

# Tensile and Dynamic Mechanical Properties of Improved Ultrathin Polymeric Films

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**ABSTRACT:** Tensile and dynamic mechanical properties of improved ultrathin polymeric films for magnetic tapes are presented. These films include poly(ethylene terephthalate) or PET, poly(ethylene naphthalate) or PEN, and aromatic polyamide (ARAMID). PET film is currently the standard substrate used for magnetic tapes; thinner tensilized-type PET, PEN, and ARAMID were recently used as alternate substrates with improved material properties. The thickness of the films ranges from 6.2 to 4.8  $\mu\text{m}$ . Young's modulus of elasticity, F5 value, strain-at-yield, breaking strength, and strain-at-break were obtained at low strain rates by using a tensile machine. Storage (or elastic) modulus,  $E'$ , and the loss tangent,  $\tan \delta$ , which is a measurement of viscous energy dissipation, are measured by using a dynamic mechanical analyzer at temperature ranges of  $-50$  to  $150^\circ\text{C}$  (for PET), and  $-50$  to  $210^\circ\text{C}$  (for PEN and ARAMID), and at a frequency range of 0.016 to 29 Hz. Frequency-temperature superposition was used to predict the dynamic mechanical behavior of the films over a 28 decade frequency range. Results show that ARAMID and tensilized films tend to have higher strength and moduli than standard PET and PEN. The rates of decrease of storage modulus as a function of temperature are lower for PET films than those for PEN and ARAMID films. Storage modulus for PEN films are higher than that for PET films at high frequencies, but this relationship reverses at low frequencies. ARAMID has the highest modulus and strength among the films in this study. The relationship between polymeric structure and mechanical properties are also discussed. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2225–2244, 2002

**Key words:** dynamic mechanical analysis; storage modulus; loss tangent; polymer film; magnetic tape

## INTRODUCTION

Poly(ethylene terephthalate), or PET, is currently the most widely used polymeric substrate mate-

rial for magnetic recording tapes.<sup>1</sup> Thinner substrates and higher areal densities (track density  $\times$  linear density) are required to meet the demand for advanced magnetic storage devices with high volumetric densities, especially for computer data storage tapes. For higher areal densities, a substrate with high dimensional stability under various environmental conditions is required. For high track densities, lateral contraction of the substrates due to viscoelastic, thermal, hygroscopic, and shrinkage effects must be minimal during storage on a reel and use in a drive.<sup>1</sup> To

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minimize stretching and damage during use, the thinner substrates should be a high-modulus and high-strength material with low creep and shrinkage characteristics. Furthermore, because high-coercivity magnetic films on metal evaporated tapes are deposited and/or heat treated at elevated temperatures, a substrate with stable mechanical properties up to 100–150°C or even higher is desirable. Elastic, viscoelastic, and shrinkage measurements were performed on PET and alternative substrates by various investigators.<sup>1–5</sup>

Viscoelasticity refers to the combined elastic and viscous deformation of a substrate when external forces are applied, and shrinkage occurs when residual stresses present in the substrate are relieved at elevated temperatures. If a substrate of a magnetic tape shrinks or deforms viscoelastically, then the head cannot read information stored on the tape. Various long-term reliability problems including uneven tape-stack profiles (or hard bands), mechanical print-through, instantaneous speed variations, and tape stagger problems can all be related to the viscoelastic properties of substrates.<sup>1</sup> To minimize these reliability problems, it is not only important to minimize creep strain, but the rate of increase of total strain needs to be kept to a minimum to prevent stress relaxation in a wound reel. The elastic and viscoelastic behavior of the substrate is also important to determine how the tape responds as it is unwound from the reel and travels over the head. This elastic/viscoelastic recovery and subsequent conformity of the tape with the head occurs in just a few milliseconds and requires optimization of the substrate's dynamic properties. The properties are measured by using dynamic mechanical analysis (or DMA), and the information acquired from this analysis includes storage or elastic modulus,  $E'$ , and loss tangent,  $\tan \delta$  (a measure of the amount of viscous or nonrecoverable deformation with respect to the elastic deformation). Both storage modulus and loss tangent are measured as a function of temperature and deformation frequency, and results can be used to predict the dynamic response of substrates over several orders of magnitude. Substrates of magnetic tapes were recently substantially improved.<sup>1–5</sup> Weick and Bhushan<sup>6</sup> also used DMA data to predict tape-to-head conformity. A lack of tape-to-head conformity can lead to an increase in wear of the head, as demonstrated by Hahn.<sup>7</sup>

The main objective of this study was to measure tensile and DMA properties of improved ultrathin polymeric films that are either used or being developed for magnetic tape substrates for ultrahigh recording media applications. DMA experiments were carried out at temperatures ranging from –50 to 150°C (for PET) and –50 to 210°C [for poly(ethylene naphthalate) (PEN) and aromatic polyamide (ARAMID)], which cover the glass transition temperatures ( $T_g$ ) of PET and PEN films. On the basis of these data, master curves were generated by using frequency-temperature superposition to predict the mechanical properties of the films. Tendencies of storage modulus, loss tangent, and effects from advanced processing were related to the structural characteristics of each polymeric film.

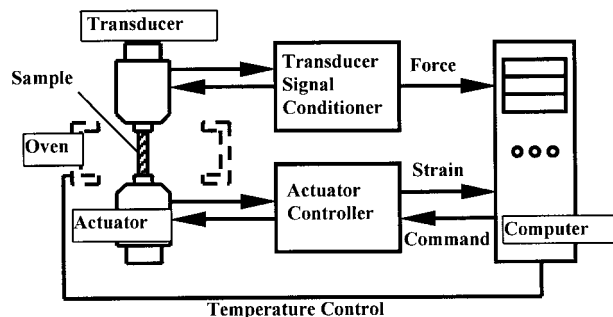
## EXPERIMENTAL

### Test Apparatus and Procedure

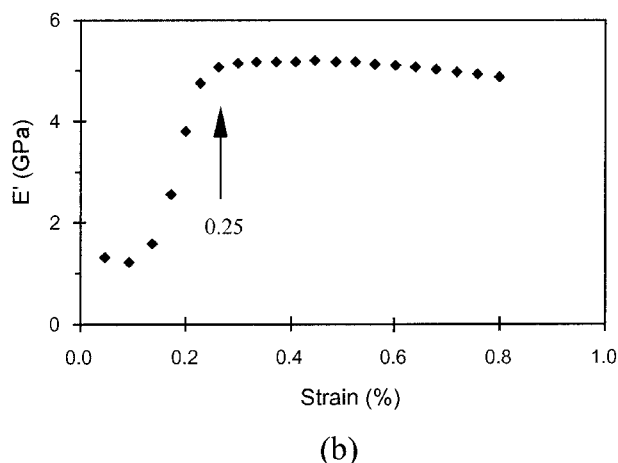
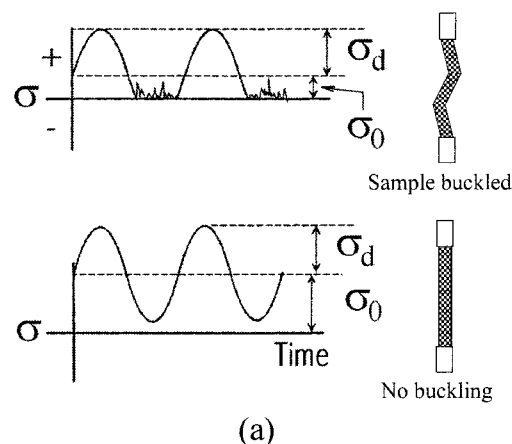
Tensile measurements were made by using a MTS (MTS Systems Corp., MN) model 804 tensile machine with a 50-lb. load cell manufactured by Sensotech Ltd. (Ohio). The tests were conducted at ambient temperature (19–22°C) and uncontrolled humidity [25–33% relative humidity (RH)]. In a previous work,<sup>8</sup> the ASTM D 1708 standard was used to measure the tensile properties of dog-bone-shaped microtensile specimens. The dog-bone-shaped test specimens were used so as to ensure failure in the thinner region. In this ASTM method, the gauge length was assumed to be equal to the distance between the grips. For thin plastic sheets thinner than 1 mm, another standard test method according to ASTM D 882–97 is recommended for measurement of tensile properties and is used here. According to this standard, a width–thickness ratio of at least 8 shall be used, because narrow specimens magnify effects of edge strains or flaws, or both. Rectangular 10-mm-wide  $\times$  150-mm-long samples with the grip distance of 100 mm were selected to measure the Young's modulus (modulus of elasticity), F5 value (the stress at 5% elongation), strain-at-yield, breaking strength, and strain-at-break. The sample length was limited by the available sample sizes. Young's modulus of all samples was measured at the strain rate of 0.1/min. For the properties other than Young's modulus, according to this standard, a strain rate of 0.1/min should be used if the strain-at-break of

the specimen is lower than about 20%, and a rate of 0.5/min should be used if the strain-at-break is 20–100%. Based on this recommendation, the selected strain rate was 0.1/min for ARAMID and 0.5/min for other samples. Incidentally, as the breaking strength and yield strength may vary according to the sample geometry and test conditions, the F5 value proved to be stable and independent and is commonly used in industry as the representative of mechanical strength for polymers. A minimum of five tests were performed for each sample. The reproducibility of the data was within about 5% for Young's modulus and F5 value and about 10% for strain-at-yield, breaking strength, and strain-at-break.

