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Elastic Properties of a Polyimide Film Determined by Brillouin Scattering and Mechanical Techniques*

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ELASTIC PROPERTIES OF A POLYIMIDE FILM DETERMINED BY BRILLOUIN SCATTERING AND MECHANICAL TECHNIQUES

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ABSTRACT

We discuss here the complete determination of the elastic properties of a polyimide film using two experimental techniques. One technique employs the polymer film as a vibrating membrane and allows a direct determination of the 'macroscopic' biaxial modulus. Brillouin scattering, which measures the elastic properties on a ~100 μ scale, allows for a complete characterization of the elastic behavior. The results obtained by the two techniques are in agreement within the reported error bars.

INTRODUCTION

Thermal and mechanical characteristics of a polymeric film usually dictate its level of performance in a given application. Mechanical properties of interest are usually stiffness, strength, toughness and creep. Properties such as impact and tear resistance of polymeric films cannot easily be related to material characteristics such as molecular structure and organization since processing history, testing conditions, sample imperfections and specimen geometry strongly influence these failure-related properties. The usual testing procedures leading to measurements of toughness and strength of polymeric films are destructive in nature.

Stiffness on the other hand, is a much simpler property to understand since it measures the resistance of a material to deformation. While it is constitutive in nature, it can be correlated with the structure of the material. Stiffness describes the elastic behavior of materials in the small strain region. As an extension of Hooke's law, the most general definition of 'stiffness' is through either the elastic stiffness constants (C_{ij}) or the elastic compliance constants (S_{ij}):

$$\sigma_i = \Sigma\, C_{ij}\, \epsilon_j \text{ or } \epsilon_i = \Sigma\, S_{ij}\, \sigma_j \qquad (1)$$

Where σ_i are components of stress and ϵ_j are components of strain.

In many cases it is useful to define simpler relationships such as the bulk modulus, Young's modulus, Poisson's ratio, etc. As will be discussed below, these are special cases of eq 1, and each one of these moduli can be expressed as a combination of C_{ij} or S_{ij} (see Appendix A).

The experimental methods commonly used to obtain elastic moduli can roughly be classified as follows: (i) macroscopic (static) stress-strain measurements, (ii) macroscopic dynamic mechanical methods, (iii) ultrasonic methods, and (iv) Brillouin scattering. For thin film polymers ultrasonic methods are very hard to apply and are almost never used. In such cases it is necessary to resort to less conventional techniques such as Brillouin scattering, and as a result, a complete determination of the elastic tensor is not always possible. Brillouin scattering is not a novel technique in polymer science, and many review articles have discussed the usefulness of the technique in this field.[1] Research

Further narrowing down of the symmetry of Kapton® requires some additional assumptions. If we assume that the orientation of the molecules does not distinguish between the top and bottom of the film, the symmetry cannot be triclinic. An equivalent assumption about any in-plane axis fixes the symmetry as orthorhombic. This is the symmetry we will take as a starting point for our investigation. The resulting C_{ij} array is given by

$$C_{ij} = \begin{matrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{matrix} \qquad (2)$$

with its 9 independent parameters. If this array is not sufficient to account for the measured results, some of the previous symmetry assumptions must be incorrect.

RESULTS AND DISCUSSION

(i) *Brillouin scattering*

From the spectra collected in the backscattering geometry we obtain the dependence of the Brillouin shift as a function of α (α is defined in Figure 1); the results are shown in Figures 2a and 2b. We note that both the longitudinal and transverse modes exhibit an angular dependence indicating that the film properties normal to the film are different from those in the plane. The platelet results, which reflect in-plane behavior, are shown in Figures 3a and 3b. They show no clear evidence for any angular dependence in either the transverse or longitudinal Brillouin peaks.

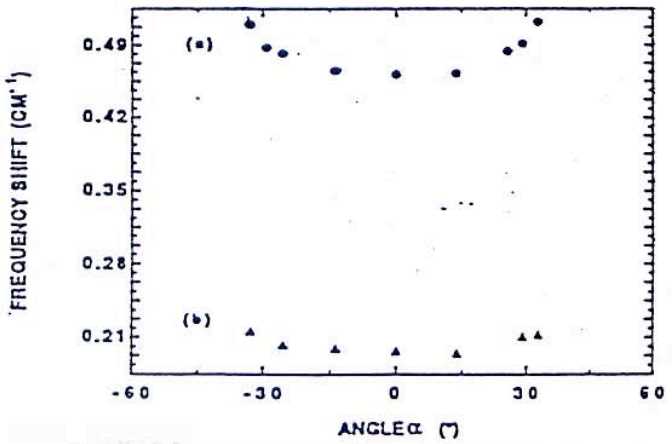

Figure 2.
Angular dependence of Brillouin peak in the backscattering geometry: longitudinal (a) and transverse (b).

