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Dynamic mechanical properties of paper: effect of density and drying restraints

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The tensile dynamic mechanical properties of paper sheets with densities between 300 and 1000 kg m^{-3} have been measured at room temperature in the frequency range 0.1 to 10 Hz. Two series of sheets have been investigated; one which had been restrained during drying and the other which had been allowed to shrink freely. In general, paper was found to be a non-linear viscoelastic material. The dynamic modulus decreased and the mechanical loss factor increased as the strain amplitude of the applied sinusoidal deformation was increased. The non-linear character of paper was more pronounced at lower sheet densities. The modulus increased strongly with increasing sheet density and was always higher for sheets that had been restrained during drying. The sheets were anisotropic and the ratio of the modulus in the machine direction (MD) to that in the cross-direction (CD) was of the order of 2 to 3.5 depending on the density and the drying conditions. The mechanical loss factor (extrapolated to zero strain amplitude) decreased with increasing sheet density and was always higher in the CD than in the MD. The freely dried sheets were characterized by a higher value of the mechanical loss factor, tan δ, than sheets that had been restrained during drying. It is suggested that the influence of the sheet density and the drying restraints on the dynamica mechanical properties of paper is associated with interfibre friction and/or bending and shearing of the cellulose fibres.

1. Introduction

Within polymer science, evaluation of dynamic mechanical properties is a valuable procedure for characterizing materials. It is well known that measurements of the dynamic storage modulus and of the mechanical loss factor at different temperatures can be used to gain knowledge of, for example, the glass transition and secondary transitions corresponding to local molecular motions [1–3]. Dynamic mechanical analysis applied to polymers thus provides information concerning the molecular characteristics of materials. The dynamical properties of paper have been investigated to some extent, see e.g. [4–6], but the volume of literature appears to be substantially smaller than that for synthetic polymers.

Paper is a rather heterogeneous material which on a structural level can be regarded as a dense network of cellulose fibres. The anisotropic fibres are normally oriented to some extent in the machine direction of the paper sheet. The mechanical properties of paper are primarily determined by the corresponding fibre properties, the fibre network structure and in some situations also by the adhesive forces between the individual fibres. Furthermore, the mechanical properties also depend on the conditions under which the paper is dried, e.g. a freely dried sheet normally has a lower modulus (stiffness) than a sheet which has been restrained or stretched during the drying process [6].

The primary aim of the present communication is to report on the dynamic mechanical properties of different paper structures. The main structural parameter considered here is the density which is varied between 300 and 1000 kg m^{-3}. The degree of fibre orientation relative to the machine direction was kept approximately constant in all the sheets. The effect of drying restraints was also included in this investigation, the sheets either being allowed to shrink freely or being biaxially restrained during the drying process.

2. Experimental details

2.1. Material

The paper used was made from a commercial never-dried bleached sulphate pulp of pine (*Pinus silvestris*) beaten to 17°SR. The number average fibre length was 2.11 mm and the corresponding weight average 2.70 mm. The sheets were made on a Formette Dynamique sheetformer [7] with a basis weight of $\sim 250\,\mathrm{g\,m^{-2}}$. They were made under conditions chosen to produce the same degree of fibre orientation with regard to the machine direction (MD) regardless of density and drying conditions. In the following discussion this has been assumed to be the case. The sheets were wet-pressed to different densities using pressures from 0 to 7 MPa. They were dried at 50% r.h., 23° C either freely or restrained in drying frames [6]. The mechanical anisotropy, i.e. the ratio of the tensile modulus in the MD to that in the cross direction (CD) was between 2 and 3.5 depending on the drying conditions and the density. The density of the sheets was measured according to SCAN standard procedures at 50% r.h. and 23° C.

2.2. Dynamic mechanical analysis

The dynamic mechanical properties of the sheets in the MD and CD were measured in the tensile mode at 50% r.h. and 23° C using a dynamic mechanical analyser, Dynastat, Imass. The versatility of this instrument is briefly described by Yang *et al.* [8]. The measurements were made on specimens having a width of 10 mm and an effective length of 45 mm. The absolute value of the complex dynamic modulus $|E^*|$, the storage modulus E', the loss modulus E'', and the mechanical loss factor $\tan\delta$ $(= E''/E')$ are obtained. For the paper samples used here the difference between $|E^*|$ and E' is negligible. For the viscoelastic characterization of the paper sheets $|E^*|$ and $\tan\delta$ have been used. The experiments were in most cases confined to three frequencies; 0.1, 1 and 10 Hz.