A Rheometrics (Piscataway, NJ) RSA II dynamic mechanical analyzer was used to measure the dynamic mechanical properties of the polymeric films. Figure 1 shows the functional block diagram of this test apparatus. The analyzer was used in a tension/compression mode, and rectangular 6.35-mm-wide  $\times$  22.5-mm-long samples were used. In this mode, rectangular samples are fastened vertically between the grips and a sinusoidal strain is applied to the specimen. Frequency/temperature sweep experiments were performed for a 0.1–182  $\text{rad s}^{-1}$  (0.016–29 Hz) range, and 14 data points were taken. For each frequency, tests sweep at 11 different temperature levels ranging from  $-50$  to  $150^\circ\text{C}$  for the PET films, and 14 temperature levels ranging from  $-50$  to  $210^\circ\text{C}$  for PEN films and ARAMID film. The temperature increment was  $20^\circ\text{C}$ , and the soak time for each temperature level was 10 s. For PET and PEN films, the upper limits for the test temperatures were set to cover the peak temperatures for loss tangent related to glass transition, which are just above the glass transition temperatures. The glass transition temperature for PET, PEN, and ARAMID are 80, 120, and  $280^\circ\text{C}$ , respectively.



**Figure 1** Functional block diagram of DMA test apparatus—Rheometrics Inc. RSA II.



**Figure 2** (a) Schematic showing the effect of pre-tension (static force) on the sample buckling and (b) an example of storage modulus ( $E'$ ) measurement in a strain-sweep test of a Standard PET sample.  $E'$  remains steady after a strain of about 0.25%; sample buckles below this strain value.

The analyzer was operated in autotension mode with a static force on the samples. This prevented buckling of the thin films by applying the peak dynamic forces (corresponding to a strain of 0.0025) while using the static force as a mean, as shown in Figure 2(a).<sup>9</sup> It was found that a static strain of more than 0.25% was needed to prevent buckling [see Fig. 2(b) for an example for standard PET]. Therefore, the initial static force of 110 g was used for standard PET and ARAMID in the machine direction (MD), and 65 g was used for other samples, which is equivalent to strain offset of about 0.25%.

Equations used to calculate the storage (or elastic) modulus,  $E'$ , and loss tangent,  $\tan \delta$ , are as follows:

$$E' = \cos \delta \left[ \frac{\sigma}{\varepsilon} \right] \quad (1a)$$

$$E'' = \sin \delta \left[ \frac{\sigma}{\varepsilon} \right] \quad (1b)$$

$$|E^*| = \sqrt{(E')^2 + (E'')^2} \quad (1c)$$

$$\tan \delta = \frac{E''}{E'} \quad (1d)$$

$$\varepsilon = \frac{D}{L} \quad \sigma = FgK_\sigma \quad (1e)$$

where  $E'$  is the storage modulus,  $E''$  is the loss (or viscous) modulus,  $|E^*|$  is the magnitude of the complex modulus,  $\varepsilon$  is the applied strain,  $\sigma$  is the measured stress,  $\delta$  is the phase angle shift between stress and strain,  $D$  is the displacement from the strain transducer,  $K_\sigma$  is the a stress constant equal to  $100/wt$ ,<sup>9</sup>  $w$  is the width of the sample,  $t$  is the thickness of the sample,  $g$  is the gravitational constant ( $9.81 \text{ m s}^{-2}$ ), and  $F$  is the measured force on the sample from the load cell. A minimum of two tests was performed on each sample and reproducibility was within a few percentages.

In simple terms, at each temperature level the analyzer operates by applying a strain on the sample in a sinusoidal fashion for each of the 0.1–182  $\text{rad s}^{-1}$  frequencies. The strain is measured by a displacement transducer, and the corresponding sinusoidal load on the sample is measured by a load cell. Because the polymeric films are viscoelastic, there will be a phase lag between the applied strain and the measured load (or stress) on the specimen. The storage modulus,  $E'$ , is therefore a measure of the component of the complex modulus which is in-phase with the applied strain, and the loss modulus,  $E''$ , is a measure of the component which is out-of-phase with the applied strain. The in-phase stress and strain results in elastically stored energy which is completely recoverable, whereas out-of-phase stress and strain results in the dissipation of energy which is nonrecoverable and is lost to the system. The loss tangent,  $\tan \delta$ , is simply the ratio of the loss modulus to the storage modulus.<sup>1</sup>

### Test Samples

Table I provides a list of the polymeric films examined in this study, along with thicknesses and

**Table I List of Substrates Used in This Study**

Sample	Symbol	Thickness ( $\mu\text{m}$ )
Standard PET	Standard PET	14
Tensitized PET	T-PET	6.1
Supertensitized PET	ST-PET	6.1
	Standard	
Standard PEN	PEN	6.2
Tensitized PEN	T-PEN	6.2
Supertensitized PEN	ST-PEN	6.2
ARAMID	ARAMID	4.8

The glass transition temperatures for PET, PEN, and ARAMID are 80, 120, and 280°C, respectively.

symbols used throughout the article. PET films include three kinds of films: standard PET, tensitized PET, and supertensitized PET. A 14- $\mu\text{m}$ -thick standard PET film is the typical substrate used for videocassette recorder (VCR) tapes. Standard PET is drawn biaxially about 300% (stretch ratio  $\sim 4$ ) in both MD and transverse direction (TD) during processing. Thinner tensitized-type PET films, which include tensitized PET (T-PET) and supertensitized PET (ST-PET), are further drawn in MD and have a 6.1  $\mu\text{m}$  thickness. The tensitized-type PET films are used for advanced magnetic tapes, especially computer data storage tapes. Similarly, PEN films have 6.2  $\mu\text{m}$  thickness and include three kinds of films: standard PEN, tensitized PEN (T-PEN), and supertensitized PEN (ST-PEN). PEN films have begun to be used as substrates for advanced magnetic tapes, especially long-play videotapes and computer data storage tapes. Both PET and PEN films are manufactured by a biaxial drawing process. On the other hand, ARAMID film is manufactured by using a solution-casting process followed by a slight drawing process. ARAMID film used for advanced magnetic tapes has a thickness of 4.8  $\mu\text{m}$ .

The unit structures of the polymer films are illustrated in Figure 3. PET and PEN have identical hydrocarbon backbones indicative of polyester materials. PET contains a single benzene ring in each repeating unit, whereas PEN contains a naphthalene ring that is slightly more rigid. However, naphthalene groups have high mobility from ambient temperature to 60°C.<sup>10</sup> Typical crystallinities of PET and PEN films are 40–50 and 30–40%, respectively. ARAMID contains amide groups with intermolecular hydrogen bonds that are stronger than the intermolecular interactions

for PET and PEN. As a result, ARAMID enables the formulation of high-strength, high-modulus films.

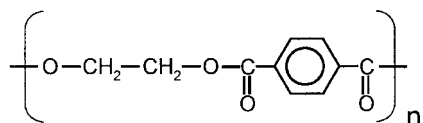
Because of the different stretch ratios along the MD and the TD during manufacture, all the materials were anisotropic and were tested along the MD and TD. It was confirmed that the MD corresponds to the direction of orientation of crystals in biaxial films by using a cross-polarizer in which optical axes show the extinction of light. Two linear polarizing films of 50.8 mm (2 in.) square (Tech Spec<sup>TM</sup> Quality J43-781, Edmund Scientific) were used. As examples, Figure 4 shows the orientation of the major axis with respect to the MD of PET films. The difference between the major axis and the MD is below  $\pm 5$  degrees.

## RESULTS AND DISCUSSION

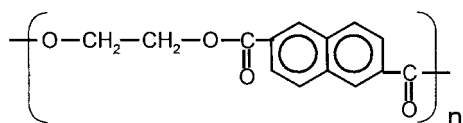
### Tensile Properties

The engineering stress–strain curves of the films are shown in Figure 5 along the MD and TD. All the samples extended uniformly during the test, and no neck was formed. The yield point is then approached by determining the intersection of the two tangents to the initial and final parts of the stress–strain curve.<sup>11</sup> Table II and Figure 6(a) give summaries of tensile properties of various films. Figure 6(b) shows the effect of strain rate

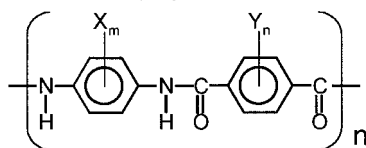
PET : Poly(ethylene terephthalate) Lumirror<sup>®</sup>



PEN : Poly(ethylene 2,6-naphthalate) Teonex<sup>®</sup>

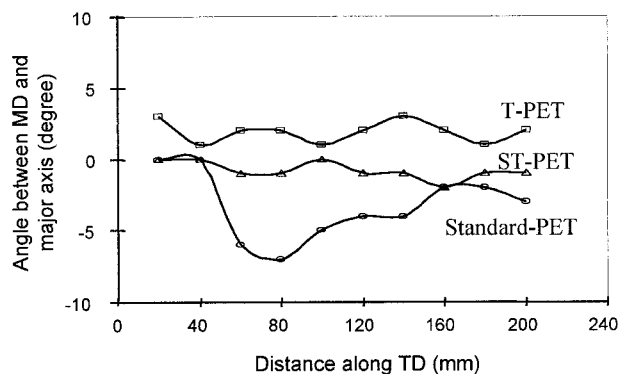


ARAMID : Aromatic poly(amide) Micron<sup>TM</sup>

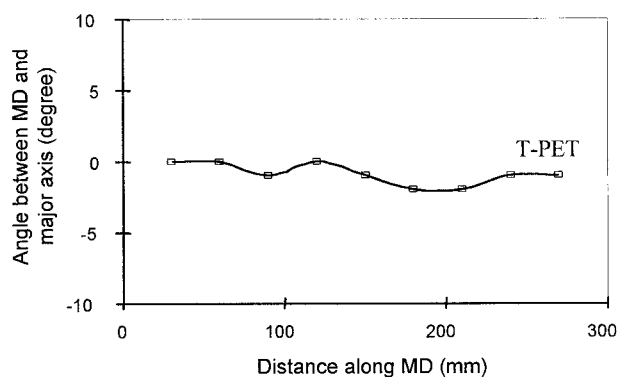


X, Y : Substituent

**Figure 3** Chemical unit structures of various polymeric films.



(a)