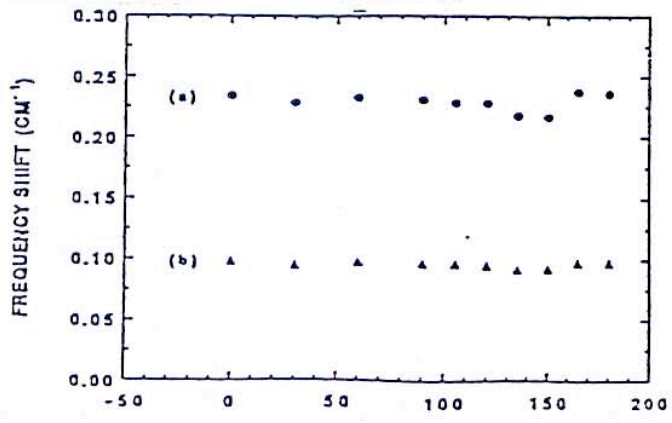

Figure 3.
Angular dependence of Brillouin peak in the platelet geometry: longitudinal (a) and transverse (b).

with polymers using Brillouin scattering has primarily been concerned with characterization of dynamics (segmental motion, relaxation, etc.) in the glassy state although the technique was employed to measure the in-plane elastic properties of stretch-oriented polymers.[2] We also describe in this paper a novel experimental technique for the direct measurement of the biaxial modulus of the polyimide film.

EXPERIMENTAL SECTION

The Brillouin scattering apparatus consists of an intense monochromatic source of well collimated light (in this case a single moded argon ion laser), and a tandem Fabry-Perot interferometer to frequency analyze the scattered light, a detector and a data acquisition system.[3] The two scattering geometries used here are shown in Figure 1, denoted as backscattering (a) and platelet (b). In the backscattering geometry, phonons with wavevector $q = 2nk_L$ (where n is the refractive index and k_L is the wavevector of the incident light) propagating close to the film normal can be probed. In the platelet geometry, phonons with $q = \sqrt{2}\, k_L$ propagating in the plane of the film are investigated: a simple rotation about the surface normal allows selection of any direction in the plane.

The other experimental technique we used to measure the biaxial elastic modulus involves the determination of resonance frequencies of a radially (and isotropically) stretched circular membrane. The experimental setup used to determine the biaxial modulus is described in detail in reference 4. Since the material has to be conductive for this method to be applicable, a thin (200Å) layer of Al was evaporated onto the Kapton® polyimide film (obtained from DuPont Co.).

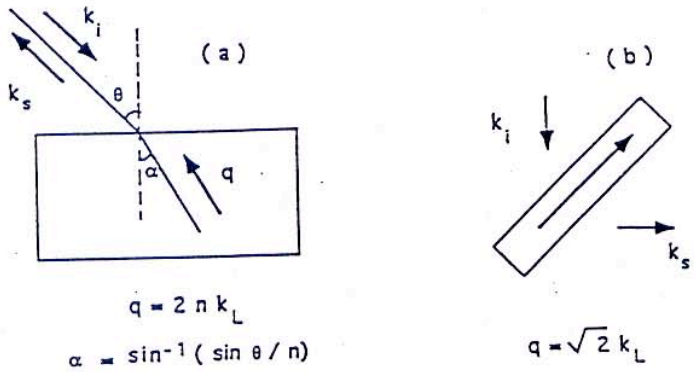

Figure 1. Scattering geometries used in Brillouin scattering experiment: back scattering (a) and platelet (b); k_i, k_s and q are the incident, scattered and phonon wave vectors respectively. α is the scattering angle.

THEORY AND ASSUMPTIONS

Before attempting to calculate individual C_{ij} from experimental results, it is necessary to determine the non-zero elements and the number of independent elements in the C_{ij} array. Although the structure of Kapton® has been reported to be either monoclinic or orthorhombic,[7] it is not clear what symmetry is to be expected for the elastic constant matrix, in the absence of information on preferential molecular orientation. Since the material is birefringent in the plane of the film, the film normal can have at most 2-fold symmetry. Furthermore, if the film normal is structurally different from any in-plane axis, the symmetry of the C_{ij} array must be orthorhombic or lower.

