

A series of model HASE polymers was synthesized using the emulsion polymerization process, as detailed in Tirtaatmadja et al. [6]. The HASE polymer consists of a backbone of 49 mol % methacrylic acid and 50 mol % ethyl acrylate, with approximately 1 mol % macromonomers containing a $C_{20}H_{41}$ alkyl chain. This model polymer is designated as RDJ31-5 and the chemical structure is given in Fig. 1. The hydrophobic groups are separated from the polymer backbone via a spacer of approximately 31–35 mol poly(ethylene oxide), which is coupled to the backbone with a urethane linkage. As synthesized, the polymers are in the form of insoluble latexes in aqueous solution at pH between 3 and 4. When neutralized to pH 6.5 and above, the carboxylic acid of the backbone is ionized and the chains expand due to the electrostatic repulsive force of negative charges along the polymer backbone.

In this work, solutions of 1 wt % latex dispersions of RDJ31-5 model polymer were prepared in 10^{-4} M KCl solution. The latexes were neutralized using either 1 M NaOH solution or AMP to pH between 9 and 9.5. These pH values were determined after the solutions had been left to equilibrate overnight. The flow properties of the solutions were then measured at one week after preparation using a controlled stress Carri-Med model CSL500 rheometer equipped with a cone-and-plate fixture (with a 40 mm, 2° cone). All measurements were carried out at 25 ± 0.1 °C. The properties of the solutions left standing at room temperature (varying between 23 and 26 °C) were measured at two other intervals of 4 and 6 weeks. In addition to the steady shear and oscillatory flow measurements, the technique of superposition of oscillation onto steady shear flows [7] were also employed. The technique enables the viscoelastic properties of the polymer under different shear conditions to be determined.

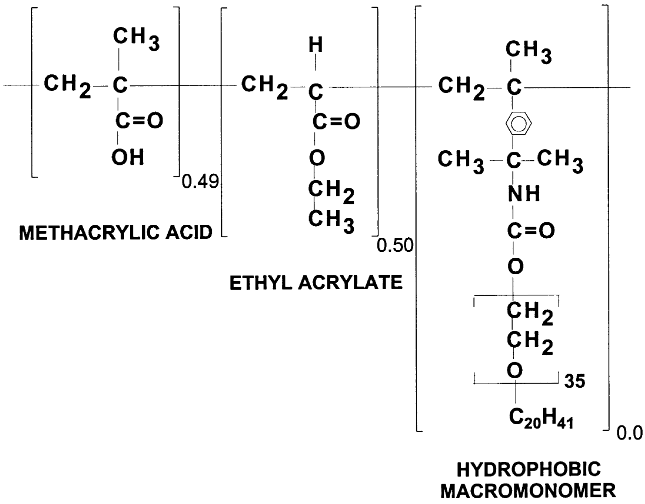

Fig. 1 Chemical structure of the model hydrophobically modified alkali-soluble emulsion polymer

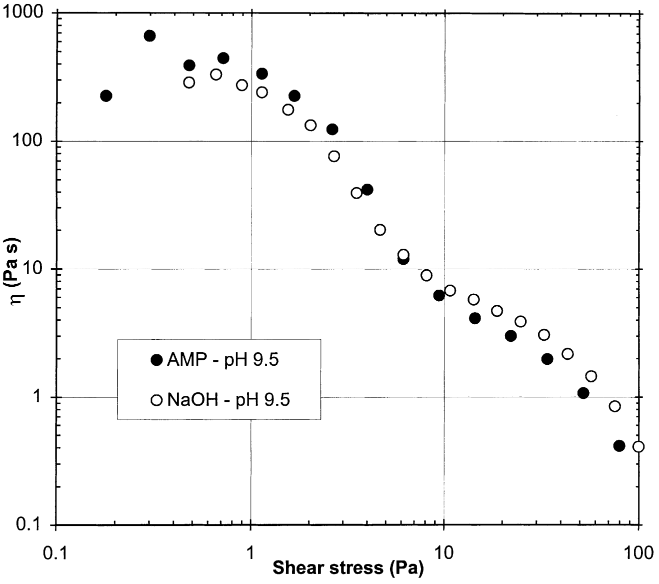

Fig. 2 Comparison of steady shear viscosities of 1 wt % RDJ31-5 neutralized using 1 M NaOH and 1-amino-1-methylpropanol (*AMP*)