3. Results and comments

3.1. Effect of the applied strain amplitude

The dynamic mechanical properties of the sheets were determined in the tensile (stretching) mode. Prior to application of the periodic deformation

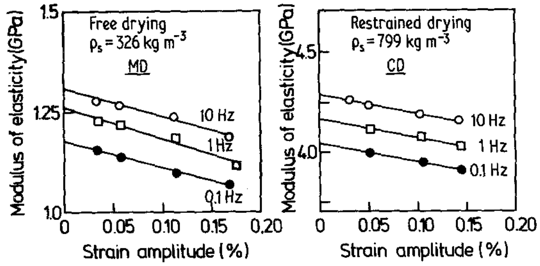

Figure 1 The complex dynamic modulus $|E^*|$ plotted against the strain amplitude, ϵ_a, at 0.1, 1 and 10 Hz. The left-hand figure refers to a freely dried sheet with a density of $326\,\mathrm{kg\,m^{-3}}$ in the MD and the right-hand figure to a restrained dried sheet (CD) with a density of $799\,\mathrm{kg\,m^{-3}}$.

the specimens were pre-strained $\sim 0.3\%$. The amplitude of the subsequently applied sinusoidal deformation was always kept lower than 0.3% in order to avoid buckling of the flexible paper strips. The strain amplitude (ϵ_a) was varied from $\sim 0.2\%$ and downwards and for each value of ϵ_a and each frequency the complex modulus ($|E^*|$) and the mechanical loss factor ($\tan\delta$) were evaluated.

Fig. 1 shows two typical examples of the effect of strain amplitude on the complex modulus of the specimens. The left-hand part of Fig. 1 refers to the MD-direction of a sheet with density (ρ_s) $326\,\mathrm{kg\,m^{-3}}$ which has been dried freely, and the right-hand part to a specimen (CD) with $\rho_s = 799\,\mathrm{kg\,m^{-3}}$ which has been biaxially restrained during drying. Increasing the strain amplitude evidently brings about a reduction in the complex modulus. For the sample with the lower density ($326\,\mathrm{kg\,m^{-3}}$) the modulus decreases by about 7% when ϵ_a increases up to 0.15% (from zero), whereas the corresponding decrease for the other sheet is lower, $\sim 3.5\%$.

In general, the percentage decrease in $|E^*|$ with increasing ϵ_a is greater in the CD than in MD. It is also greater in the low density region and is more pronounced for freely dried sheets than for sheets that have been restrained during drying. The greatest decrease in $|E^*|$ when the amplitude is increased up to 0.15% is observed in the CD of a freely dried sheet of low density ($326\,\mathrm{kg\,m^{-3}}$) and is almost 15%, whereas the smallest is observed in the MD of a sheet of high density which has been biaxially restrained during drying ($< 3\%$). The influence of the strain amplitude, ϵ_a, on the complex modulus appears to be similar for the three frequencies used here, cf. Fig. 1. As expected, an increase in frequency shifts the stiffness to higher values (for all values of the strain amplitude).

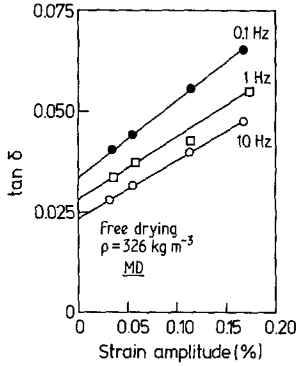

Figure 2 The mechanical loss factor tan δ plotted against the strain amplitude ϵ_a at 0.1, 1 and 10 Hz for a freely dried sheet (MD) with a density of $326\,\mathrm{kg\,m^{-3}}$.

Figs. 2 and 3 show the influence of ϵ_a on the mechanical loss factor, tan δ, for the same samples as in Fig. 1. The loss factor increases linearly with increasing applied strain amplitude. This is true for all specimens used here and for all frequencies. It must be underlined that, in absolute values, the effect of ϵ_a on tan δ is considerable, cf. Fig. 2. Again the influence of ϵ_a is larger in the CD, at lower densities and for freely dried sheets. When the amplitude is increased up to 0.15% (from zero) the increase in tan δ is ~ 0.03 at 0.1 Hz for freely dried sheet in CD with a density of $326\,\mathrm{kg\,m^{-3}}$, while the corresponding change in the MD at a high density ($1064\,\mathrm{kg\,m^{-3}}$) is of the order of 0.015 (restrained drying).

