

# Stress relaxation of polymer films in bending

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Stress-relaxation functions in bending and in tension were obtained for several polymer films with widely different microstructures and relaxation characteristics. For all the films tested, non-linear viscoelastic response is observed at strains exceeding 0.8%, with the relaxation time being generally lower the higher the strain. It is also observed that, within the linear viscoelastic range, the relaxation spectra of the bending and tensile moduli are qualitatively different, with the bending modulus relaxing generally more slowly than the tensile modulus. This difference is attributed mainly to a temporal change in Poisson's ratio, which can be estimated directly from the bending and tensile relaxation functions. Other possible causes for the observed differences in relaxation response are discussed.

(Keywords: stress relaxation; bending; films)

## INTRODUCTION

In a recent study<sup>1</sup> we presented an analytical model for the bending recovery effect in polymer films and reported experimental data for various polymers over a wide range of conditions. The model was based on a simple extension of the classical plate bending theory to linear viscoelastic materials and was fairly successful in describing most of our observations. However, a systematic deviation of the analytical predictions from the data for all the polymers studied forced us to assume that the relaxation processes in the tensile and compressive bands in the film during the bending test are generally dissimilar. This *ad hoc* 'correction' seemed to remove all the discrepancies between theory and data, but could not be tested critically at the time. In an attempt to resolve this question, we have taken a closer look at the relaxation process in bending, which is a key element of the bending recovery problem.

Stress-relaxation phenomena in solid polymers have been studied extensively over the years, both empirically and theoretically<sup>2-4</sup>. Various molecular and phenomenological theories have been advanced to explain these phenomena in glassy and semicrystalline polymers<sup>4-6</sup>, but none is completely satisfactory<sup>7</sup>, as no clear connection between the observed macroscopic relaxation and molecular relaxation processes has been established. It is generally agreed, however, that the macroscopic relaxation process involves some molecular 'cold' flow, i.e. relative translation of large molecular domains within the solid matrix. Interpretation of stress-relaxation data is often confounded by ageing effects<sup>8</sup>, which are strongly coupled to the stress-relaxation process<sup>9-11</sup> and may have a significant impact on the rate of relaxation. Another complicating feature, first noted by Sternstein and Ho<sup>12</sup>, is that relaxation rates are coupled to the strain fields in which they are observed even within the limits of linear

viscoelasticity, i.e. relaxation rates in uniaxial tension, torsion or compression may be generally different. Similar observations, although in a somewhat different vein, were made by Koppelman<sup>13</sup> and by Yee and Takemori<sup>14</sup>. In this study we focus on the relaxation process in bending and its correspondence to the tensile stress-relaxation response for several polymer films with different microstructures.

## EXPERIMENTAL

### Materials

Several commercial polymer films with a wide range of relaxation behaviour were used in this study. All films were tested as received. Following is a list of the materials studied: (a) *Cellulose acetate* (CA), a solvent-cast film from Eastman Kodak Company. CA has a degree of substitution of 2.85 and is plasticized with 12 wt% of triphenyl phosphate. The solvent content of this film is estimated at 0.3 wt% of cyclohexanone. (b) *Poly(ethylene terephthalate)* (PET), a standard production-grade Estar film produced by Eastman Kodak Company. The film is melt-extruded and biaxially oriented. (c) *Polypropylene* (PP), a biaxially oriented Extrel XPP-323 film from Exxon Chemical Company. (d) *Polycarbonate* (PC), a solvent-cast Lexan 8010P film produced by General Electric Company.

It should be noted that the solvent-cast films, CA and PC, can be considered to be transversely isotropic, whereas the films produced by biaxial stretching (PET and PP) are anisotropic.

The thicknesses and some pertinent physical properties of the test films are listed in *Table 1*. The steady-state mechanical properties of all the films were measured in the 'machine' direction at 21°C/50% r.h. using a Syntec Automated Tensile Tester. The thermodynamic transitions were determined with a DuPont 990 Differential Thermal Analyzer and the dynamic-mechanical properties

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**Table 1** Physical properties of test films

Film	Thickness ( $\mu\text{m}$ )	$E_0$ (GPa)	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$\lambda_n^a$ ( $10^6$ s)
CA	127	4.02	131	—	2.20
PET	180	4.59	75	255	9.53
PP	211	1.08	—	165	1.42
PC	292	2.16	150	—	9.57

<sup>a</sup>Average relaxation time in tension,  $\lambda_n \equiv \sum_{i=1}^n E_i \lambda_i$  (see equation (11))

of the films were measured with a MkII Dynamic Mechanical Thermal Analyzer (Polymer Labs).