Results and discussion

The two HASE polymer solutions neutralized using NaOH and AMP showed fairly similar steady shear viscosity when measured 1 week after preparation, as can be seen from the results shown in Fig. 2. It has previously been shown that the shear viscosity of the model HASE polymer with attached alkyl hydrophobic groups increased sharply at pH 6.5 and became almost constant above pH 7 [5, 8, 9]. The dynamic results of the two solutions were also similar, although not identical, as shown in Fig. 3a. The solution neutralized with NaOH showed slightly higher viscoelastic properties in both storage modulus G' and loss modulus G''. The slight difference in the viscosity and viscoelastic properties between the two solutions might be due to the fact that NaOH, being a stronger base than AMP is more effective in the neutralization of the methacrylic-acid groups on the polymer backbone.

The behavior of 1.0 wt % RDJ31-5 solution, neutralized with NaOH or with AMP, was examined over a period of 6 weeks and the rheological stability was monitored over this time period. The solution neutralized with AMP showed no change with time in either the steady shear viscosity or the viscoelastic properties up to 6 weeks after preparation, as shown in Figs. 4 and 5, respectively. Not only were the viscoelastic properties of the solution at rest the same, but the values of both G' and G'' also remained unchanged even with applied stresses up to 20 Pa (Fig. 5a–d). In contrast, the solution neutralized with NaOH showed no change in the steady shear viscosity up to 4 weeks (see Fig. 6), but displayed a gradual decrease in both the storage and loss moduli with time (see Fig. 7). The loss in the elastic component of the solution was particularly prominent when comparing the G' curves of the solution at an applied stress of 10 and 40 Pa (Fig. 7c, d respectively). At this applied stress condition, the network junctions were possibly being broken at a much faster rate than the rate of junction formation, and the network was significantly disrupted from its rest state. The terminal region of the viscoelastic curves was shifted to within the frequency range of the measurements. The G' curve was greatly reduced especially in the terminal region where G' is proportional to ω^2. The longest relaxation time of the solution, which could be determined from the terminal region of the viscoelastic behavior, i.e., $\tau_x = \lim_{\omega \to 0}\left[[G'(\sigma_s, \omega)]/[\omega^2 \eta'(\sigma_s, \omega)]\right]$, where σ_s is the applied shear stress and $\eta' = G''/\omega$ is the dynamic viscosity, was different between the two solutions. Thus the relaxation time of the solution was greatly curtailed with increasing aging of the NaOH-neutralized polymer solution. At longer time of up to 6 weeks after its preparation, the solution with NaOH was further degraded such that the steady shear viscosity started to decrease, in particular in