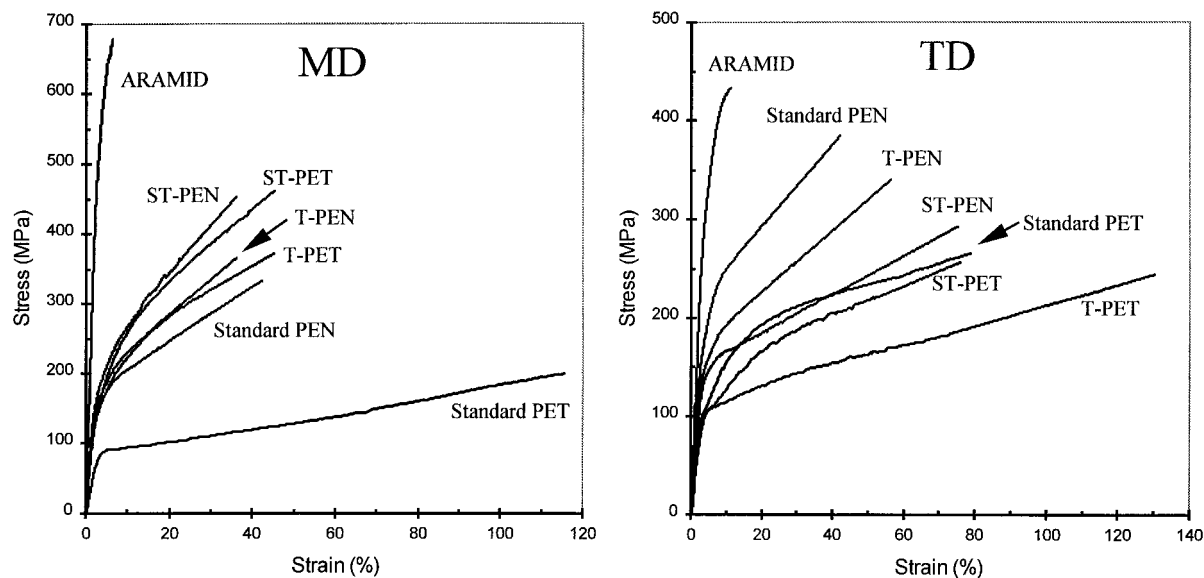


(b)

**Figure 4** Orientation of the optical major axis with respect to the MD of PET films (a) along the TD and (b) along the MD.

on tensile properties on T-PET and T-PEN. An increase in strain rate results in increases in Young's modulus, F5 value, breaking strength, and decreases in strain-at-yield and strain-at-break. T-PEN appears to be more strain-rate dependent than T-PET: when strain rate increases from 0.1 to 0.5/min, the Young's modulus for T-PEN (MD) increases by 1.2 GPa, whereas that for T-PET increases only by 0.3 GPa [Fig. 6(b)]. The strain rate could be related to the frequency in DMA tests, where the storage modulus of PEN in DMA tests appears to be more frequency dependent.

Tensilization significantly increases the Young's modulus, F5 value, and breaking strength of PET films in the MD. For example, the Young's modulus of Standard PET (3.5 GPa) is doubled after tensilization (T-PET: 7 GPa) and supertensilization (ST-PET: 7.35 GPa). However, the deformation properties, strain-at-break and strain-at-



**Figure 5** Engineering stress–strain curves of various polymeric films. Strain rate for PETs and PENs was 0.5/min, strain for ARAMID was 0.1/min.

yield, are decreased after tensilization. These tendencies reverse in the TD, as the Young's modulus changes from 4.8 GPa for Standard PET to 4.5 GPa for T-PET, and strain-at-break changes from 79% for Standard PET to 130% for T-PET.

Standard PET shows a fairly low work-hardening ratio ( $d\sigma/d\varepsilon$ ) after the elastic limit is reached for the MD samples. This increases as a result of the stretching process in the case of T-PET and ST-PET. The increase in the hardening ratio as a result of stretching arises because the chain segments in the amorphous regions are already extended in a variety of directions, thereby limiting the freedom that can occur during additional stretching (e.g., during tension test). The stress–strain curve for T-PET in the TD is similar to that for Standard PET along the MD. Furthermore, it is supposed to have been stretched at a low ratio in this direction during the manufacturing process. Comparatively, ST-PET may have a higher stretch ratio in both the MD and the TD than T-PET.

Tensilization has similar effects on PEN films as on PET films, but is not that significant. For example, the modulus for Standard PEN increases from 7 to 7.7 GPa (T-PEN) and 8.5 GPa (ST-PEN) in the MD and decreases from 7.25 to 6.1 GPa (T-PEN) and 5.5 GPa (ST-PEN) in the TD after tensilization.

ARAMID has a high Young's modulus, strength, and low elongation, and it is more aniso-

tropic than PET and PEN films. The Young's modulus along the MD and TD are 20.4 and 11.3 GPa, respectively, as compared to 9.5 GPa (MD) and 10.5 GPa (TD) in a previous article.<sup>8</sup> This is probably due to an improvement in tensilization along the MD during the manufacturing process.

## DMA Properties

### PET Data

Results from the DMA for PET films are shown in Figure 7; storage moduli are plotted in Figure 7(a), and the loss tangents are plotted in Figure 7(b). In addition to the two-dimensional representations of storage modulus and loss tangent as a function of frequency and temperature, a three-dimensional representation of these parameters is also shown for each material. From the three-dimensional surfaces, it can be seen that higher elastic moduli correspond with higher deformation frequencies and lower temperatures, whereas lower elastic moduli correspond with lower deformation frequencies and higher temperatures. This can also be seen from the two-dimensional representations of the data.

For all the PET films, the rate of decrease of storage moduli as a function of temperature is low before a certain temperature is reached; then the rate suddenly increases and the storage moduli drop to a very low level. This change corresponds to the character of the loss tangents in Figure 7(b), where the loss tangents remain low below

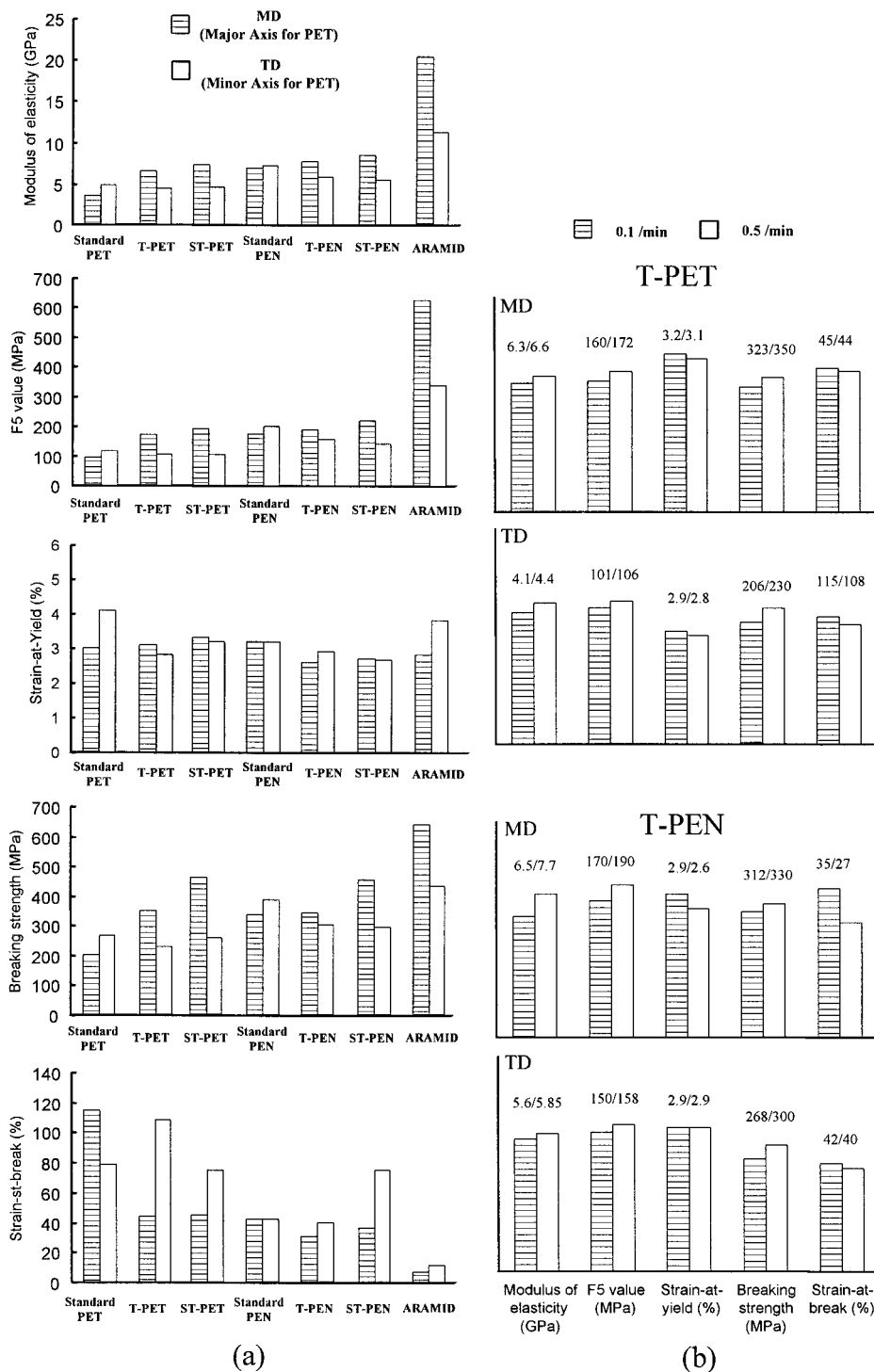
**Table II Summary of Mechanical Properties of Various Substrates**