#### Uniaxial tensile stress relaxation

Uniaxial tensile stress-relaxation experiments were conducted on an Instron Tensile Tester at  $21^{\circ}\text{C}/50\%$  r.h. Air-pressurized jaws were used to grip the film and prevent slippage. Strips 15 mm wide  $\times$  100 mm long (gauge length) were attached to the jaws and pulled initially at a rate of  $100 \text{ mm min}^{-1}$  up to a final strain of 0.5, 0.8, 1.3 or 1.6%. This strain was then held constant and the tensile force was recorded as a function of time. Measurements on a  $51 \mu\text{m}$  stainless-steel shim have been used to confirm the integrity of the gripping technique, i.e. the absence of slippage during the relaxation test.

#### Stress relaxation in bending

The film bending experiment was conducted with a commercial Bending Resistance Tester (Lorentzen & Wettre, Sweden). A 15 mm wide  $\times$  20 mm long film strip was bent to a fixed angle of  $15^{\circ}$  and the corresponding bending force was measured as a function of time. All measurements were performed in the 'machine' direction at  $21^{\circ}\text{C}/50\%$  r.h. In addition to measurements on the test films, we have also studied the bending relaxation of a CA/steel laminate. The purpose of this test was to evaluate the difference (if any) between the relaxation response of the CA film in uniaxial compression and in tension. In this test the  $127 \mu\text{m}$  thick CA film was laminated onto a  $51 \mu\text{m}$  thick stainless-steel shim with a silicone (Loctite Superflex) adhesive. The unlaminated steel shim was tested first to confirm that it does not relax in bending, i.e. that it is purely elastic. The bending test was then repeated with the CA layer either in tension (CA on convex side) or in compression (CA on concave side). It should be noted that the neutral axis of this laminate lies within the steel layer in either case, so that the CA layer is either in a state of pure tension or in uniaxial compression, depending on the direction of bending.

#### THEORY

When a thin plate (film) is subjected to cylindrical bending, a linear strain profile is established across its thickness:

$$\epsilon = y\Lambda \quad (1)$$

where  $\epsilon$  is the uniaxial strain acting along the contour of the bent film,  $y$  is the cross-film coordinate with its origin at the midplane (assuming that the midplane is

the neutral surface) and  $\Lambda$  is the curvature (reciprocal of radius of curvature) of the film (see *Figure 1*). For a transversely isotropic, elastic film, the curvature is related to the applied bending moment through:

$$M = ID_0\Lambda \quad (2)$$

where  $I$  is the moment of inertia of the film and  $D_0$  is the instantaneous bending modulus:

$$D_0 = E_0/(1 - \nu^2) \quad (3)$$

$E_0$  and  $\nu$  are, respectively, the tensile modulus and Poisson's ratio. Equation (2) can be generalized to the linear viscoelastic case by:

$$M(t) = I \int_0^t D(t - \xi) \dot{\Lambda}(\xi) d\xi \quad (4)$$

where  $D$  is the time-dependent bending modulus and  $\dot{\Lambda}$  is the rate of change of the curvature with time. When a flat viscoelastic film is bent at  $t=0$  to a fixed curvature  $\Lambda_0$ , all the strata in the film are effectively subjected to a step strain and equation (4) gives:

$$M(t) = I\Lambda_0 D(t) \quad (5)$$

The corresponding bending force per unit width is:

$$P(t) = M(t)/L \propto D(t) \quad (6)$$

where  $L$  is the length of the film. If Poisson's ratio of the film is not dependent on time, then:

$$D(t) = E(t)/(1 - \nu^2) \quad (7)$$

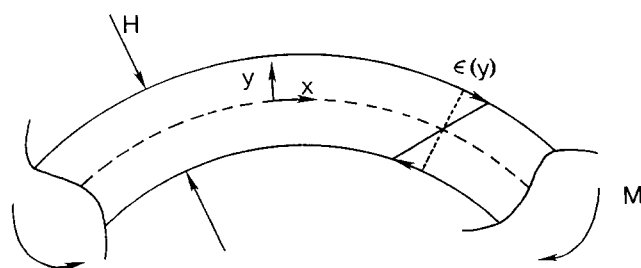
where  $E(t)$  is the relaxation modulus in tension. In general, however,  $D$  is related to the tensile modulus through the convolution theorem:

$$\bar{D} = \bar{E}/(1 - s^2\nu^2) \quad (8)$$

where overbars denote the Laplace transform and  $s$  is the transform variable. Thus, independent measurements of  $D(t)$  and  $E(t)$  can be used to estimate  $\nu(t)$  through equation (8).