It should be pointed out that the variation in $|E^*|$ and tan δ with ϵ_a is reversible; i.e. no permanent structural changes are induced by application of the periodic deformation. It was also ascertained that the effect of ϵ_a was not due to slippage in the clamps of the dynamic analyser. The increase in tan δ with ϵ_a is, as already noted, quite large and cannot be attributed solely to the corresponding decrease in E' ($\tan\delta = E''/E'$). The primary reason for the higher values of tan δ is an increase in the loss modulus, E''.

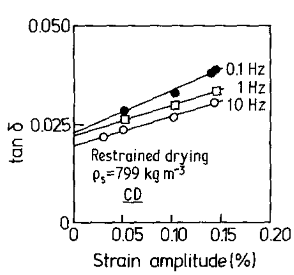

Figure 3 Same as Fig. 2 but for a sheet which has been restrained during drying ($\rho_s = 799\,\mathrm{kg\,m^{-3}}$, CD).

The data shown in Figs. 1 to 3 clearly indicate that the effect of the strain amplitude must be taken into account when the dynamic mechanical properties of paper are measured. To compare different paper structures in this respect all data have been extrapolated to zero strain amplitude as indicated in Figs. 1 to 3.

3.2. Variation of stiffness and loss factor with frequency

Fig. 4 shows the complex modulus $|E^*|$ and the mechanical loss factor tan δ as a function of the frequency in the range 0.1 to 30 Hz. The values of $|E^*|$ and tan δ have been obtained by extrapolating the experimental data to zero strain amplitude. Fig. 4 refers to the CD direction of a freely dried sheet with a density of $777\,\mathrm{kg\,m^{-3}}$. Obviously no dramatic changes in the dynamic mechanical properties occur in this frequency region. This is not surprising since the frequency range used is rather narrow and normally transitions, if there are any, in composite materials (which we may consider paper to be) are not very pronounced. With increasing frequency the modulus increases and the loss factor decreases somewhat. This is to be expected for a solid polymeric material not undergoing any structural transition on a molecular level, cf. [1–3]. The behaviour displayed in Fig. 4 is typical of all paper structures studied here.

3.3. The effect of density on the dynamic modulus

In this section the modulus is discussed in terms of the specific modulus, i.e. $|E^*|/\rho_s$, this being an adequate way of expressing moduli for heterogeneous materials. The modulus is then related to

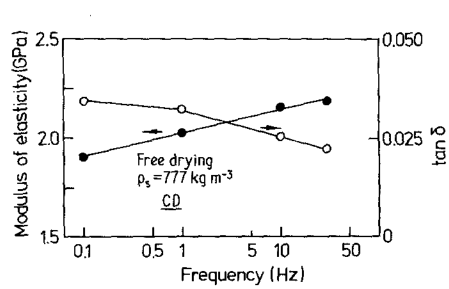

Figure 4 The dynamic modulus and loss factor plotted against the frequency for a freely dried sheet (CD) with a density of $777\,\mathrm{kg\,m^{-3}}$. The mechanical data shown are obtained by extrapolating to zero strain amplitude.

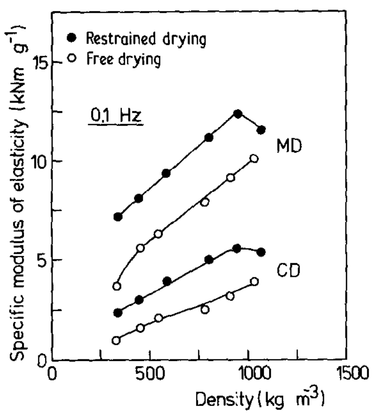

Figure 5 The specific dynamic elastic modulus in the MD and CD plotted against sheet density for paper sheets that have been freely dried and restrained during drying. The frequency was 0.1 Hz and the data are obtained by extrapolating to zero strain amplitude.