Data Resource	Data From This Study									
	Manufacturers' Data				Tensile					DMA
	Modulus of Elasticity (GPa)	F5 Value (MPa)	Breaking Strength (MPa)	Strain at Break (%)	Modulus of Elasticity <sup>a</sup> (GPa)	F5 Value <sup>b</sup> (MPa)	Strain at Yield <sup>b</sup> (%)	Breaking Strength <sup>b</sup> (MPa)	Strain at Break <sup>b</sup> (%)	Modulus of Elasticity <sup>c</sup> (GPa)
Standard PET										
MD	4.4	113	295	130	3.30	95	3.00	200	115	4.12
TD	6.2	143	340	100	4.54	117	4.10	266	79	5.05
T-PET										
MD	7.2	180	440	70	6.30	172	3.10	350	44	6.40
TD	4.5	108	270	130	4.10	106	2.80	230	108	4.20
ST-PET										
MD	8.5	229	533	50	7.15	195	3.30	461	45	7.38
TD	5.2	121	327	106	4.47	107	3.20	257	75	4.96
Standard PEN										
MD	7.0	173	438	69	6.25	175	3.20	334	42	6.42
TD	7.3	202	450	62	6.90	200	3.20	384	42	6.70
T-PEN										
MD	8.0	184	465	61	6.50	190	2.60	340	30	7.30
TD	6.5	161	410	81	5.60	158	2.90	300	40	6.50
ST-PEN										
MD	9.0	217	623	52	7.80	220	2.70	452	36	7.79
TD	6.0	139	340	103	5.42	144	2.65	293	75	5.37
ARAMID										
MD	19.3	590	655	10.6	20.4	628	2.80	638	6.4	17.2
TD	11.5	390	414	6.4	11.3	338	3.80	433	11	12.1

<sup>a</sup> Data for all samples taken at 0.1/min strain rate.

<sup>b</sup> Data for all PETs and PENs taken at 0.5/min strain rate, and for ARAMID at 0.1/min strain rate.

<sup>c</sup> Data taken at 0.016 Hz, 20°C.



**Figure 6** (a) A summary of tensile properties of various polymeric films. For Young's modulus, data for all samples were taken at 0.1/min strain rate. For other properties, data for PETs and PENs were taken at 0.5/min strain rate, and for ARAMID were taken at 0.1/min strain rate. (b) Effects of strain rate on tensile properties for T-PET and T-PEN.



50°C, indicating that a small amount of energy is dissipated. The amounts of loss tangent generally reflect the mobility of molecules, and larger loss tangent shows high mobility of molecules. The loss tangents begin to rise at 70–90°C (corresponding to different frequencies) and peak at the elevated temperatures of 110 to 130°C, which means the molecules begin to change their shape/orientation on a large scale. For example, rotation could occur along the junctions in the backbone of the chain, such as the —O— bond in PET. The temperature at which the loss tangent starts to increase corresponds to the glass transition temperature,<sup>12</sup>  $T_g$ . Above this temperature, the polymeric material behaves as a viscoelastic rubber due to the rotation of molecules. The glass transition temperature of PET measured in this study is consistent with that reported by Ward,<sup>11</sup> which was 80°C, for amorphous PET. Below  $T_g$ , PET films have lower loss tangent. This result indicates that PET films have less mobility at ambient temperature below  $T_g$ .

The temperature at which the peak of the loss tangent occurs is a function of frequency<sup>13</sup>; it shifts to a lower value and higher temperature as the frequency increases [Fig. 7 (b)], because of the frequency dependence of relaxation processes. For example, the loss tangent peak for Standard PET shifts from 0.22 at 110°C to 0.12 at 130°C as the deformation frequency increases from 0.016 to 29 Hz. Essentially, the faster the applied stimulus, the less time the molecules have to respond to it. At lower frequencies, the molecules have a longer time to respond to the applied strain, whereas at high frequencies, the time is too short and the response is considered to be glassy (i.e., the molecules cannot move rapidly). Therefore, in general terms, a high temperature is needed to energize molecular movement at high frequencies. On the other hand, at a constant temperature, as the stimuli are applied over a range of frequencies, the glass transition is seen first for the lower frequencies. Minimal movement of the molecular chain at high frequencies also explains the continuous decrease in loss tangent as the frequency increases. From the frequency dependence of the loss tangent peak, it is possible to evaluate the activation energy for the process.<sup>13</sup>

#### **PEN Data**

Figure 8(a,b) shows the storage modulus and loss tangent for Standard PEN, T-PEN, and ST-PEN. There are some common points among PET and

PEN films: the storage modulus increases as the frequency increases and temperature decreases, the magnitude of the loss tangent peak shifts toward a lower value, and it occurs at higher temperature as the frequency increases. Unlike the PET films of which the storage modulus keeps almost constant at the glassy state, the storage modulus of PEN films decrease in a certain slope in the whole temperature range. A high rate of decrease of storage modulus of PEN films corresponds to a high value of loss tangent, as shown in Figure 8(b). For example, the loss tangents for PEN films at 30°C are 0.05 to 0.09, whereas that for PET films are only 0.01–0.03. Also for PEN films, there is a minor loss tangent peak at 50–70°C in addition to the peak that is related to the glass transition (140 to 170°C), and this minor peak is absent for PET films. These peaks are responsible for a drop in the storage modulus near these temperatures.

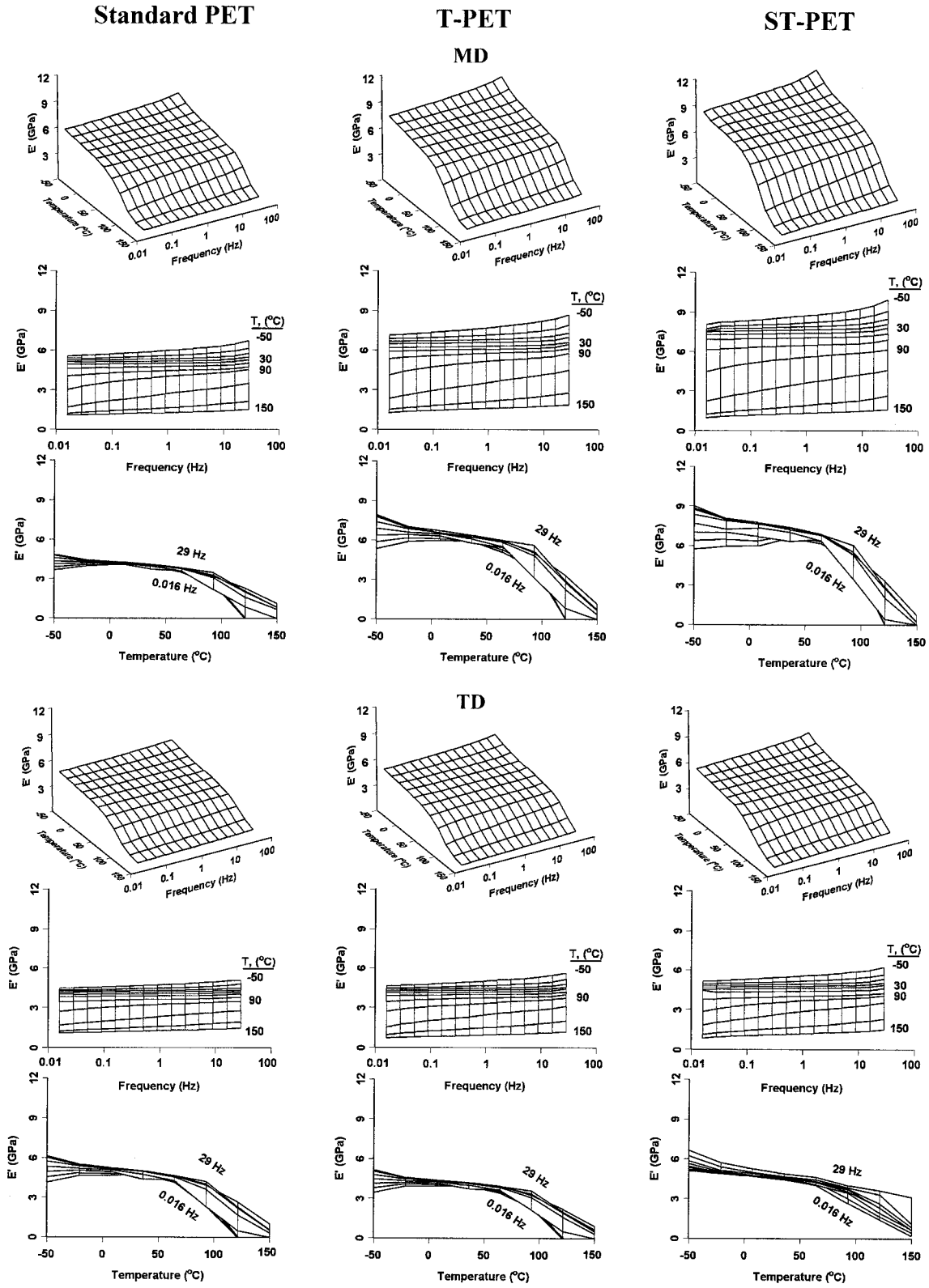
#### **ARAMID**

The storage modulus and loss tangent for ARAMID as a function of frequency and temperature are presented in Figure 9. ARAMID has a significantly higher storage modulus than PET and PEN films. It also has good temperature resistance; for example, the storage moduli remains above 6 GPa even at 200°C in both the MD and the TD.

The glass transition temperature for ARAMID is typically reported as 280°C, so there is no glass transition peak in the loss tangent-temperature diagram in this study; instead, only a steady increase is present in the 170–210°C range. However, similar to the curves of PEN films, a minor loss tangent peak at 50°C (at 0.016 Hz) to 130°C (at 29 Hz) is present, which is responsible for a drop in the storage modulus near this temperature. The loss tangent for ARAMID at elevated temperatures (above ambient) is 0.5–0.8, similar to that for PEN films and higher than that for PET films. As a result, the storage modulus for ARAMID keeps on decreasing at elevated temperatures, and there is no sudden drop as in the storage modulus-time-temperature 3D diagram for PET.