For the general case where the relaxation times in tension and in compression are dissimilar, equation (6) can be scaled by:

$$P(t) \propto [D_t(t) + D_c(t)]/2 \quad (9)$$



**Figure 1** Schematic film geometry

where  $D_t$  and  $D_c$  are the bending moduli in tension and compression, respectively (assuming that the neutral surface coincides with the midplane).

Thus, based on equations (7)–(9):

$$D(t)/D_0 = E(t)/E_0 \quad (10)$$

if, and only if, the polymer is linear viscoelastic throughout the strain range of the bending experiment ( $D(t) \neq f(y)$ ), the relaxation responses in tension and compression are identical ( $D_t(t) = D_c(t)$ ) and Poisson's ratio is constant throughout the relaxation experiment ( $\nu \neq f(t)$ ). Violation of any of these conditions should give rise to differences in the relaxation response in tension and in bending.

## RESULTS AND DISCUSSION

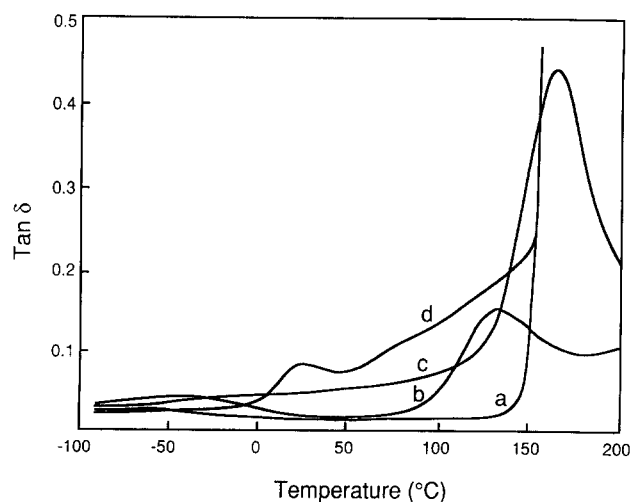
Dynamic-mechanical spectra of the test films, represented by the isochronous loss tangent ( $\tan \delta$ ) vs. temperature, are shown in Figure 2. The results clearly underlie the qualitative differences in relaxation response among the various films. It is noteworthy that CA and PC are essentially amorphous glasses at 21°C (temperature of the relaxation tests) while PET and PP are semicrystalline solids. Also, the test temperature lies below the glass transition temperature of PET but is within the  $\alpha$  transition range of PP (see Figure 2).

The normalized moduli of CA, PET, PC and PP in bending and in tension (at various strain levels) are shown in Figures 3–6. The experimental data are fitted via the regularization method by a generalized Maxwell function of the form:

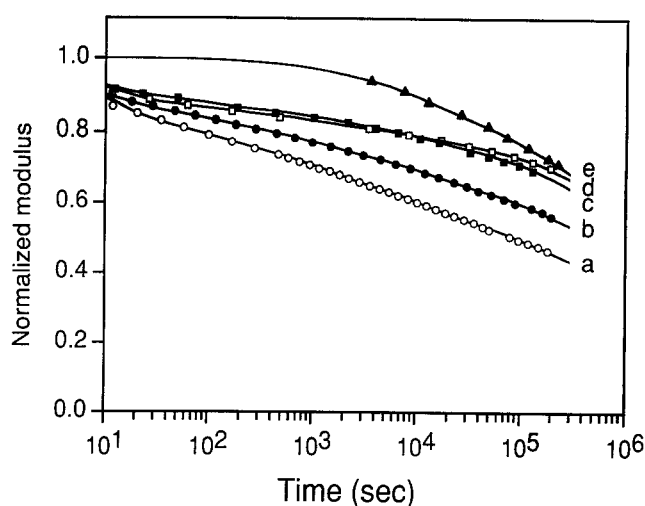
$$G(t)/G_0 = \sum_{i=1}^n G_i \exp(-t/\lambda_i) \quad (11)$$

where  $\lambda_i$  and  $G_i$  are the discrete relaxation times and moduli of the film and  $G_0$  is its instantaneous modulus. In the tensile tests  $G(t)$  is the tensile relaxation modulus  $E(t)$ , while in the bending experiment  $G(t)$  is its time-dependent bending modulus  $D(t)$ .