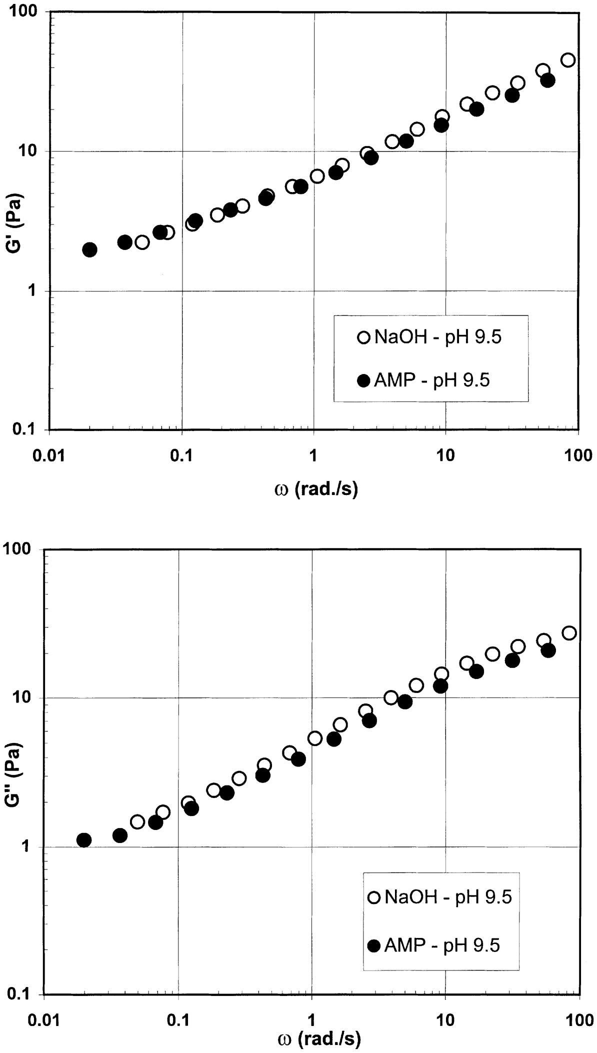

Fig. 3 Comparison of dynamic storage and loss moduli of 1 wt % RDJ31-5 neutralized using 1 M NaOH and AMP

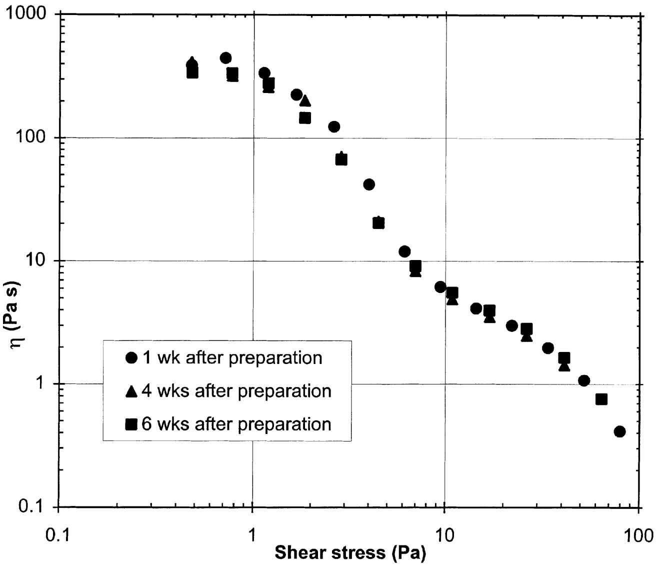

Fig. 4 Steady shear viscosities of 1 wt % RDJ31-5 neutralized using AMP at 1, 4 and 6 weeks