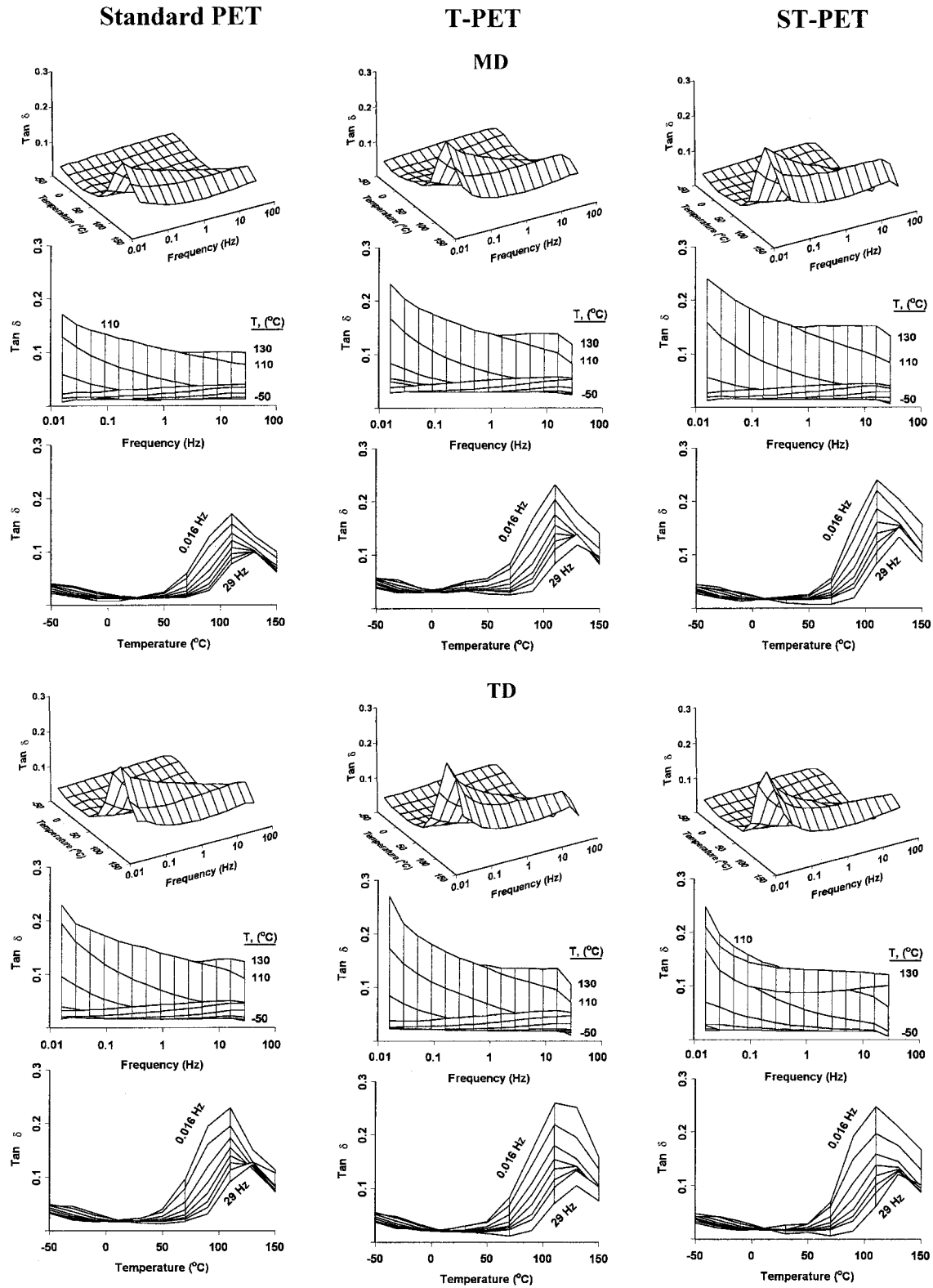
#### **Comparison of DMA Data at 30°C and 0.016 Hz**

Figure 10 shows the effects of frequency (and temperature) on the DMA properties of various polymeric films at 30°C (and 0.16 Hz) along the



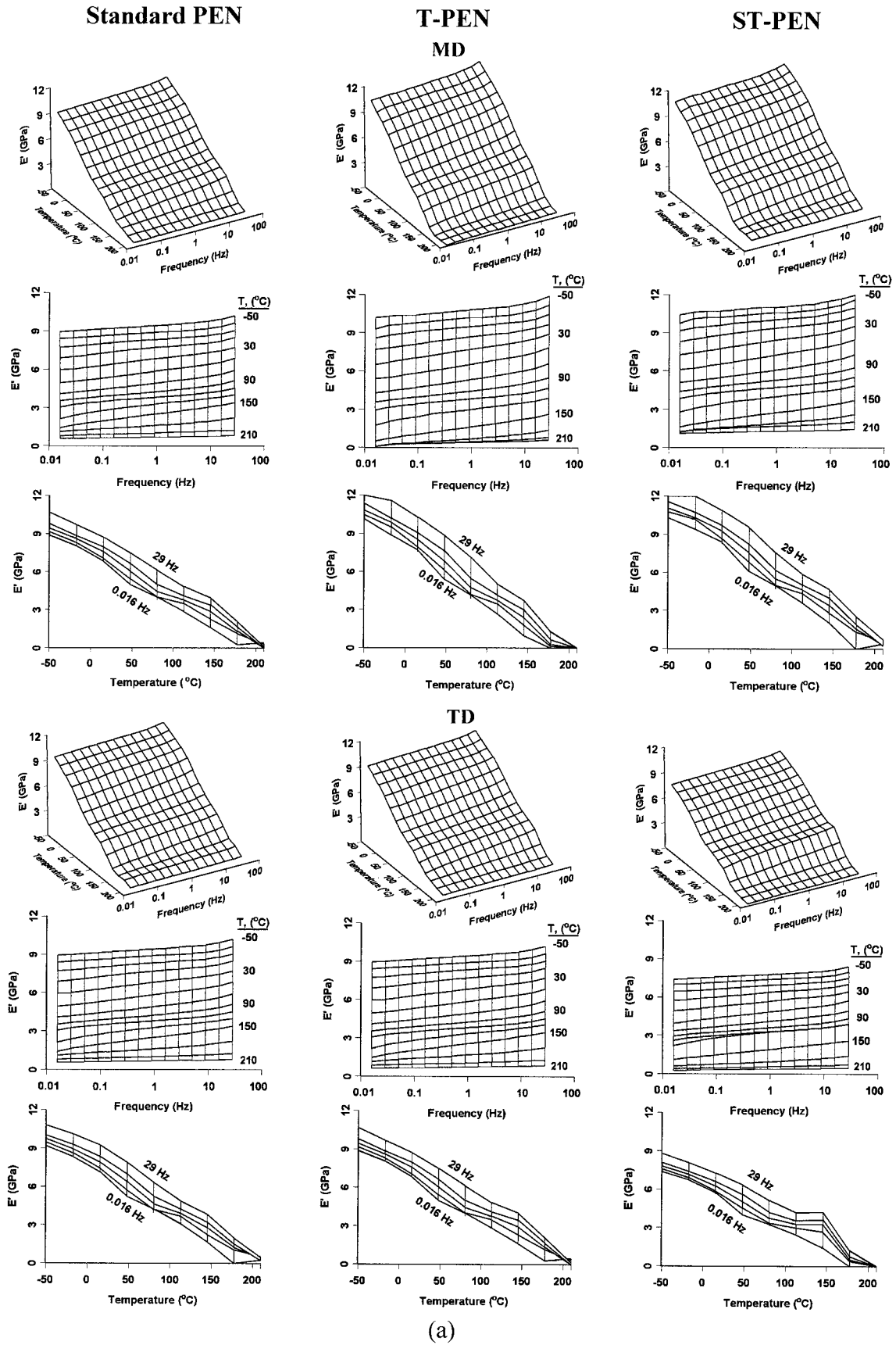
(a)

Figure 7 (a) Storage modulus ( $E'$ ) and (b) loss tangent ( $\tan \delta$ ) of PET films as functions of frequency and temperature.