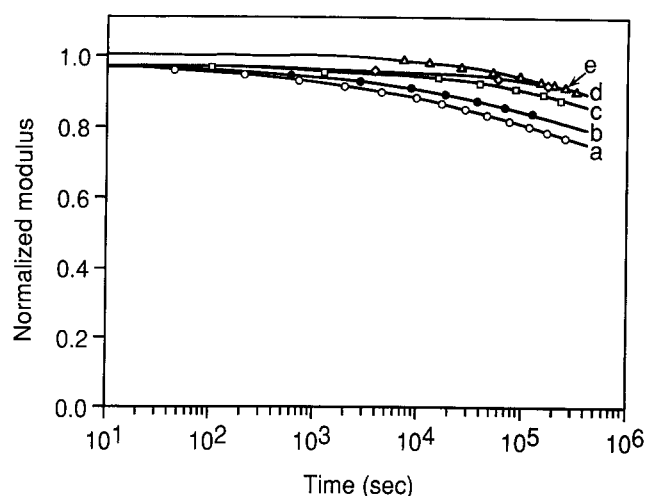
The data in Figures 3–5 reveal that PET, CA and PC exhibit a distinct non-linear viscoelastic response at



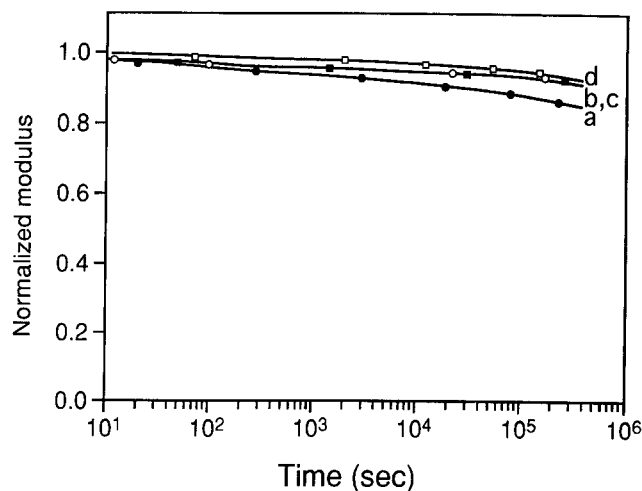
**Figure 2** Isochronous loss tangent (at 10 Hz) vs. temperature for test films: (a) PC, (b) PET, (c) CA, (d) PP



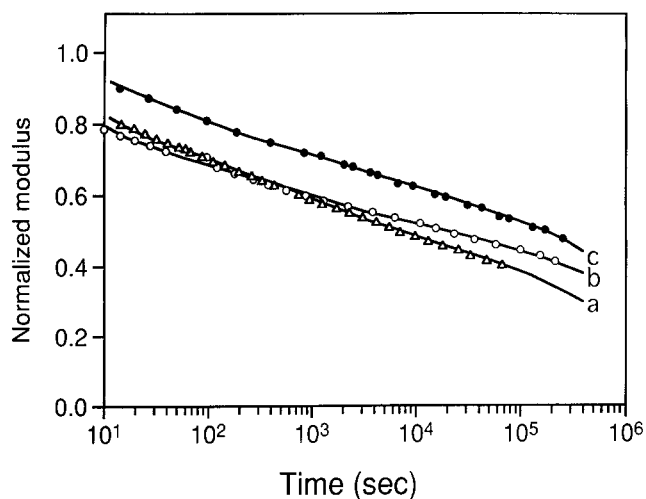
**Figure 3** Normalized relaxation moduli vs. time for CA at various strain levels: (a) tension, 1.6%; (b) tension, 1.3%; (c) tension, 0.8%; (d) tension, 0.5%; (e) bending. Points, experimental data; curves, regression fits based on equation (11)