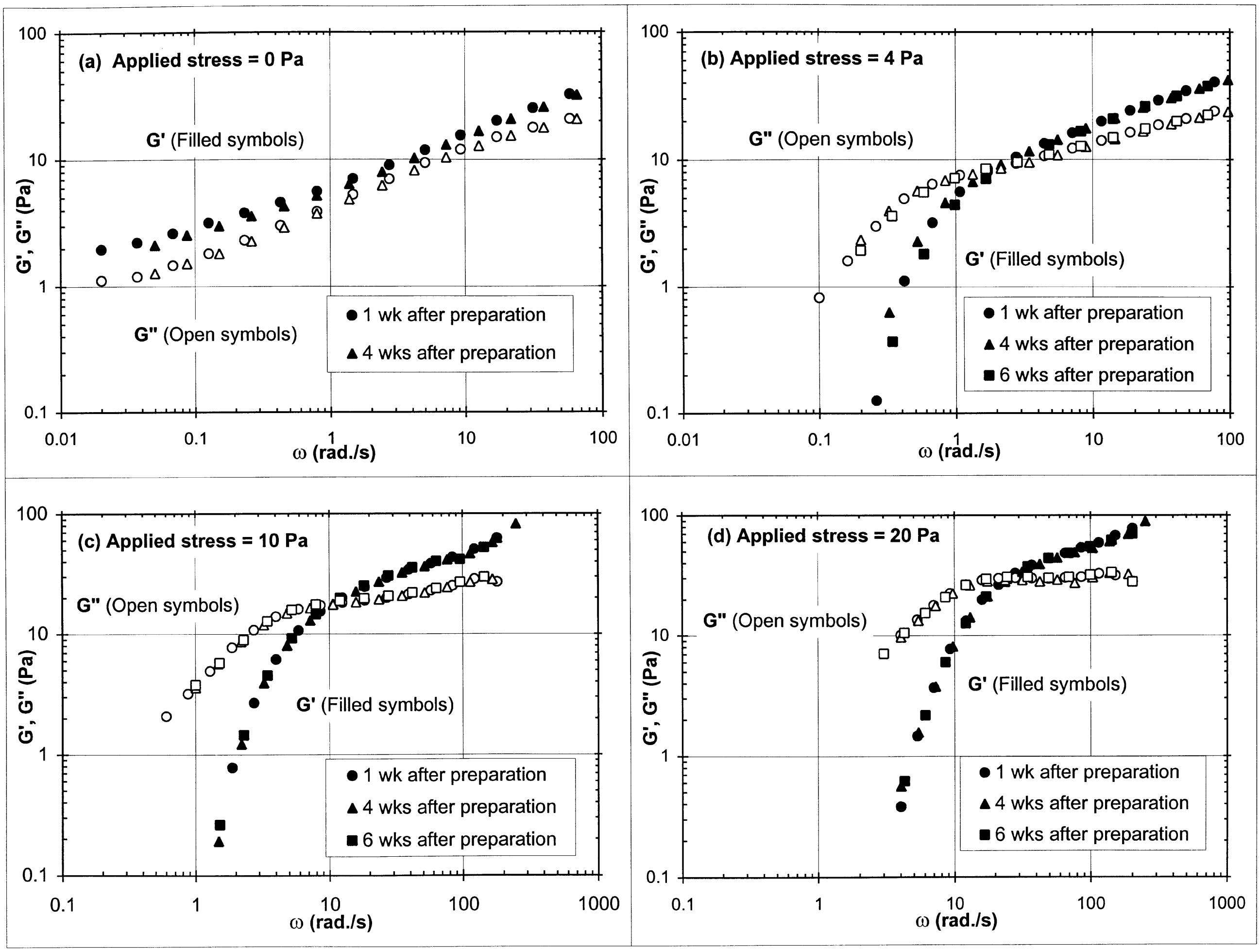

Fig. 5 Viscoelastic storage and loss moduli of 1 wt % RDJ31-5 neutralized using AMP at 1, 4 and 6 weeks at applied stresses of **a** 0, **b** 4, **c** 10 and **d** 20 Pa

the low shear region, as shown in Fig. 6. This was accompanied by a further decrease in both the *G′* and *G″* curves (Fig. 7a, b). The loss of low-shear viscosity of solutions of HASE polymer neutralized with NaOH has been reported to be about 13–15% on heating at 70 °C for 30 days: this is in contrast to a reduction in viscosity of 40–50% when a mixture of triethanolamine/KOH was used.

The loss in shear viscosity and, more importantly, the elastic properties of HASE polymer in the presence of a strong base such as NaOH was probably due to a hydrolysis reaction. Experiments carried out at Union Carbide have shown no difference in the thermal stability test with or without oxygen present and hence an oxidative reaction as the cause of degradation of HASE polymer has been eliminated. Hydrolysis probably occurred at the urethane groups of the macromonomers, thereby causing a cleavage of the

