

Temperature Dependency of Elastic Moduli and Internal Dilational and Shear Frictions of Polyetherimide

Mikio Fukuhara*

Technology Center, Toshiba Tungaloy, 2-7 Sugawacho, Tsurumi, Yokohama, 230-0027, Japan

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ABSTRACT: To investigate the thermally activated structural change of polyetherimide, longitudinal and transverse wave velocity, six kinds of elastic parameters (Young's, shear, and bulk moduli, Lamé parameter, Poisson's ratio, and Debye temperature), and dilational and shear internal frictions were simultaneously measured over a temperature range 69–474 K, using the ultrasonic pulse method. All elastic moduli decreased with increasing temperature, suggesting a lowering of molecular bonding strength. From shear internal friction, the 190, 314, 371, 395, and 430 K peaks are interpreted as the γ - [derived from $-C(=O)-$ motion], β_1^* -

(interplane slippage between benzene rings), β - (softening-glass transition) peaks, and rotational vibration of main benzene rings and a local relaxation of the main chain, respectively. The abrupt increase peak from 449 K in dilational friction would be a low-temperature side shoulder of the α -glass-transition peak. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 759–764, 2003

Key words: polyimide; molecular dynamics; modulus; relaxation; glass transition

INTRODUCTION

Aromatic polyetherimide (PEI) is one member of the polyimide family for which mechanical and electrical properties have been extensively studied.¹ It is characterized by incorporation of the proper ether linkages into the polyimide molecular chain.² Because PEI has the highest tensile modulus, high-temperature stability, low dielectric constants,¹ and good chemical and environmental stability,³ its properties are attractive for microelectronic applications. In particular, the longer-term thermal stability of PEI is consistent with the well-known stability of the aromatic imide moiety.¹ Thus we selected PEI as a representative engineering polymer with high performance.

To investigate these properties more comprehensively, it is necessary to observe the acoustic characteristics of PEI. Ultrasonics is the only method available for measurement of high-frequency elastic parameters and losses, which arise from molecular motions underlying relaxation processes.^{4–8} Internal friction is a property that depends on the nonideal elastic behavior (anelasticity), which yields information about the various stages of incipient crystallization such as relief of strain, softening, rotation of side chains, and micro-Brownian motion. Thus it is clear that the elastic parameters and internal frictions are convenient probes for structural investigation of engi-

neering polymers. Our interest lies in studying the thermally activated structural relaxation of PEI in the temperature regions of interest on the basis of molecular morphology associated with viscoelasticity.

Using an ultrasonic pulse method that we developed, we investigated longitudinal and transverse velocities, elastic parameters [Young's, shear ($=C_{44}$ in elastic constant matrix), and bulk moduli, Lamé parameter ($=C_{12}$), Poisson's ratio, and Debye temperature], and dilational and shear internal frictions for PEI in the temperature range between 69 and 474 K. We observed many peaks in molecular morphology associated with structural relaxation. In particular, given that characterization of various relaxation transitions, observable in a wide temperature region, is important in relation to the stress–strain properties of solid polymers⁹ (i.e., to the impact strength and to anomalies in the temperature and time dependency of strength), the origins of damping of various β -groups have to be clarified in view of dilational and shear modes, taking into consideration chemical bond morphology. As far as we know, no previous research has been done on simultaneous measurement of phonon velocities, elastic parameters, and dilational and shear internal frictions for PEI. Neither have we seen any temperature-dependent elastic data for PEI.

For phonon studies of PEI, longitudinal and transverse wave velocities as a function of temperature have not been extensively studied. Johnson and Burlhis¹ measured flexural modulus and tensile strength between 223 and 353 K. They did not observe any anomalies for these elastic parameters, except for flexion points at around 313 and 413 K, respectively.

*Email: a80010@tungaloy.co.jp.

EXPERIMENTAL

Materials and sample preparation

The amorphous PEI sample used in this study was a commercial material (ULTEM-1000) produced by General Electric Company (New York). Characteristics of the PEI sample are listed in Table I.¹⁰ The specimen was a short rod fastened to the waveguide of PEI with a thread pitch of 1.75 mm, using a domed cap nut of copper. This eliminated the generation of spurious signals attributed to mode conversion at the sides.¹³

The density was precisely determined by the Archimedes method; the specimen was weighed in air and in distilled water.