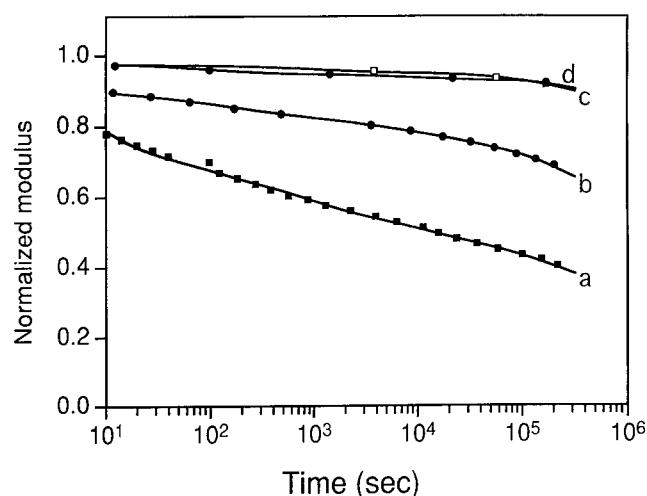
**Figure 4** Normalized relaxation moduli vs. time for PET at various strain levels: (a) tension, 1.6%; (b) tension, 1.3%; (c) tension, 0.8%; (d) tension, 0.5%; (e) bending. Points, experimental data; curves, regression fits based on equation (11)



**Figure 5** Normalized relaxation moduli vs. time for PC at various strain levels: (a) tension, 1.6%; (b) tension, 0.8%; (c) tension, 0.5%; (d) bending. Points, experimental data; curves, regression fits based on equation (11)



**Figure 6** Normalized relaxation moduli vs. time for PP at various strain levels: (a) tension, 0.8%; (b) tension, 0.5%; (c) bending. Points, experimental data; curves, regression fits based on equation (11)



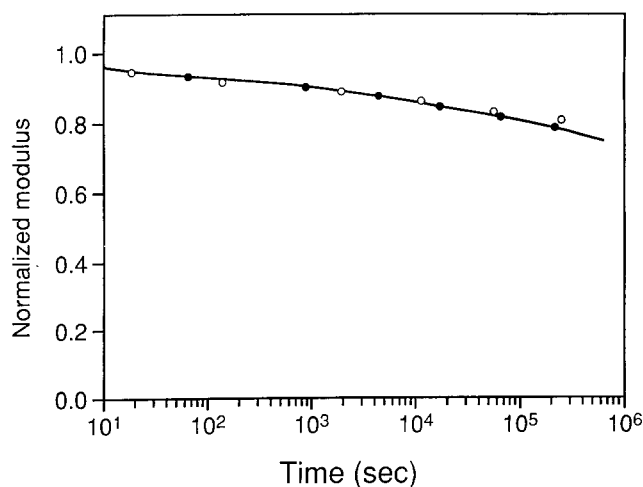
**Figure 7** Normalized tensile relaxation moduli vs. time for test films at 0.8% strain: (a) PP, (b) CA, (c) PET, (d) PC

strains  $>0.8\%$ , with the effective relaxation time becoming progressively shorter as the strain increases beyond  $0.8\%$ . In the case of PP (Figure 6), the onset of non-linearity is apparently at a strain lower than the lowest strain used in the tensile test, although the results are inconclusive on this point. Similar observations regarding the non-linearity of the stress-relaxation process have been reported for other polymers<sup>12,15,16</sup>, illustrating generally the limited range of linear response in common thermoplastic solids. Overall, however, the critical strain for the onset of non-linearity is higher than the strain generated in the bending test under the specified conditions ( $<0.3\%$ ), with the possible exception of PP.

The wide range of relaxation response of the films tested is illustrated in Figure 7 where the relaxation functions in tension (at  $0.8\%$ ) are compared for all the films. Of the films shown, PP and CA have the shortest relaxation times while PET and PC are the slowest to relax (see Table I). The relatively short relaxation times of CA and PP reflect the ability of these polymers to sustain 'cold flow', i.e. relative translation of large molecular domains under the applied strain, which are clearly related to their molecular structure and

morphology. It is interesting to note that the relaxation time is inversely proportional to the value of the loss tangent at the test temperature (Figure 2), which expresses the dissipative nature of the solid material, even though the timescales interrogated by the dynamic technique ( $\approx 0.1$  s) are much shorter than the characteristic times of the stress-relaxation test ( $\approx 10^6$  s).