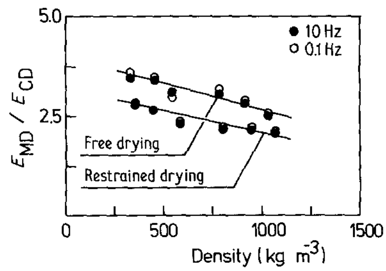

Figure 6 The mechanical anisotropy E_{MD}/E_{CD} plotted against the sheet density for freely dried sheets and sheets that were biaxially restrained during drying. Two sets of data obtained at 0.1 and 10 Hz are shown.

the amount of material per stressed area unit. In this way the modulus is independent of compacting operations such as dry pressing (calendering), which do not produce any increased adhesion between fibres.

Fig. 5 shows the complex dynamic modulus plotted against the sheet density in the MD and CD for both sheets that were allowed to shrink freely and sheets that were biaxially restrained during drying. The frequency was 0.1 Hz, but the same ρ_s dependence of $|E^*|$ is observed at 1 and 10 Hz. The effect of the drying conditions is notable in this graph. The sheets which were restrained during drying have significantly higher moduli both in the MD and CD over the density range used here. This is in agreement with the findings reported by Htun [6].

In general, the specific modulus increases, as expected, with increasing sheet density, both in the MD and CD. However, at densities exceeding 1000 kg m^{-3} there is a drop in specific modulus, both in the MD and CD, for sheets that have been restrained during drying. This is probably due to a crushing of the cellulose fibres during the wet-pressing of the sheets. For the sheets which have been dried freely, there is no corresponding decrease at high densities. It must be pointed out that the wet-pressing itself results in a certain restriction in shrinkage during drying. This is more pronounced at higher wet-pressing pressures and results in a higher stiffness than for an "ideally" freely dried sheet. Fig. 6 shows the mechanical anisotropy $|E^*_{MD}|/|E^*_{CD}|$ as a function of the sheet density. The mechanical anisotropy is here of the order of 2.6 to 3.5 for sheets that have been dried freely, and 2.1 to 2.7 for sheets that have been restrained during drying. For both sets of sheets the anisotropy decreases with increasing sheet density. This behaviour is difficult to explain in any detail at present, especially since the sheets were made so as to have the same degree of fibre orientation. It can be mentioned that the fibre orientation distribution for some of the sheets (which contained a small fraction of dyed fibres) was measured using an image analyser. The method is described by Rigdahl *et al.* [9]. For these sheets the fibre orientation distribution was approximately the same, regardless of the sheet density and the drying restraints. Although the mechanical anisotropy varies slightly, it may be reasonable to assume, in this case, that any major variations in the mechanical parameters are due to differences in the sheet density or to the drying restraints, at least to a first approximation, and not due to any difference in the fibre orientation. It should be pointed out that the level of anisotropy in these paper sheets is significantly lower than that sometimes encountered with fibre-reinforced polymer-based composites. From Fig. 6 it is obvious that the mechanical anisotropy is always higher for the freely dried sheets than for those which are restrained during drying, although the fibre orientation is the same in both sets of sheets. This effect is expected and may be traced back to the fact that, for anisotropic paper structures, the shrinkage, which is restricted in the case of biaxially restrained sheets, is larger in the CD than in the MD [10, 11].

As expected the frequency has no influence on the mechanical anisotropy, cf. Fig. 6.

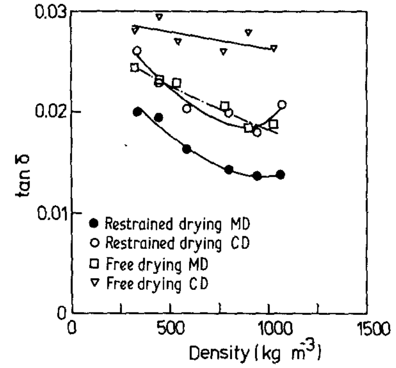

Figure 7 The mechanical loss factor tan δ plotted against the sheet density for freely dried sheets and sheets that have been biaxially restrained during drying. The frequency was 10 Hz and the tan δ values are obtained by extrapolating to zero strain amplitude.

3.4. The effect of density on the mechanical loss factor

The impact of the network structure of paper on the density dependence of the mechanical loss factor tan δ is especially interesting in this context. Fig. 7 summarizes the influence of density on tan δ for the different paper structures studied here. The values of tan δ in Fig. 7 are obtained by extrapolation to zero strain amplitude, cf. Figs. 2 and 3.