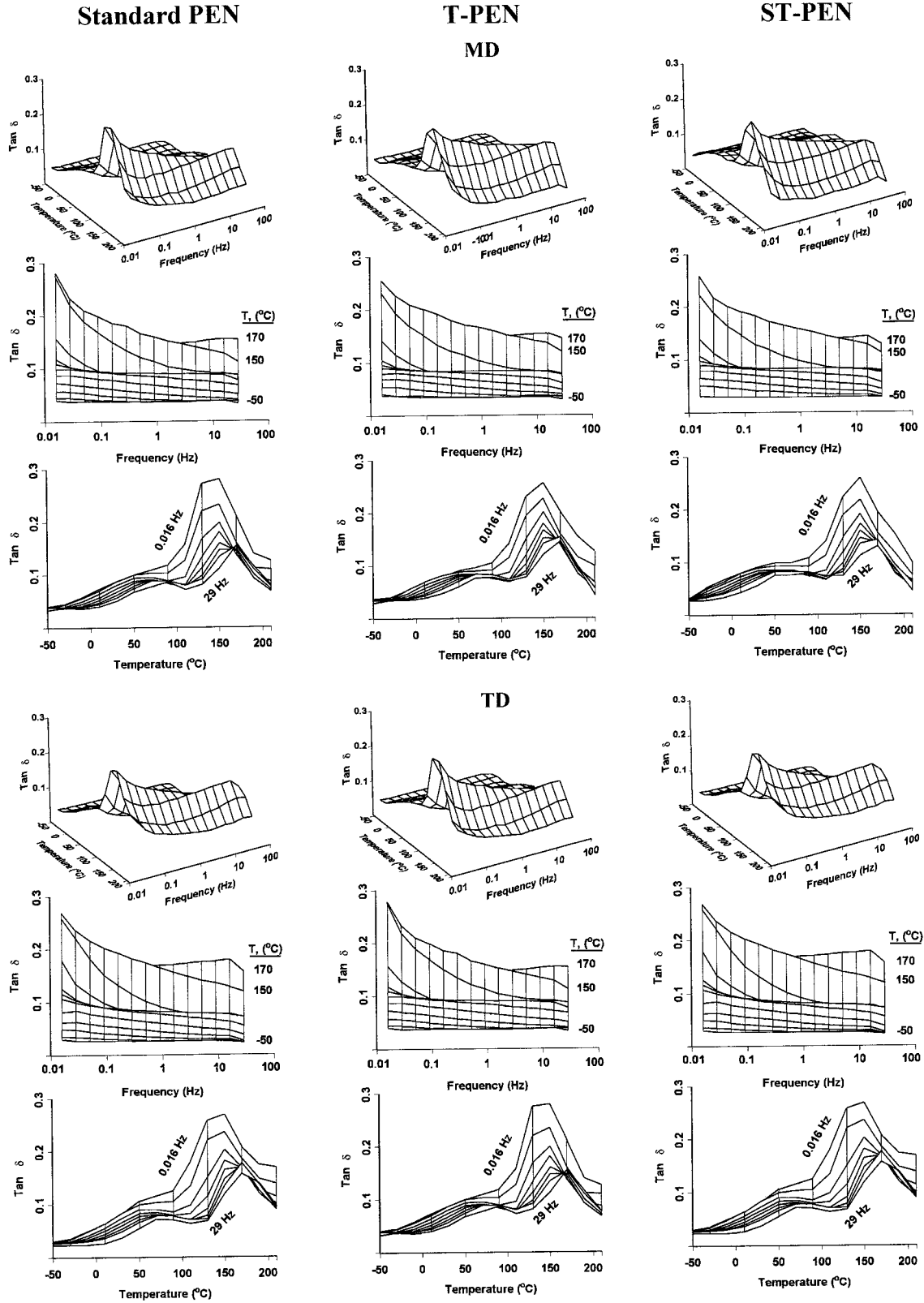


(b)

Figure 7 (Continued from the previous page)

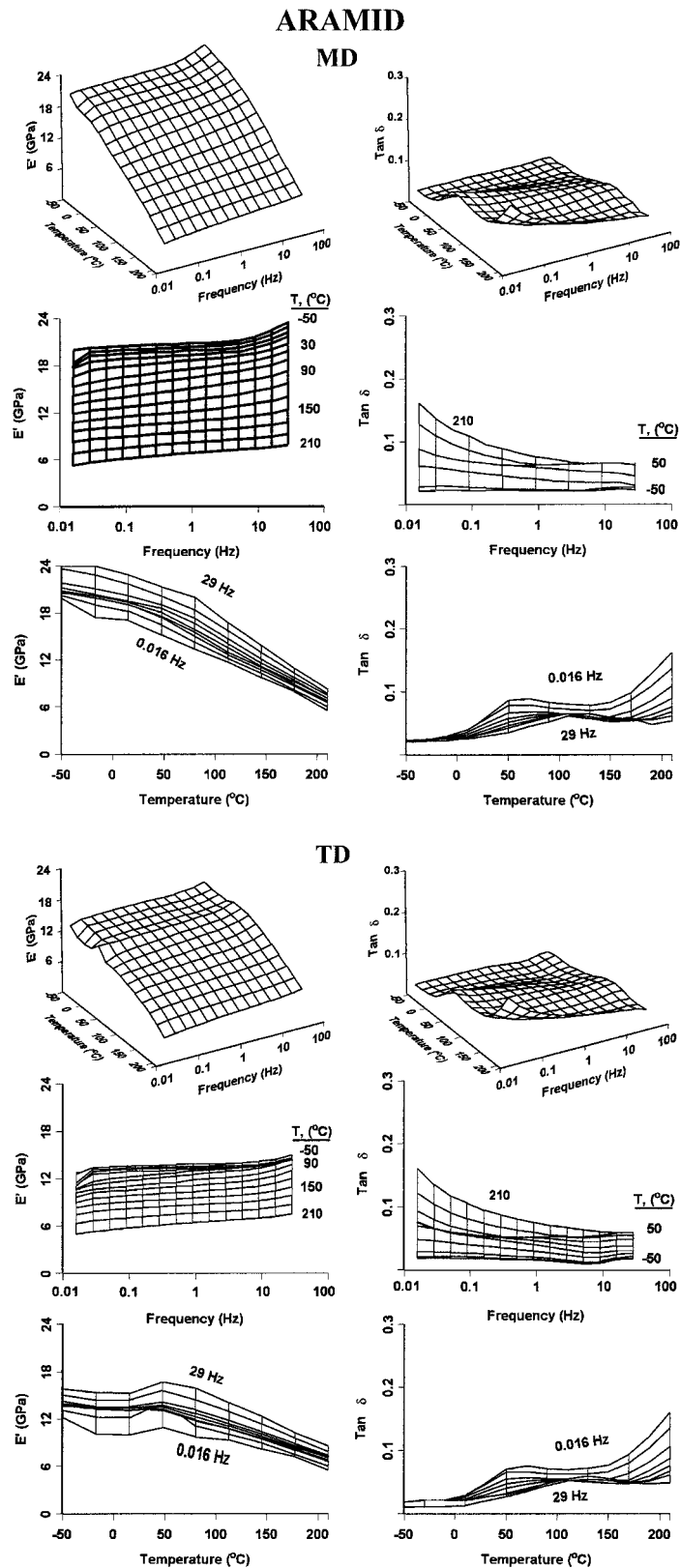


**Figure 8** (a) Storage modulus ( $E'$ ) and (b) loss tangent ( $\tan \delta$ ) of PEN films as functions of frequency and temperature.

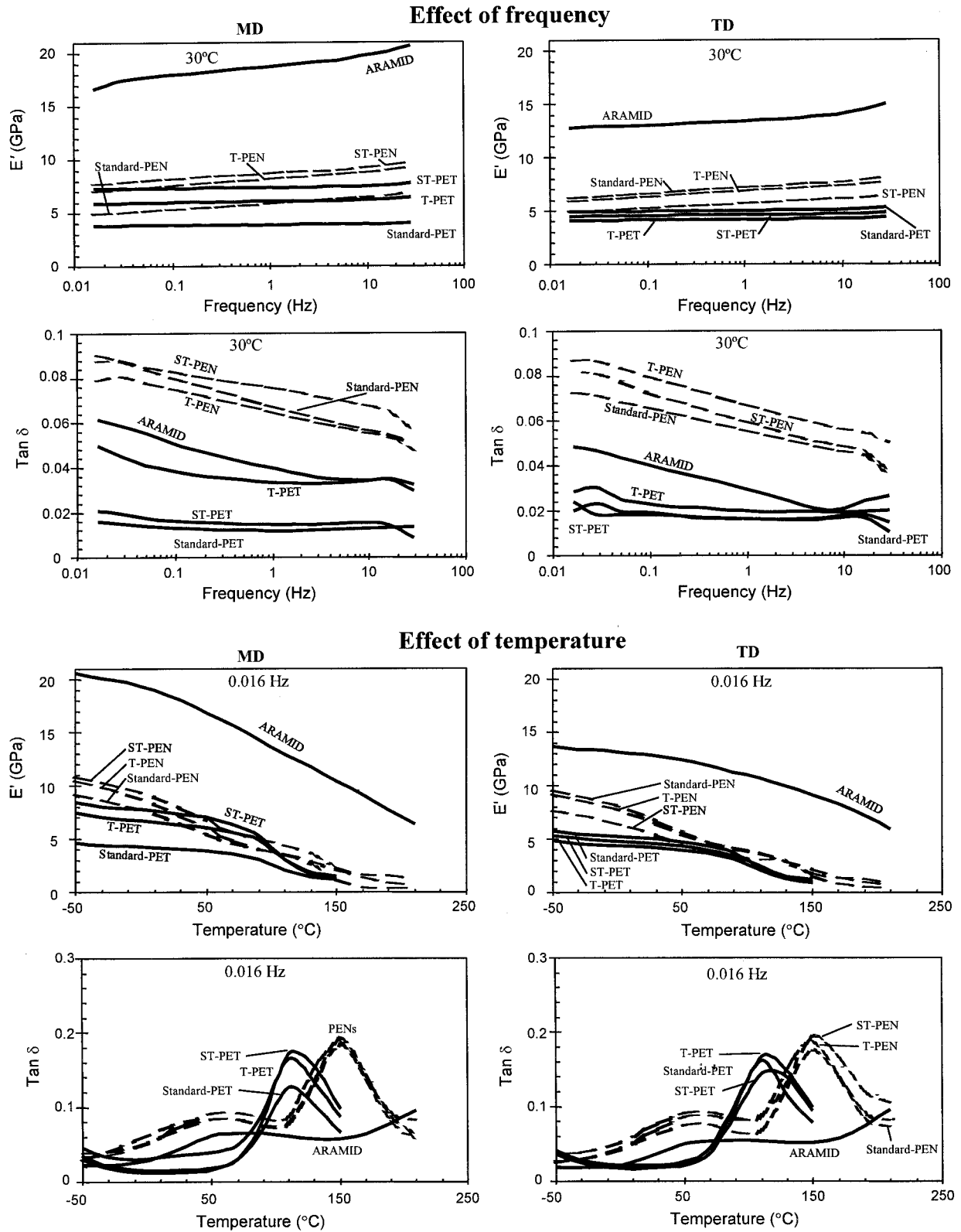


(b)