Another interesting observation that can be gleaned from Figures 3–6 is that in all cases the relaxation moduli in tension and bending are qualitatively different, with the relaxation process in tension being generally faster. This is especially evident in the case of CA. As noted above, this difference may be ascribed to one of three possible causes (cf. equation (10)): (1) the viscoelastic relaxation process is non-linear; (2) the relaxation times in tension and uniaxial compression (both deformation modes are operative in the bending test) are dissimilar even under the low strains of the bending experiment; and (3) Poisson's ratio is time-dependent. We have already noted that viscoelastic non-linearity is not likely in any of the films (perhaps except PP) under the conditions of the bending experiment since the strain level in these runs is  $<0.3\%$ . In order to evaluate the second option, we conducted a bending relaxation test on a CA/steel laminate (see 'Experimental' section). This experiment was repeated with the CA layer in a state of pure tension (CA on convex side of laminate) and in uniaxial compression (CA on concave side). Since the steel shim was confirmed to be purely elastic, any time-dependent response of the laminate may be presumed to arise from the relaxation of the CA film. Figure 8 compares the bending relaxation response of the laminate with the CA layer being in a state of either tension or compression. Clearly, the relaxation functions in both cases are identical, thus suggesting that relaxation processes in tension and compression in the case of the CA film are indistinguishable at the strain levels of the bending test. (The relatively long relaxation time of the laminate compared with the relaxation time of the homogeneous CA film is due to the retarding effect of the steel layer.) McKenna and Zapas<sup>17</sup> have made qualitatively similar observations on the relaxation of poly(methyl methacrylate) (PMMA) specimens in tension and compression.



**Figure 8** Normalized bending moduli vs. time for CA/steel laminate: (●) CA in tension, (○) CA in compression

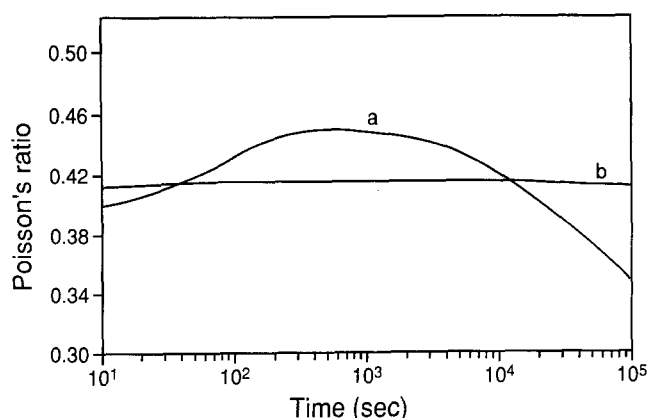


Figure 9 Poisson's ratio vs. time for: (a) CA, (b) PC. Analytical results based on equation (12)

It follows then that the only plausible explanation for the qualitative difference between the relaxation moduli in tension and in bending is the time dependence of Poisson's ratio,  $\nu(t)$ , which can be estimated from the given tensile and bending moduli via equation (8):

$$\nu(t) = \mathcal{L}^{-1} \left[ \frac{1}{s} \left( 1 - (1 - \nu_0^2) \frac{\bar{E}_N}{\bar{D}_N} \right)^{1/2} \right] \quad (12)$$

Here  $\mathcal{L}^{-1}$  is the inverse Laplace transform,  $\nu_0$  is the instantaneous Poisson's ratio and  $\bar{E}_N$  and  $\bar{D}_N$  are transforms of the normalized bending and tensile relaxation functions as expressed by equation (8). The function  $\nu(t)$  can be obtained by a numerical inversion of the expression in the argument on the r.h.s. of equation (12) and specification of  $\nu_0$ . For the CA and PC films of this study, the  $\nu(t)$  estimated from equation (12) are plotted in Figure 9. In both cases Poisson's ratio initially increases with time and then it goes through a shallow maximum, with the effect being far more pronounced for the CA film. The possibility of time dependence of Poisson's ratio in linear viscoelastic materials was conjectured by Freudenthal and Henry<sup>18</sup> and by Sternstein and coworkers<sup>3,12</sup>, and some evidence on the increase in Poisson's ratio with time was presented by LeGrand *et al.*<sup>19</sup> for polycarbonate specimens, but data on this effect are relatively scant. Freudenthal and Henry have shown that, under some conditions, linear viscoelastic materials can exhibit a time-dependent, non-monotonic Poisson's ratio if they are assumed to be elastically compressible. Yee and Takemori<sup>14</sup> observed that the dynamic tensile modulus of PMMA has a qualitatively different spectrum than the dynamic bulk modulus (or Poisson's ratio), which they attribute to the fact that the  $\beta$  relaxation in this polymer is not a purely internal motion but is somehow coupled to the bulk. In general, however, the temporal change in Poisson's ratio can be related to volume relaxation phenomena since  $\nu$  is, by definition, a function of volume. For uniaxial deformation of elastic materials,  $\nu$  is related to volume through:

$$\Delta V/V = (1 - 2\nu)\epsilon \quad (13)$$

where  $\Delta V$  is the change in volume induced by strain. Volume-relaxation phenomena are commonly observed in glassy and semicrystalline polymers<sup>8</sup>, and are usually

coupled in some complex manner to the applied strain field.