Several features of Fig. 7 are noteworthy. For both freely-dried and restrained-dried specimens in the MD and CD, the loss factor decreases as the sheet density increases. For sheets that have been restrained during drying there is, however, a tendency for tan δ to approach a limiting value at higher densities. For sheets that have been restrained during drying, the loss factor increases somewhat at densities greater than 1000 kg m^{-3}. This is especially pronounced in the CD. This effect is probably due to crushing of the fibres during the wet-pressing, cf. also the earlier discussion regarding the stiffness. At a given sheet density the damping is always higher in the CD than in the MD. Furthermore, freely dried sheets have higher tan δ values than sheets that have been restrained during drying, at a given density and in a given direction (MD or CD). Apparently, the paper structure has a significant influence on the mechanical loss factor. In Fig. 7 tan δ varies from almost 0.03 to below 0.015.

The data shown in Fig. 7 refer to 10 Hz, but the same pattern is also observed at 0.1 and 1 Hz.

4. Discussion

The results here reported show that the dynamic mechanical properties of anisotropic paper depend strongly on sheet density and on the drying strategies adopted. Both of these factors may be said to have a significant effect on the network structure of paper, cf. [12], but the drying conditions may also affect the mechanical properties of the cellulosic fibres.

Figs. 1 to 3 further show that the dynamic modulus decreases and the mechanical loss factor increases as the applied strain amplitude increases. The increase in tan δ has also been observed by Riemen and Kurath [5] for paper ($\rho_s \approx 840 \text{kgm}^{-3}$) using a vibrating reed technique operating at ~ 50 Hz. They attributed this phenomenon to a non-linear viscoelastic property of cellulose itself. This may well be the case since semicrystalline polymers are often non-linear in behaviour even at very low levels of deformation, cf. e.g. [13], while amorphous polymers may often be linear viscoelastic materials up to higher strains, cf. [14]. It should, however, be pointed out that fibre-to-fibre friction (interfibre friction) may also contribute to the observed behaviour. Such an effect should be more pronounced at lower sheet densities, which is the case found in the work reported in this communication.

Whether the effect of strain amplitude on the dynamic properties is due to the inherent polymeric properties of cellulose or to the network structure, it is clear that paper is a non-linear viscoelastic material. Consequently, the concepts of linear viscoelasticity should be used with caution when applied to this material, e.g. the strain or load levels used should always be stated. For natural reasons this also applies to creep and stress relaxation experiments.

The effect of structure on tan δ as shown in Fig. 7 may deserve some additional comment. The difference in damping between the MD and the CD is not surprising, since for oriented synthetic polymers there is often a corresponding difference in loss behaviour [3, 15]. Considering first the specimens which have been biaxially restrained during drying, it may be the case that the loss factor of the cellulose fibres themselves is higher in the transverse direction than in the axial direction. For wood in the wet state this is apparently the case [16]. This would explain why the tan δ values are higher in the CD of paper (also at high densities where there is a tendency for the loss factor to level out). However, if the tan δ values of paper were solely attributable to the corresponding properties of the pulp fibre the mechanical loss factor would be expected to increase with increasing density due to the higher fraction of fibre crossings at higher densities, i.e. the transverse properties of the crossing fibres would have a greater influence at higher densities. This is not observed here. Instead it can be suggested, but not proved, that the high values of tan δ at low densities may be due to fibre-to-fibre surface friction (or some similar mechanism). This surface friction is not primarily associated with the fibre crossings, where the fibres are bonded together, but rather to the segments between the bonds. During the periodic deformation such segments belonging to different fibres can make contact with each other. The interfibre friction should contribute to the loss factor to a greater degree in networks with fewer bonding sites, i.e. at lower densities. It is also likely that at lower sheet densities, the individual fibres are, relatively speaking, more deformed in the bending and the shearing modes, which presumably also makes an additional contribution to the mechanical losses. It is at present not possible to distinguish between the contributions from interfibre friction and those from the bending and shearing of the fibres. The primary cause of these factors is, however, the same, i.e. the lower bond site density along the fibres at lower sheet densities.

The importance of interfibre friction for the viscoelastic properties has earlier been pointed out for textile structures [3, 17, 18]. Murayama [17] has devised a method for transforming the coulomb friction (interfibre friction) into an equivalent viscosity which may then be used to evaluate the fibre-to-fibre surface friction.