Based on the above data we conclude, within our experimental accuracy, that Kapton® exhibits isotropic behavior in plane and anisotropic behavior out of plane. Thus the polymeric film resembles a material with hexagonal symmetry in its elastic response. This indicates either an accidental degeneracy or that the accuracy of our measurements is not sufficient to resolve the in-plane anisotropy. With the indicated increased symmetry, defining the z axis to be the film normal, the C_{ij} array (eq 2) has the following additional restrictions: $C_{22} = C_{11}$, $C_{23} = C_{13}$, $C_{44} = C_{55}$ and $C_{66} = (C_{11}-C_{12})/2$ which reduces the number of independent parameters from 9 to 5.

These five elastic constants can be determined from the Brillouin spectra acquired in different scattering geometries. The Brillouin frequency shifts are related to the velocities (v_q) of acoustic phonons by

$$\Delta\omega = 2n\omega_o (v_q/c) \sin (q/2) \qquad (3)$$

where n is the refractive index, ω_o the frequency of the incident light, c the velocity of light and q the scattering angle. The subscript q emphasizes that the velocity depends on the direction of propagation. Since the velocities along different directions are related to different C_{ij}'s, the latter are easily determined.

Thus from the backscattering geometry at $\alpha = 0$, C_{33} is obtained from the velocity of the longitudinal phonons and C_{44} from the velocity of the transverse phonons. Similarly, from the in-plane longitudinal and transverse phonon velocities, we can calculate C_{11} and C_{66} respectively. C_{12} can be computed from $C_{66} = (C_{11}-C_{12})/2$. The remaining elastic constant C_{13} is obtained only indirectly from the angular dependence given in Figures 2a and 2b through a complex expression[5] which involves C_{11}, C_{33}, C_{44} and α. Alternatively, C_{13} can be estimated independently from expressions for the biaxial modulus (A-4) and the in-plane Young's modulus (A-2); for the biaxial modulus we use the value (5.26 ± 0.26 GPa) determined by the mechanical technique discussed below. For the Young's modulus we use the literature value of 3.0 ± 0.3 GPa reported for Kapton®.[8] The C_{ij} obtained from our Brillouin results and those calculated from other techniques are summarized in Table I. From Table I we note that elastic constants obtained from different methods are in agreement within the reported error bars.

Table I
Elastic Constants of Kapton® Film

Elastic Constants GPa	C_{11}	C_{33}	C_{13}	C_{12}	C_{44}	C_{66}
Brillouin Scattering	8.9±0.3	5.84±0.12	5.6±0.5	5.8±0.3	1.2±0.2	1.57±0.03
Mechanical[a] Technique			5.2±0.5			
Literature[b]			5.9±0.2			

[a] Value calculated from the measured biaxial modulus.
[b] Value calculated from the reported Young's modulus in reference 8.

(ii) *Biaxial modulus*

The normal modes (of vibration) of a film fixed on a circular boundary of radius a are well characterized.[6] The film behaves as a membrane when the restoring force is dominated by the tension T (force per unit area) applied to the film boundary. However, when the tension is negligible compared to the elastic stiffness of the film, it is called a plate, and its elastic response is different from that of a membrane. Whether a given material responds like a membrane or a plate depends on the ratio of its thickness to its diameter and also on its C_{ij}. Experimentally we found that our composite film (polymer + 200 Å aluminum) responds like a membrane, with the fundamental resonance (ν_{01}) given by

$$\nu_{01} = 0.38274/a(\sqrt{T/\rho}) \qquad (5)$$

where ρ is the mass density. The higher resonances (γ_{ij}) are given by

$$\nu_{ij} = \beta_{ij}\, \nu_{01} \qquad (6)$$

Where i is the number nodal lines and j is the number of nodal circles.
β_{ij} are numbers; for the lowest modes they are β_{11}= 1.5933, β_{21}= 2.1355, β_{02}= 2.2954.[4,6]

The measured strain versus the square of the resonant frequency is plotted for the polyimide film in Figure 4. Since ν^2 is a measure of the applied stress, Figure 6 basically depicts the stress-strain behavior of the polymeric film. The biaxial modulus therefore can be calculated from the slope of the straight line in Figure 4. Using the density 1.42 g/cc for the polyimide film, we obtain a biaxial modulus of 5.26 + 0.26 GPa.