Velocity measurement

Longitudinal and transverse wave velocities, V_l and V_t , respectively; elastic parameters; and internal friction values were accurately measured under a vacuum pressure of 0.1 MPa, using an ultrasonic pulse method with zero cross-time detection. The experimental procedure is described in detail in previous studies.^{4-8,11,12} The specimen, vertically mounted in cryostat with a liquid nitrogen cooling system under vacuum, was measured from 69 to 474 K at a heating rate of approximately 0.08 K/s, during which the transverse wave disappeared. The temperature was first reduced to 69 K by decompressing the pressure over liquid nitrogen. The transducer and the specimen were joined to both sides of the waveguide using a water-free glycerin grease (Sonicoat SH, Nichiyo Acetylene, Osaka, Japan). Because trailing pulses are generated when a longitudinal sound wave is propagated through a rod, accurate longitudinal and transverse velocities are simultaneously determined in one run using mode conversion,^{11,14} even if there is a temperature gradient, and the resulting velocity gradient occurs through the waveguide between room temperature and the cooled or heated sides. To avoid propagation loss arising from high frequencies and inaccurate measurements attributed to lower frequencies, we used a longitudinal wave-generation PZT transducer (Harisonic, CT) with a frequency of 1.7 MHz. Thus we could not use a wide frequency range, although we know that it is necessary for PEI to study the frequency dependency of these parameters.

Debye temperature measurement

Ultrasonic wave velocity measurements are related to the long-wavelength acoustic phonons,¹⁵ enabling the elastic Debye temperature Θ_D to be obtained from

$$\Theta_D = \left(\frac{h}{k}\right) \left(\frac{3N}{4\pi V}\right)^{1/3} V_m \quad (1)$$

where h and k take their usual values and N denotes the number of mass points in an average atomic volume V . The mean velocity V_m can be calculated by

$$V_m = \frac{1}{3} \left(\frac{1}{V_l^3} + \frac{2}{V_s^3}\right) \quad (2)$$

Internal friction measurement

Increasing rates of internal friction Q_l^{-1} and Q_s^{-1} at temperature t for longitudinal and transverse waves, respectively, were calculated using the ratio of logarithmic echo amplitude of the ultrasonic pulse wave at t to the corresponding amplitude measured at the lowest test temperature.¹¹

RESULTS AND DISCUSSION

Temperature dependency of wave velocity

Sound velocity provides a sensitive tool for locating phase transitions, determining phase diagrams, and studying the phase-transition order. Figure 1 shows the longitudinal and transverse wave velocities as a function of temperature. The transverse wave velocities in the temperature region over 475 K could not be determined because of the low level of transverse wave damping. Both velocities decrease substantially with increasing temperature, as well as those of metals,^{16,17} ceramics,^{11,18} and other polymers such as poly(methyl methacrylate) (PMMA),⁴ polyimide (PI),⁵ polycarbonate (PC),⁶ and poly(vinyl chloride) (PVC).⁷ This suggests a decrease in molecular bonding strength. In particular, a distinct temperature slope change in transverse wave velocity takes place from 368 K. This change is coupled with a shear damping, described later. Indeed, a noticeable change in the slope of allowable stress was reported at 367 K.¹⁰

TABLE I
Characteristics of PEI Used in This Study

Density (kg/m ³)	T_g (K)	Copolymer (%)	Water absorption (%)	Tensile yield strength (MPa)	Crystallinity (%)	Thermal expansion coefficient $\times 10^5$ (1/K)	Dielectric constant 1 kHz, 300 K
1.294	217	0	0.25	105	0	5.6	3.15

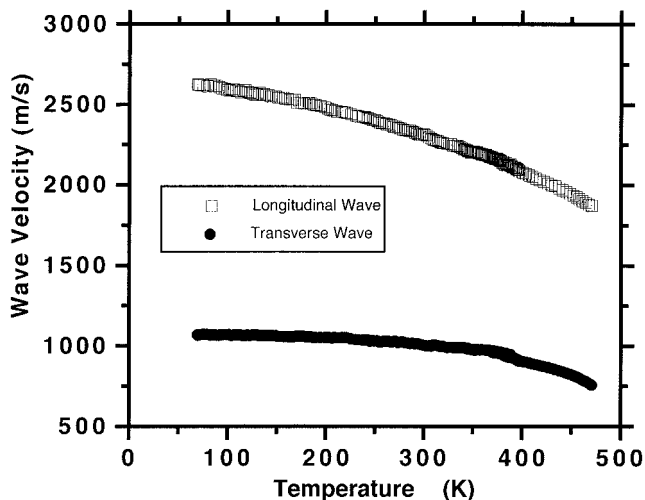


Figure 1 Temperature dependency of longitudinal and transverse wave velocities of polyetherimide.