The freely dried sheets have a higher damping capacity than sheets that have been restrained during drying. There can be several reasons for this. First it should be noted that the relative bonded area in the sheets, i.e. the product of the number of bonding sites and the bonded area of individual fibre crossings, is approximately the same for freely dried sheets and for sheets that have been restrained during drying. This has been evaluated from light scattering experiments [10]. The increase in tan δ cannot thus be traced to a change in the bonded area. However, the cellulose fibres in a freely dried sheet often have a more irregular shape; they can be slightly deformed and are more curled (also between the bond sites). This can lead to an increase in interfibre friction and the fibres may also be more bent and sheared when the network is deformed than the fibres in a sheet which has been restrained during drying. Felty and Murayama [19] measured the dynamic mechanical properties of textile assemblies of crimped fibres (polyamide 66) and found that tan δ for of the fibre masses (in the glassy region of the polymer) increased as the crimp frequency increased and they interpreted this in terms of an increase in interfibre friction.

The increase in the mechanical loss factor for the freely dried sheets may also be due to a change in the morphology of the cellulose fibres. The cellulosic material constituting the fibres may be schematically divided into ordered (crystalline) and disordered zones [6]. In the wet state, the disordered regions are plasticized by the water [6]. If the sheet is restrained during drying and thus prevented from shrinking, the disordered zones become "oriented" and this affects the mechanical properties, e.g. the fibre modulus increases compared with that of a freely dried fibre [12]. It is likely that the loss behaviour of the fibre is also affected by the same mechanism and this may give lower values of tan δ for restrained dried sheets (and fibres) than for freely dried ones.

As a final point, it can be mentioned that dry-formed sheets are normally characterized by a low degree of interfibre adhesion (if no binding material is added). Such structures have, as expected, a relatively high mechanical loss factor of the order of 0.033 [20]. In this case, the low degree of adhesion between crossing fibres may make a relatively large contribution to the interfibre friction and may also increase the proportion of fibre bending and shearing.

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References

1. I. M. WARD, "Mechanical Properties of Solid Polymers" (Wiley-Interscience, London, 1971).
2. J. D. FERRY, "Viscoelastic Properties of Polymers", (Wiley, New York, 1961).
3. T. MURAYAMA, "Dynamic Mechanical Analysis of Polymeric Materials" (Elsevier, North-Holland, Amsterdam, 1978).

4. J. KUBAT, L. NYBORG and B. STEENBERG, *Sv. Papperstidn.* **66** (1963) 714.
5. W. P. RIEMEN and S. H. KURATH, *Tappi* **47**(10) (1964) 629.
6. M. HTUN, PhD thesis, Royal Institute of Technology, Stockholm, Sweden (1980).
7. S. GAURET, H. THRINH and G. LETEBVRE, *Das Papier* **23**(1) (1969) 8.
8. P. YANG, L. CARLSSON and S. S. STERNSTEIN, *Polym. Comp.* **4** (1983) 104.
9. M. RIGDAHL, H. ANDERSSON, B. WESTERLIND and H. HOLLMARK, *Fibre Sci. Technol.* **19** (1983) 127.
10. N. L. SALMEN and M. RIGDAHL, Paper presented at the International Paper Physics Conference, Harwichport, Massachusetts, USA, 18–22 September (1938).
11. M. HTUN, H. ANDERSSON and M. RIGDAHL, *Fibre Sci. Technol.* **20** (1984) 165.
12. R. W. PERKINS and R. E. MARK, in "The Role of Fundamental Research in Paper Making", edited by J. Brander (Mechanical Engineering Publications Ltd, London, 1983) p. 479.
13. W. RETTING, *J. Polymer Sci. Symp.* **42** (1973) 605.
14. I.V. YANNAS, *J. Polymer Sci. Macromol. Rev.* **9** (1974) 163.
15. J. H. DUMBLETON and T. MURAYAMA, *Kolloid Z. Z. Polymer* **238** (1970) 411.
16. N. L. SALMÉN and C. FELLERS, *Pulp Pap. Mag. Can., Trans. Technol. Sec.* 8(4) (1982) TR93.
17. T. MURAYAMA, *J. Appl. Polymer Sci.* **24** (1979) 1413.
18. C. C. CHANG and K. E. DUCKETT, *Text Res. J.* **42** (1972) 51.
19. D. C. FELTY and T. MURAYAMA, *J. Appl. Polymer Sci.* **26** (1981) 987.
20. M. RIGDAHL, B. WESTERLIND, H. HOLLMARK and A. DE RUVO, *ibid.* **28** (1983) 1599.

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