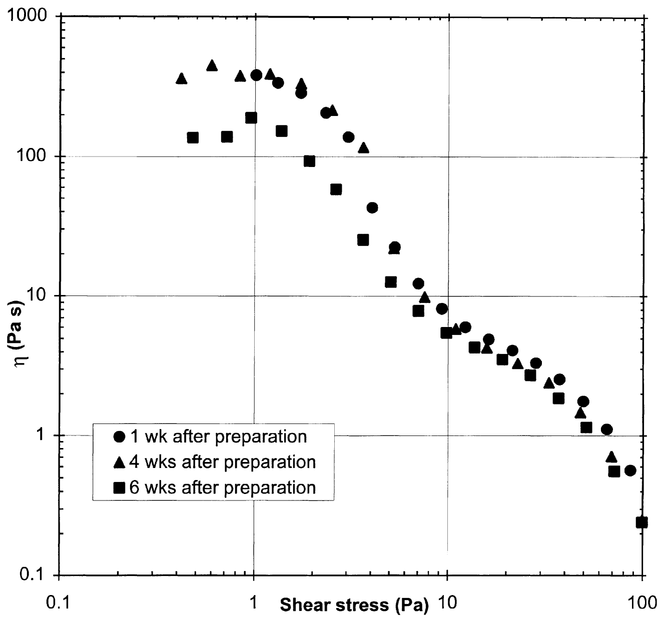

Fig. 6 Steady shear viscosities of 1 wt % RDJ31-5 neutralized using NaOH at 1, 4 and 6 weeks