Temperature dependency of elastic parameters

The temperature dependencies of Young’s, shear, and bulk moduli, Lamé parameter, and Poisson’s ratio were calculated using both longitudinal and transverse wave velocities, with a measurement error within 5% allowance. These results are presented in Figures 2 and 3, respectively. Young’s and shear moduli show a gradual decrease except for a notable decrease from 367 K, as the temperature increases. The temperature slope change from 367 K would be generated from the motion of PEI’s main chain, corresponding to shear friction mechanisms, as described later. To the best of our knowledge, no one has ever reported any theoretical model that anticipates or predicts such a change for Young’s and shear moduli.

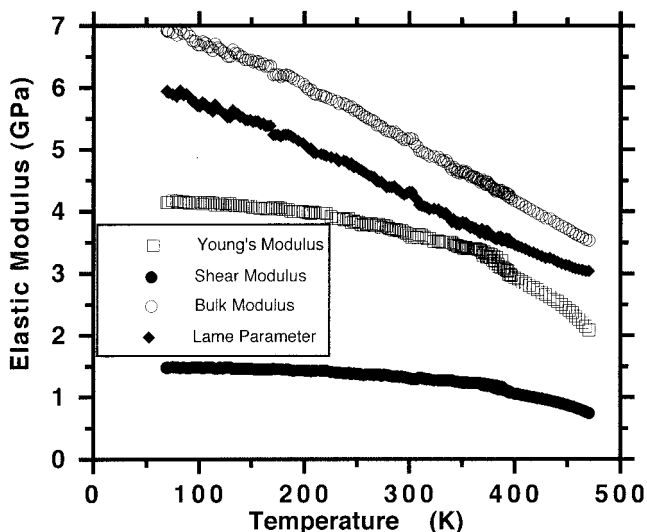


Figure 2 Young, shear, and bulk moduli and Lamé parameter of polyetherimide as a function of temperature.

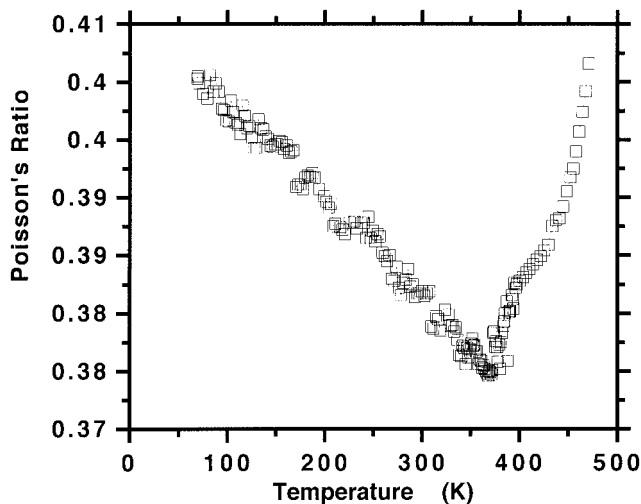


Figure 3 Poisson’s ratio of polyetherimide as a function of temperature.

On the other hand, the bumpy curves of bulk modulus and the Lamé parameter show a faster decrease compared with those of Young’s and shear moduli. The bumpy behavior of the bulk modulus and Lamé parameter indicates that a thermal structural change of PEI is more sensitive to two- or three-dimensional volume-nonpreserving distortion such as bulk modulus and Lamé parameter, than to simple (uniaxial) volume-preserving tension and shear such as Young’s and shear moduli, respectively. Here, we note that bulk modulus and the Lamé parameter do not show a distinct temperature slope change from 367 K. Although we have not determined the second phase transition based on specific heat and bulk thermal coefficient in the temperature regions of interest, the existing thermodynamic theory for a second-order phase transition predicts that the bulk modulus will show discontinuity at a specific temperature.¹⁹ Thus it is clear that the 367 K change in Young’s and shear moduli is not the second-order phase transition from the disordered to the ordered phase of molecular structure. In other words, the 367 K change may be associated with volume-preserving molecular displacement of the first order.