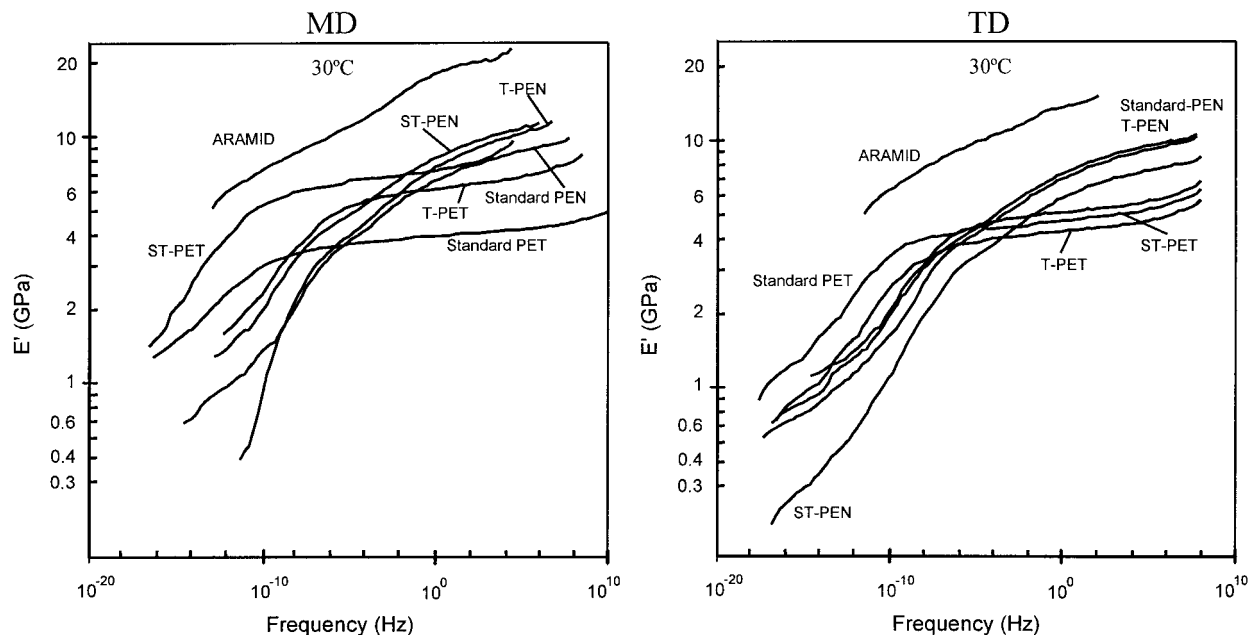
Figure 8 (Continued from the previous page)



**Figure 9** Storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of ARAMID as functions of frequency and temperature.



**Figure 10** Effects of frequency (at 30°C) and temperature (at 0.016 Hz) on storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of various polymeric films.



**Figure 11** Master curves of storage modulus ( $E'$ ) of various polymeric films at 30°C.

MD and TD, so that we can have a general comparison with different films.

ARAMID has significantly higher storage modulus than that for PET and PEN films in both the MD and the TD. The storage moduli for PEN films are slightly higher than that for PET films, but the difference is reduced as the deformation frequency decreases during the test. In general, the storage modulus at higher frequency is mainly determined by the elastic elements, and the viscoelastic deformation, creep deformation, predominates at lower frequency. Tensile test data in Figure 6(b) also show that frequency dependence on modulus for PEN is higher than for PET. The storage moduli of the same material (such as standard PET, T-PET, and ST-PET) have similar slope against frequency. In the previous research,<sup>4,5</sup> PEN films have slightly more creep deformation compared with tensilized-type PET. Thus, it appears that PEN is superior to PET in elastic properties, whereas it is inferior in viscous properties. In this study, the loss tangents of PEN films are the highest among the three kinds of materials at ambient temperature.

Tensilization increases the storage modulus in the MD and decreases the storage modulus in the TD, which makes the material more anisotropic. It also generally increases the loss tangent for both PET and PEN. Temperature has a reverse effect on the storage modulus of the polymeric

films. The same material (such as PET films) show a similar rate of decrease of storage modulus versus temperature.

#### **Prediction of Mechanical Behavior Using Time-Temperature Superposition**

A technique known as frequency-temperature superposition was used to predict the storage moduli over a wider frequency range at a specific reference temperature.<sup>14,15</sup> The superposition is carried out by using DMA data taken over a relatively narrow frequency range at different temperature levels. For instance, the storage modulus versus frequency curves in Figure 7(a) are used as the starting point, and a reference temperature of 30°C is selected. Curves at temperatures higher than 30°C are shifted to the left until they fit together smoothly, and the curves corresponding to the temperatures lower than 30°C are shifted to the right. The shift direction corresponds with the viscoelastic nature of polymeric films. Storage moduli measured for a polymer at high frequencies under ambient conditions will be equivalent to those measured at lower frequencies and colder temperatures.

Based on the time-temperature superposition, master curves are generated. Two plots are shown in the MD and TD in Figure 11. The results are shown on a logarithm-logarithm scale,




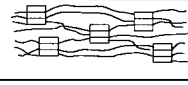
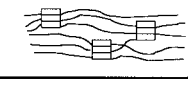

which indicates the storage modulus along the MD and TD over a frequency range from  $10^{-18}$  to  $10^{10}$  Hz. The storage modulus curves for PET films can be identified as two regions according to the slopes separated at about  $10^{-10}$  Hz. As a matter of fact, the storage modulus data for PET films at frequencies lower than  $10^{-10}$  Hz come from the storage moduli at temperatures higher than  $T_g$ . Thus, the curves can be regarded as composed of two regions: a glassy region and a rubbery region. This has more academic meaning rather than practical meaning, because  $10^{-10}$  Hz means the load cycle lasts 317 years. The data for PEN films can also be identified as glassy and rubbery regions, separated at about  $10^{-7}$  Hz, although the change of slope is not as significant as that observed for PET films. This is more realistic, or, more critical, because the PEN films would begin to act rubbery when the load cycle lasts for about 4 months. In the MD, the storage modulus for PEN films is higher than that for PET films at high frequencies, and this relationship reverses at low frequencies. The storage modulus curves for Standard PET and Standard PEN cross at the frequency of  $10^{-5}$  Hz (cross-frequency). Tensilization shifts the storage modulus curves for PET and PEN films to a higher value. Tensilization also shifts the cross frequency toward higher frequencies. However, tensilization does not obviously affect the threshold frequencies for transition from glassy to rubbery. There is no glass transition for ARAMID in the frequency range corresponding to the temperature range used in this study; the whole curve is within the glassy region.

ARAMID, over the available frequency range ( $10^{-10}$  to  $10^5$  Hz), has a superior storage modulus than other polymeric films, although the decreasing rate of storage modulus as a function of frequency is relatively high. PEN films appear to be stiffer than PET films at the frequencies higher than  $10^{-2}$  Hz (for MD) and  $10^{-6}$  Hz (for TD), but PET has a lower storage modulus slope in the glassy range. It is interesting to find that at low frequencies ( $10^{-2}$  Hz for MD and  $10^{-6}$  Hz for TD), the storage moduli for PET films are higher than those for PEN films. The modulus at the cross-frequency is about 3–5 GPa.

### Relationship between Mechanical Properties and Polymeric Structure

#### PET Films

The mechanical properties of polymeric films are dependent on their chemical composition and

Substrates	Structure	Comments
Standard PET		<ul style="list-style-type: none"> <li>• less oriented chains</li> <li>• larger fraction of crystalline structure</li> </ul>
Tensilized-type PET		<ul style="list-style-type: none"> <li>• more oriented chains</li> <li>• larger fraction of crystalline structure</li> </ul>
PEN		<ul style="list-style-type: none"> <li>• more oriented chains</li> <li>• smaller fraction of crystalline structure</li> </ul>
ARAMID		more oriented chains (rigid units, hydrogen bonds)

**Figure 12** Schematic of structures of various polymeric films.

physical structure, such as crystallization and molecular orientation, which in turn are affected by the manufacturing process.

The crystallinity (the portion of crystal region in the whole material) of PET is higher than that of PEN and ARAMID, as schematically shown in Figure 12. However, the molecules of Standard PET have a higher mobility because of less oriented chains, and distortion of the intermolecular bonds such as van der Waals attractions could contribute to the lower modulus of elasticity. Tensilized-type PET films, including T-PET and ST-PET, contain more oriented chains than Standard PET, which effectively restrain the molecular deformation along the drawing direction. Cakmak and Wang<sup>16</sup> suggested that the increase in crystallinity and orientation of chains in the amorphous region results in a reduction in creep strains for PET. At the same time, tensilization stores mechanical energy in the material as it increases the entropy and leaves residual stresses in the system. As a result, the loss tangent has a higher peak magnitude for T-PET and ST-PET than Standard PET [Fig. 7(b)]. The long-range molecular motion at a temperature higher than  $T_g$  is less affected by the molecular orientation than by the deformation frequency. As presented in Figure 10, the loss tangent peak positions are not affected by tensilization; that is,  $T_g$  is independent of manufacturing processes such as stretching.

In Figure 10, PET films show less temperature dependence than PEN films and ARAMID except at the range from 90 to 130°C where PET transfers from a glassy to a rubbery state. The reason for this is that crystallization can effectively stabilize the polymer. Mascia and Fekkai's work<sup>17</sup> indicated that when the degree of crystalline of

PET reached 43%, the shrinkage would be completely suppressed.

Tensilization also increases the stress needed to start the molecular rotation; because the angle between molecular orientation and applied load is small, a higher load is required to reach the critical partial shear stress to rotate the segment. As a result, the yield strength is increased.