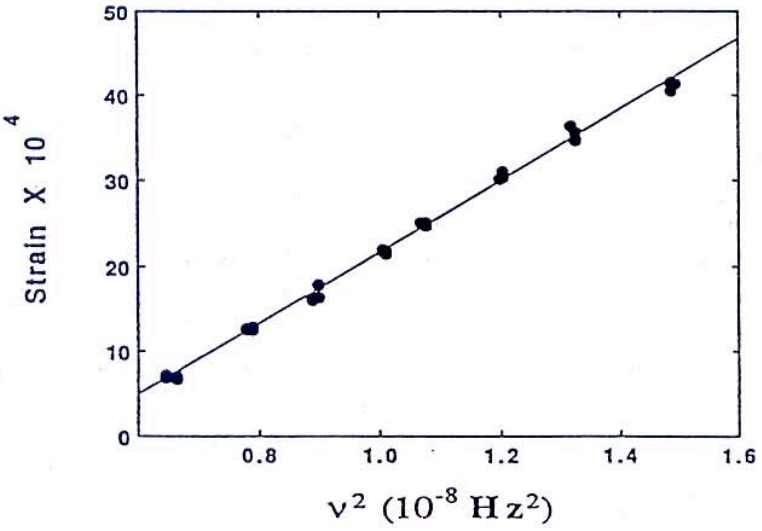

Figure 4. Strain versus the square of the fundamental frequency for Kapton® film.

Using the complete set of C_{ij} obtained from the Brillouin scattering experiments we can calculate any modulus corresponding to a particular deformation. Since within our experimental accuracy Kapton® is hexagonal, we have summarized in the appendix expressions relating the particular moduli to the C_{ij} relevant to this case. In Table II we list the numerical values of these moduli which may be of interest in various applications.

We see from Table II that the moduli measured by different techniques are in good agreement.

Table II
Elastic Moduli of Kapton® Film Calculated from the Elastic Constants Determined from Brillouin Scattering

Elastic Modulus GPa	B	E_Y^{in}	E_Y^{out}	E_b	G_{in}	G_{out}
Brillouin Scattering	5.8±0.1	3.5±1.0	1.6±0.8	4.0±2.0	1.57±0.03	1.02±0.02
Mechanical[a] Technique				5.26±0.26		
Literature[b]		3.0±0.3				

Since our Brillouin spectroscopic measurements could not resolve the anisotropic elastic properties in the film plane, the maximum value of the elastic modulus measurable by macroscopic testing is given by its tensile modulus value of 3 GPa.[8] A higher measured biaxial modulus therefore indicates significantly enhanced stiffness in applications involving biaxial deformations, than that indicated by macroscopic tensile test result. This conclusion is valid as long as the elastic response of the film remains Hookean (as evidenced by the linear stress-strain behavior). Thus we believe that direct measurement of biaxial modulus by the technique given here provides a reliable means to predict the performance of polymeric films in their most popular application: packaging.

CONCLUSIONS

Polymer morphology plays a very important role in governing the thermomechanical properties. Any experimental technique that provides determination of properties through preservation of polymer morphology is desirable. The Brillouin spectroscopic technique described here is nondestructive and allows a thorough characterization of the elastic properties of polymeric films. Since both experimental techniques described here basically measure fundamental material constants, we should be able to establish structure-property relationships in a straightforward manner, through similar measurements on a number of polymeric systems.

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APPENDIX

In this appendix we define and derive expressions for various moduli of a material with hexagonal symmetry.

(i) Bulk modulus (B):

$$B = (C_{11}C_{33} + C_{12}C_{33} - 2C_{13}^2)/(2C_{33} + C_{11} + C_{12} - 4C_{13}) \qquad (A.1)$$

(ii) In plane Young's modulus (E_Y^{in}):

$$E_Y^{in} = (C_{11} - C_{12})\{1 - (C_{13}^2 - C_{12}C_{33})/(C_{11}C_{33} - C_{13}^2)\} \qquad (A.2)$$

(iii) Out of plane Young's modulus (E_Y^{out}):

$$E_Y^{out} = C_{33} - 2C_{13}^2/(C11 + C12) \qquad (A.3)$$

(iv) Biaxial modulus (E_b):

$$E_b = C_{11} + C_{12} - 2C_{13}^2/C_{33} \qquad (A.4)$$

(v) In plane shear modulus:

$$G_{in} = \sigma_{xy}/\epsilon_{xy} = C_{66} \qquad (A.5)$$

(vi) Out of plane shear modulus:

$$G_{out} = \sigma_{xz}/\epsilon_{xz} = C_{44} \qquad (A.6)$$

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