Because a ratio E (Young’s modulus)/ K (bulk modulus) can be conveniently taken as a measure of elasticity,²⁰ the ratio is compared with those of other representative materials.^{4-7,11,15-17,21,22} Table II shows that the ratio of PEI is the second lowest value, showing high elasticity near that of rubber.²³

Poisson’s ratio linearly decreases up to 367 K and then increases abruptly as the temperature increases. This behavior also resembles that of PMMA,⁴ PI,⁵ PC,⁶ and PVC.⁷ The abrupt increase from 367 K suggests a softening attributed to the viscoelastic nature,²⁴ corresponding to a temperature slope change in Young’s and shear moduli (Fig. 2). The decrease in Poisson’s

TABLE II
Ratio of Young's Modulus E to Bulk Modulus K for Polyetherimide, Low Carbon and Stainless Steels,¹⁷ Ti-6Al-4V, Inconel 718,¹³ Al₂O₃, ZrO₂, Si₃N₄,¹¹ Fused Quartz,²¹ Polymethyl Methacrylate,⁴ Polyimide,⁵ and Urethane Rubber²² at Room Temperature

Polyetherimide	Low carbon steel	Stainless steel	Ti-6Al-4V	Inconel 718	Al ₂ O ₃	ZrO ₂	Si ₃ N ₄	Fused quartz	Polymethyl methacrylate	Polyimide	Urethane rubber
0.697	1.261	1.249	1.225	1.657	1.560	1.103	2.137	1.974	1.025	0.910	0.595

ratio is qualitatively interpreted as being analogous to the case of rubber stretching.^{25,26} However, we cannot state clear intrinsic reasons for the gradual decrease, which needs further investigation.

We next note a change in the effective atomic distance of the temperature region of interest. The Debye temperature (Fig. 4) shows a gradual decrease up to 367 K and then a rapid decrease. The decrease in Debye temperature (i.e., the decrease in the maximum frequency allowed) leads to an increase in effective atomic distance. Thus the rapid decrease from 367 K could be derived from an increase of atomic distance in the amorphous phase or crystal lattice in the crystalline phase, which reflects a soft phonon mode, associated with structural relaxation; it would be the former, assumed from noncrystallinity in Table I.

Temperature dependency of internal frictions

The temperature dependency of wave velocities and elastic parameters we observed provides clear evidence of molecular displacement. In this section, internal friction curves for longitudinal and transverse waves were measured as a function of temperature (Fig. 5). The dilational friction shows a large peak at 209 K and a small one at 351 K, and an abrupt increase

from 449 K. Sliding or rotation of crystals and a variation in potential energy between atoms for metallic, organic, and inorganic materials cause the dilational friction.^{4-8,11,16-18} From the physics of dilational friction and the molecular structure of PEI,¹ the 209 K peak is probably attributable to the γ -relaxation peak attributed to $-C(=O)-$ motion.²⁷ The abrupt increase from 449 K would be a low-temperature side shoulder of an α (glass-transition) peak at 490 K,¹ associated with a variation in potential energy, analogous to the dilational friction in PMMA,⁴ PI,⁵ PC,⁶ PVC,⁷ and anthracene single crystal (ASC).⁸ The α -peak is associated with micro-Brownian motion of the main chain in amorphous regions, accompanied by a pronounced dielectric loss derived from dipole dissociation.¹ Because the temperature and magnitude of the α -relaxation are critically dependent on the chain rigidity, ordered structure, and cooperativity of the segment motion in the PI family, the α -transition temperature of the PEI is lower than that of PI with rigid *p*-phenylene in the backbone. Indeed, it is well known that the glass transition for polymers does not necessarily occur at a very narrow range of temperature, but in a rather wide range.²⁸ In addition, we cannot elucidate the origins of the small 351 K peak. This would be