The presence of residual strain and the general anisotropy of the films studied may also contribute to the difference between  $D(t)$  and  $E(t)$ , but these effects are apparently insignificant since a qualitatively similar result is obtained for films produced by solvent casting and biaxial drawing processes, which possess different microstructures. The relatively large difference in the case of the CA film may be attributed, in part, to uneven distribution of residual solvent, moisture and plasticizer within the film and a corresponding strain-induced solvent redistribution during the relaxation test.

## SUMMARY

Stress-relaxation experiments in bending and in tension were conducted on polymer films with different relaxation characteristics and microstructures. In all cases the bending and tensile relaxation functions are dissimilar and the corresponding relaxation times are always longer in the bending mode. This difference is partly due to non-linearity in the relaxation response of the polymer, but even within the linear viscoelastic range the difference between the bending and tensile data persists. The possibility of inherent differences in relaxation rate between the tensile and compressive bands in the bent film has been ruled out based on experimental data on a CA/steel laminate. Another explanation for the apparent 'sluggish' relaxation in the bending test is the time dependence of Poisson's ratio, which may be related to volume-relaxation effects and/or residual solvent redistribution. This possibility requires further study and corroborating data before it can be conclusively accepted as the cause for the apparent discrepancy.

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## REFERENCES

- Greener, J., Tsou, A. H., Ng, K. C. and Chen, W. A. *J. Polym. Sci. (B)* 1991, **29**, 843
- McLoughlin, J. R. and Tobolsky, A. V. *J. Colloid Sci.* 1952, **7**, 555
- Sternstein, S. S. in 'Treatise on Materials Science' (Ed. J. M. Schultz), Academic Press, New York, 1977, Vol. 10B, p. 541; see also Sternstein, S. S. *Adv. Chem. Ser.* 1983, **203**, 123
- Pink, E. *Rev. Deform. Behav. Mater.* 1977, **2**, 37
- Högfors, C., Kubát, J. and Rigdahl, M. *Rheol. Acta* 1985, **24**, 250; Kubát, J. *Phys. Status Solidi* 1982, **111**, 159
- LeGrand, D. G., Olszewski, W. V. and Bendler, J. T. *Ann. NY Acad. Sci.* 1986, **484**, 307
- Struik, L. C. E. in 'Failure of Plastics' (Eds. W. Brostow and R. D. Corneliussen), Hanser, New York, 1987, p. 209
- Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
- Kubát, J., Maurer, F. H. J., Rigdahl, M. and Welander, M. *Rheol. Acta* 1989, **28**, 147
- Vleeshouwers, S., Jamieson, A. M. and Simha, R. *Polym. Eng. Sci.* 1989, **29**, 662
- Spinoza, A. and Aklonis, J. J. *Polym. Eng. Sci.* 1993, **33**, 486

- 12 Sternstein, S. S. and Ho, T. C. *J. Appl. Phys.* 1972, **43**, 4370
- 13 Koppelman, J. *Rheol. Acta* 1958, **1**, 20
- 14 Yee, A. F. and Takemori, M. T. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **20**, 205
- 15 Tieghi, G., Fallini, A. and Levi, M. *Polym. Commun.* 1991, **32**, 245
- 16 Brüller, O. S. and Laws, R. *Kunststoffe* 1983, **73**, 367
- 17 McKenna, G. B. and Zapas, L. J. in 'Rheology', Vol. 3, 'Applications' (Eds. G. Astarita, G. Marrucci and L. Nicolais), Plenum, New York, 1980, p. 299
- 18 Freudenthal, A. M. and Henry, L. A. in 'Solid Propellant Rocket Research' (Ed. M. Summerfield), Academic Press, New York, 1960, p. 33
- 19 LeGrand, D. G., Olszewski, W. V. and Bendler, J. T. *Thermochim. Acta* 1990, **166**, 105