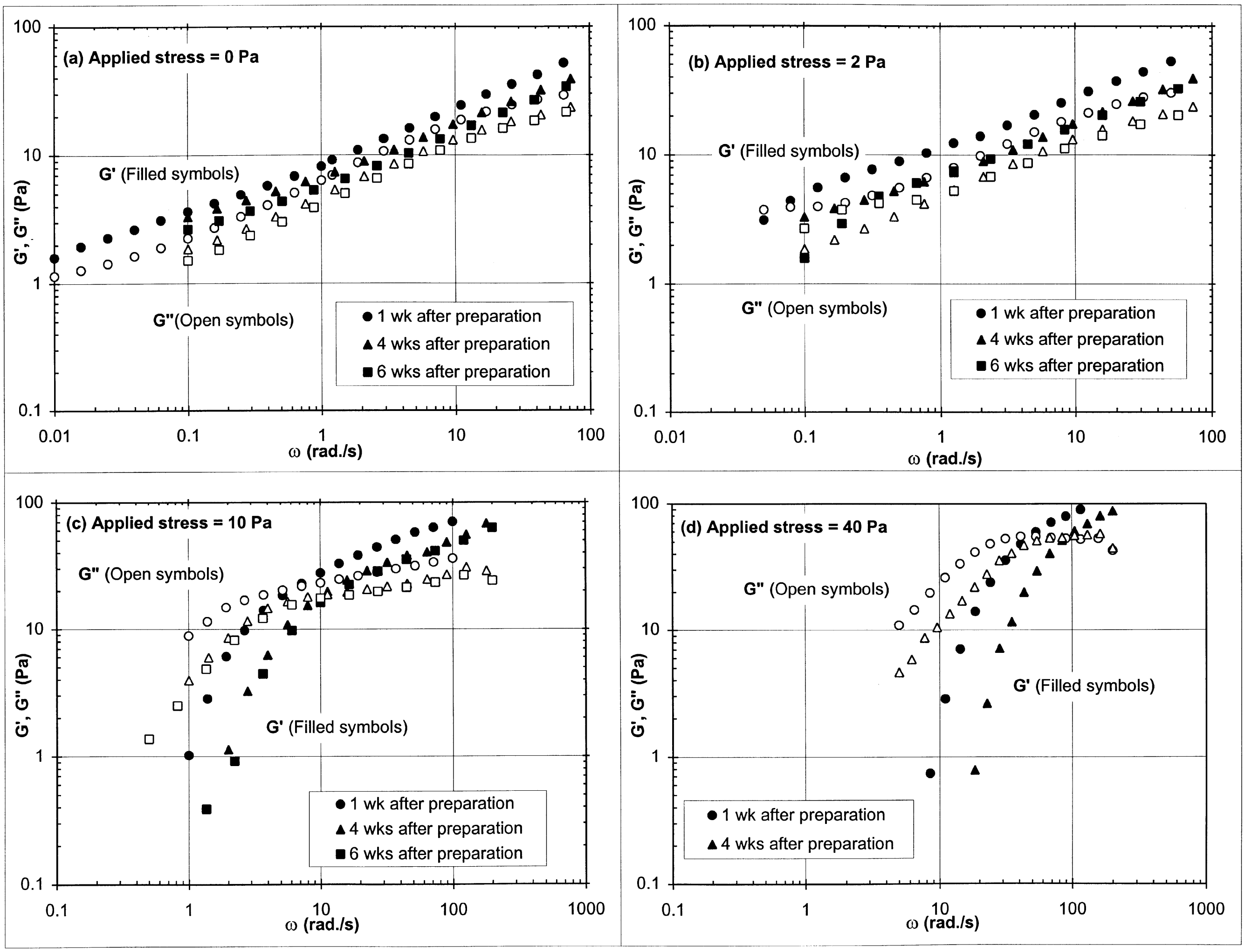

Fig. 7 Viscoelastic storage and loss moduli of 1 wt % RDJ31-5 neutralized using NaOH at 1, 4 and 6 weeks at applied stresses of **a** 0, **b** 2, **c** 10 and **d** 40 Pa

hydrophobes from the polymer. Hence this loss in the association of part of or some of the polymer chains from the network would result in a significant decrease in the elastic property of the solution, which is a function of the junction density. While the viscosity of the polymer is a function of the volume of the network in solution, the initial loss of some hydrophobic groups from the polymer backbone and hence loss of associations to the network junctions might not be significant enough to affect its shear viscosity. Only when a larger number of hydrophobes had been cleaved off its backbone was the loss in solution viscosity evident. From the results reported here, it was apparent that a slight degradation of the HASE polymer due to loss of some hydrophobic groups was detectable when the solution viscoelastic properties determined under applied shear stress conditions were considered.

The mechanism for the reduction in the viscoelastic properties observed in the presence of a strong base was attributed to the hydrolysis reaction of the urethane groups in the macromonomers. Since the concentration of macromonomers is low (0.9 mol %), the hydrolysis by-products are difficult to detect experimentally with established spectroscopic techniques. However, there is documented evidence that the resistance to hydrolysis by a base decreases in the following order: ether, urethane, ester groups [10, 11]. Based on the chemical structure of the model polymer (Fig. 1), it is reasonable to conclude that hydrolysis of the urethane group is preferred compared to the ether group.

It would be useful to point out that various types of linkages were used to graft the hydrophobes onto the hydrophilic polymer backbone. These include maleic anhydride, alkyl vinyl ether, isocyanate and vinyl ester [12]. Traditionally, vinyl esters are widely used to attach the hydrophobes onto the polymer backbone. In a patent by Shay et al. [15], it was claimed that by using a urethane instead of an ester group, a more superior and hydrolytically stable associative thickener with better performance in aqueous alkaline medium can be obtained. It is evident that the choice of an appropriate linkage group to connect the hydrophobes to the polymer backbone is critical for achieving the desired performance in aqueous coating applications.

Conclusions

The use of a strong base, NaOH, in the neutralization of HASE polymer to effect its solubility caused the degradation of the polymer over a period of several weeks. NaOH caused hydrolysis of the urethane groups resulting in a reduction in the number of hydrophobic groups on the polymer.

The use of an organic base, AMP, for the neutralization of the HASE polymer was shown to induce stability in the rheological properties of the solution. Not only was the steady shear viscosity of the solution unchanged over a period of 6 weeks, but the dynamic storage and loss moduli at rest and under various shear stress conditions were also found to remain the same over a 6-week period.

The technique of superposition of oscillations onto steady shear flows has been found to be a sensitive tool for detecting changes occurring in associative polymers in solution. It can be used to detect changes in the network structure even when steady shear and viscoelastic properties of the polymer in its rest state show negligible difference.

Acknowledgements This work was supported by the National Science and Technology Board and the Ministry of Education of Singapore.

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