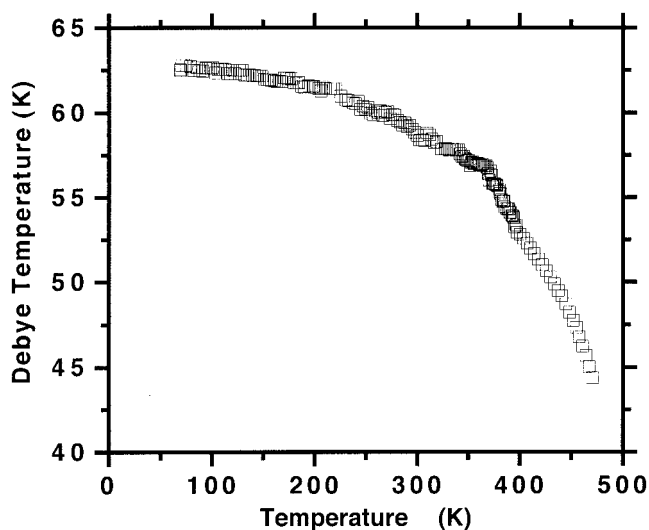


Figure 4 Temperature dependency of Debye temperature for polyetherimide.

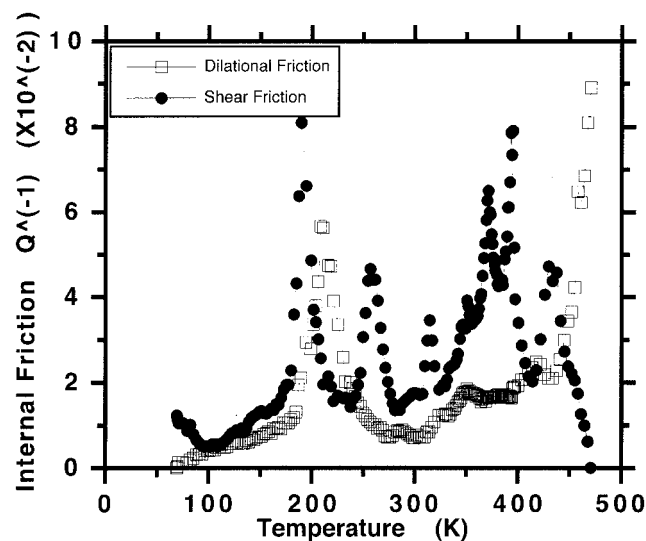


Figure 5 Temperature dependency of internal friction for longitudinal and transverse wave of polyetherimide.

attributed to thermal motions of tiny subunits in the PEI.

The shear friction shows six peaks at 190, 257, 314, 371, 395, and 430 K. The shear friction corresponds to atomic rearrangement in either the crystalline or the noncrystalline structure for metallic, organic, and inorganic materials.^{4–8,11,16–18} From the physical properties of shear friction and the molecular structure of PEI,¹ the 190, 314, 371, 395, and 430 K peaks may be linked to the γ -peak, β_1^* derived from interplane slippage between benzene rings,²⁹ the β -peak (softening-glass transition), rotational vibration of the main benzene rings,³⁰ and a local relaxation of the main chain,³¹ respectively. The β -peak is derived from rotational vibration of the phenyl rings, as assumed from Bessonov et al.⁹ Although Gilham et al.³¹ observed the β -relaxation peak at 333–370 K in PI, using the torsional braid method with 1 Hz, the various conclusions, based on experimental observations for the origin of the β -relaxation process in PI families, are not consistent and are sometimes conflicting.³³ Thus we must address the origin of the β -relaxation process in PEI, using other scientific methods. Furthermore, the origin of the 257 K peak is unclear at the present time. This would be derived from thermal motions of ether linkage units in PEI.