### PEN Films

PEN has a similar molecular structure to PET (as shown in Fig. 3). PEN contains a naphthalene ring that is slightly more rigid than the benzene ring for PET. This is why the PEN films have a higher Young's moduli and storage moduli than PET films. The glass transition temperature  $T_g$  for PEN is about 110–130°C (120°C as typically reported), higher than that for PET. Also, the zero strength temperature for PEN films (170°C) is higher than that for PET films (130–150°C). All these ensure that PEN films are superior to PET films at high temperatures. However, the large naphthalene segment inhabits the movement of the molecules during the crystallization and results in a low crystallinity. The typical crystallinities of PET films and PEN films are 40–50 and 30–40%, respectively. Crystalline and oriented chain segments play important roles in determining mechanical properties of polymers. The network structure formed by crystal region significantly improves the stiffness and mechanical stability by anchoring polymeric chains in the high-density and less mobile crystalline region. The lower density amorphous region is more temperature and frequency dependent than the crystal region and behaves viscoelastically. Higashioji and Bhushan<sup>5</sup> calculated the apparent activation energy of creep of some tensilized PETs and PENs, assuming that the viscoelastic deformation process has an Arrhenius temperature dependence. The result showed that tensilization of PET increased the activation energy from 290 to 400 kJ/mol, but this increase for PEN was only from 300 to 310 kJ/mol. It is possible that the minor loss tangent peak at 50 to 70°C for PEN films eliminates the improvement from advanced processing such as tensilization.

The investigations of Chen and Zachmann<sup>12</sup> and Ezquerro et al.<sup>18</sup> on dynamic mechanical properties of amorphous PEN revealed that there exist three peaks (or relaxations) in the loss tangent versus temperature diagram:  $\beta$  (at -50°C),  $\beta^*$  (at 60°C), and  $\alpha$  (at 80–130°C), corresponding

to short- and long-range molecular motion. The  $\beta$  relaxation is attributed to motion of the —COO— groups; the  $\beta^*$  relaxation is attributed to motions of naphthalene rings and the  $\alpha$  relaxation is attributed to glass transition. The secondary motions of  $\beta$  and  $\beta^*$  relaxation involve localized motion such as the so-called crankshaft mechanism and local-mode process, and distortion of the polymeric chains occurs through intermolecular distances.<sup>19,20</sup> Because the relaxations, especially the  $\beta^*$  relaxation, represent the deformation ability and determine the mechanical properties of the polymer close to ambient temperature, they were extensively investigated both experimentally and theoretically.<sup>12,18–20</sup> Gillmor and Greener<sup>10</sup> suggested that a possible localized motion in PEN is interlayer slippage of naphthalene ring stacked in order of a liquid crystal parallel to the plane of the film because of the rigid and planar conformation of the naphthalene ring. Cakmak and Lee<sup>21</sup> suggested that, during the deformation of PEN, the naphthalene rings are rapidly aligned parallel to the surface of the films, and they are also highly localized. Ezquerro et al.<sup>18</sup> indicated that the  $\beta^*$  relaxation could not be detected by nuclear magnetic resonance (NMR) because the frequency was too high ( $\sim 1$  MHz). Alhaj-Mohammed et al.<sup>22</sup> also found that at high frequency the motion of the naphthalene ring ( $\beta^*$ ) only becomes detectable around  $T_g$ . Localized molecular motion does not have significant effects on the Young's modulus, which is mainly determined by the polymer backbone. However, the localized motion results in high-loss tangent value (associated with the large energy dispersion) and high toughness.<sup>23</sup> This relaxation also has reversal effects on the long-term stability, as concluded in Higashioji and Bhushan's work,<sup>5</sup> that PEN films have higher creep compliance than that of tensilized PET at ambient and elevated temperatures. This can also be confirmed from the storage modulus–temperature 2D diagram in Figures 7(a) and 8(a) that when the frequency changes from 29 to 0.016 Hz, the extension of storage moduli distributions (vertically) are much wider in PEN films than in PET films. In Figure 10, at ambient temperature, the storage modulus of T-PEN drops about 3 GPa from 29 to 0.016 Hz, whereas the modulus for T-PET drops only 1 GPa. Thus, the mechanical properties of PEN are more frequency dependent. The modulus for tensilized-type PET films could be comparable with that of PEN films at lower frequency and lower strain rate.

### ARAMID Film

ARAMID consists of rigid molecular chains with a linear structure. Molecular chains normally orient themselves in a single direction during the formation of liquid crystals in a doped solution. Therefore, the molecules in solid ARAMID are highly oriented and compose the so-called rigid rod structure. There is no oxygen atom in the backbone chain; instead, it consists of an aromatic hydrocarbon group (benzene ring) combined by amide bonds, para-linked by intermolecular hydrogen bonds that are stronger than the intermolecular interactions for PET and PEN. As a result, ARAMID enables the formation of high-strength, high-modulus, and low strain-at-yield, strain-at-break polymer film. The factors that determine the superior mechanical properties of ARAMID also include the following:

- Rigid aromatic (NH—CO) bonding
- Intermolecular hydrogen bond that comes from amide group
- Highly symmetric configuration
- High interlinked density from substituent  $X_m$  and  $Y_n$  atoms
- Presence of additional polar group

Electron delocalization also contributes to high chain stiffness and various threshold temperatures. This is easily identified from the colors because color increases both in occurrence and in darkening as delocalization increases.<sup>23</sup> The PET film is transparent, whereas PEN is pearl and semi-opaque, and ARAMID appears to be yellow and opaque.

The ARAMID film used in this study (Toray Inc., Mictron<sup>TM</sup>) is manufactured by using a solution-casting process followed by a slight drawing process. The solution casting process virtually eliminates the shrinkage that is common in the drawing processes. However, the cost of the film produced by casting is higher than by drawing. The study on the secondary relaxation of ARAMID film Mictron<sup>TM</sup> has not been accumulated in detail. Different aramids have different substituent  $X_m$  and  $Y_n$  atoms; thus, they have different intermolecular reacting mechanisms and different temperatures at which the secondary relaxations occur. Studies on other aramids such as aliphatic polyamide and poly(*p*-phenylene terephthalamide) (PPTA) fiber Kevlar® and poly(*m*-phenylene isophthalamide) fiber (Nomex®) suggested

that the  $\beta^*$  relaxation was due to the hindered local motion of phenylene group.<sup>13,24</sup> Kunugi and his colleagues<sup>13</sup> studied the loss tangent peaks for PPTA fiber over  $-100$  to  $500^\circ\text{C}$  and indicated that the peak near  $60^\circ\text{C}$  was a  $\beta$  relaxation. Frosini and Butta<sup>24</sup> suggested that the relevant relaxation process was due to the motion of the free amide group which did not form inter- or intramolecular hydrogen bonds and that the presence of water molecules or other low-molecular-weight polar substances played an important role in the relaxation process.

### CONCLUSION

Tensile and dynamic mechanical properties of ultrathin polymeric films, including PET, PEN, and ARAMID, as well as tensilized-type PET and PEN films, were measured and analyzed. Tensile tests at room temperature show that the ARAMID has a higher Young's modulus, F5 value, breaking strength, and lower strain-at-break than other films. Additional tensilization of PET and PEN films along the MD increases the Young's modulus, breaking strength, F5 value, but reduces the strain-at-yield and strain-at-break along this direction, because more chain segments were oriented and aligned in the stretch direction. It has reversed effects on the properties in the TD.

Storage modulus of polymeric films increases as the deformation frequency increases and test temperature decreases. PEN films have higher frequency dependence than PET films. PET films have a low rate of storage modulus decrease as temperature increases before its glass transition temperature is reached. This is also confirmed by the low value of loss tangents for PET films at low temperatures. A sudden drop in storage moduli occurs at  $80$ – $130^\circ\text{C}$  when PET films transform from a glassy to a rubbery state, corresponding to a loss tangent peak at  $110^\circ\text{C}$  ( $0.016$  Hz) to  $130^\circ\text{C}$  ( $29$  Hz). No secondary relaxation peak for PET films was detected in the temperature range used in this study (i.e.,  $-50$ – $150^\circ\text{C}$ ). Although for PENs, besides the loss tangent peak related to glass transition at  $150^\circ\text{C}$  ( $0.016$  Hz) to  $170^\circ\text{C}$  ( $29$  Hz), a secondary relaxation,  $\beta^*$  relaxation, was identified at about  $50$ – $70^\circ\text{C}$ , which is responsible for drop in the storage modulus near this temperature. The loss tangents for PEN films are higher than that for PET films at the temperatures lower than  $70^\circ\text{C}$ . All the loss tangent peaks shift toward

low value and high temperature as test frequency increases. Tensilization does not change the position of these loss tangent peaks, but slightly increases their absolute value. ARAMID also has a secondary relaxation ( $\beta$  relaxation) at 50°C (0.016 Hz) to 130°C (29 Hz), which results in the quick drop of storage modulus at these temperatures. This is consistent with previous work<sup>5</sup> that showed ARAMID has an apparent activation energy which is lower than that for tensilized PET, which does not have a relaxation in this temperature range.

A frequency-temperature master curve was generated from the DMA data that covers the storage modulus of polymeric films over a frequency range from  $10^{-18}$  to  $10^{10}$  Hz. ARAMID has a superior storage modulus when compared to other materials through the available frequency range. The storage moduli for PET films are the lowest at high frequencies, but its rate of decrease as frequency decreases is also low until  $10^{-10}$  Hz. The storage moduli for PET films become higher than that of PEN films when frequency is lower than  $10^{-2}$  Hz (MD) and  $10^{-5}$  Hz (TD). It suggests that elastic properties of PEN films are superior, whereas viscous properties are inferior as compared to PET films. Tensilization raises the storage modulus-frequency curves to higher positions, but generally does not affect the tendencies and slope.

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