Although acoustic wave velocity, which is mainly phonon velocity, varies with temperature and pressure because of the incongruity of potential between atoms, the pressure effect in the ultrasonic method is negligible. On the other hand, flexural vibration and resonance frequency methods are subject to possible deterioration resulting from high-frequency fatigue.³⁴ In this ultrasonic method, we observed many friction peaks, compared with those of low-frequency (<15 kHz) methods such as torsional pendulum^{32,35} and resonance frequency.^{28,36} For this reason, it is known that the ultrasonic thermal relaxation losses occur when significant segments of the polymer chain oscillate at the same frequency as that of the applied wave.³⁷ Furthermore, although the frequency dependency was investigated to clarify the microscopic nature of the thermally activated anelastic relaxation process, it is difficult for torsional braid and resonance frequency methods to change frequency over a wide frequency range. Thus it is not necessarily suitable for investigation of origins of the relaxation processes to use the nonultrasonic methods under low frequencies, although little research has been carried out on the high-frequency subject. Therefore, it would be desirable for microscopic investigation of PEI to use the ultrasonic method without the fatigue effect.

As can be seen from the internal frictions in Figure 4, the thermally activated structural relaxation processes of PEI over the whole temperature region of interest are mainly divided into three categories, in order of temperature: γ -process between 170 and 240

K; β -process between 300 and 410 K; and α -process over 410 K. This shows that thermal stimulation propagates from motion or rotation of subunits to micro-Brownian motion of the main chain with increasing temperature. On the other hand, Young's and shear moduli, Poisson's ratio, and Debye temperature in Figures 2, 3, and 4, respectively, show two categories below and above 367 K. In other words, the internal friction response for structural change is more sensitive compared with the response of elastic parameters depending on main structural changes only.

It is known that relaxations for the shear and bulk responses are different within the glassy regime. The flexion point at 367 K in Figures 2, 3, and 4 corresponds to the β -peak, which is connected to softening-glass transition. The β -peak transition is unrelated to the two- or three-dimensional volume-nonpreserving distortion, as can be seen from bulk modulus and Lamé parameter in Figure 2. As deduced from the definition for C_{12} in the elastic constant matrix, the relaxation may be connected with an interlocking of two parts of the random glassy network.³⁸ Thus it is clear that the β -peak is attributed to the structural transition associated with the simple volume-preserving distortion.

When we take note of the rising curve from 367 K in Poisson's ratio (Fig. 3), we can see two upward tendencies at around 370 and 450 K. The former is the β -peak and the latter corresponds to the α -peak. Because Poisson's ratio is a viscoelastic function, these transitions closely correlate to the viscoelastic nature. The viscoelastic properties would be associated with an increase in the effective atomic distance, assumed from the Debye temperature curve in Figure 4. The viscoelasticity must be treated by a complex modulus M^* ,³⁹ as follows:

$$M^* = M_1 + i\omega\eta \quad (3)$$

where M_1 ($=\rho V^2$) is the dynamic modulus; and η ($=2\rho\delta V^3/\omega^2$) is the dynamic viscosity, where ρ is the density, δ is the logarithmic damping ratio, and ω ($=2\pi f$) is the angular frequency. Equation (3) is a function of frequency. Thus, the Poisson's ratio is dependent not only on frequency but also on temperature.⁴⁰ Loss peaks that appear in the temperature space may not appear in the frequency space. However, we could not investigate the frequency dependency in this study because of PEI's transmissibility within a narrow frequency region. In this interesting field, further study is needed to compare with other aromatic polymers.

CONCLUSIONS

To investigate the thermally activated structural change of polyetherimide, characteristic elastic and

damping behaviors were simultaneously measured as functions of temperature between 69 and 137 K in PEI, using the ultrasonic pulse method. The distinct temperature slope change in transverse wave velocity and Young's and shear moduli takes place from 368 K. The bulk modulus and Lamé parameter monotonically decreased with increasing temperature. Poisson's ratio and Debye temperature gradually decreased up to 367 K and then increased and decreased abruptly, respectively, as the temperature increased. The dilational friction showed one large peak at 209 K and the abrupt increase from 449 K, whereas the shear friction showed six peaks at 190, 257, 314, 371, 395, and 430 K. The 190 and 209 K peaks are probably attributable to the γ -relaxation peak stemming from $-C(=O)-$ motion. The 314, 371, and 395 K peaks would be softening-glass transition, associated with motion of the main benzene rings. The 430 K peak and the abrupt increase from 449 K would be the local relaxation and the relaxation process associated with α -glass transition, respectively. These results suggest that the thermally activated structural relaxation processes of PEI are characterized by α - and β -transitions associated with the simple volume-preserving viscoelastic distortion.

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