JOURNAL OF Applied Polymer SCIENCE

Dynamic Mechanical Analysis of Barium Ferrite Magnetic Tapes with Aramid and Poly(ethylene naphthalate) Substrates

Robert D. Berry, Brian L. Weick
Mechanical Engineering Department, School of Engineering and Computer Science, University of the Pacific, Stockton, California 95211
Correspondence to: B. L. Weick (E-mail: bweick@pacific.edu)

ABSTRACT: Frequency- and temperature-dependent viscoelastic characteristics of advanced materials used for high-capacity digital magnetic tapes were analyzed using a custom ultra-low frequency dynamic mechanical analyzer (ULDMA). The magnetic tapes studied both use barium ferrite (BaFe) magnetic particles. One tape uses an aromatic poly(amide) or aramid substrate, and the other tape uses a poly(ethylene naphthalate) or PEN substrate. ULDMA studies were performed for both types of tape materials using samples cut from reels and the substrates after the front and back coats were removed. Two-hour experiments were performed at 25, 30, 50, and 70°C temperatures, and four test frequencies were used at each temperature: 0.006, 0.010, 0.033, and 0.065 Hz. Properties determined were the peak strain-based elastic modulus, E, and the storage modulus, E', loss modulus, E'', loss tangent, $\tan(\delta)$, complex modulus, E^*, and complex loss, E''/E^*, expressed as a percentage. When compared with the PEN tape and substrate materials, the peak elastic modulus, storage modulus, and complex modulus were higher for the aramid materials. Substrates for each material exhibited higher elastic, storage, and complex moduli compared with their respective tapes. Through the complex loss percentage, comparisons were made between the aramid and PEN materials related to their viscoelastic characteristics. Finally, the influence of frequency was shown to have increasing relevance at higher temperatures, with the PEN tape and substrate exhibiting an increase in complex loss modulus in the 50°C range because of the β^* secondary transition. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41478.

KEYWORDS: films; polyamides; polyesters; properties and characterization; viscosity and viscoelasticity

Received 9 July 2014; accepted 31 August 2014
DOI: 10.1002/app.41478

INTRODUCTION

Background and Motivation

Overview of Advanced Tapes for Digital Storage. The use of magnetic tapes in the storage of electronic data is a well-established technology, and they are manufactured to be much thinner and longer than tapes developed in the past, allowing for much greater storage at higher long-term stability. The evolution of magnetic tapes is both a product of more advanced manufacturing techniques and continued research in tape materials to meet the specific growing demand to store more information over longer periods of time. In fact, tapes approaching 100 GB/in^2 with life spans of 100 years are being discussed and appear promising.[1] Advanced magnetic tapes available on the market today can store up to 0.25 GB/in^2 and average around 900 yards in length. These long lengths of tape are stored as reels in cartridges with approximate dimensions of 5 inches long by 4 inches wide and only three quarters of an inch thick. (Although English units are the standard descriptors for tape cartridges, testing primarily uses metric units).

Magnetic tapes recently have made the transition from primary storage media, to secondary storage media, and now to long-term storage media or archival media. Short-term storage devices such as hard drives and compact solid state drives have taken over as the hardware of choice for most computing systems as the ideal media for active software and immediate storage and backup. Further digital media such as compact disks and flash memory devices with their small to mid-range storage capabilities have been found more ideal for temporary or transitional storage. This may falsely lead to the conclusion that magnetic tapes are becoming an archaic instrument of the past. The truth is, with data being created and stored with increased ease, more and more daily information is making its way into the digital realm and needs to be stored or archived to meet user demands and protect consumer interests. With the rise of cloud computing and increased development and implementation of graphic and video-based data, the amounts of data being created is vast in today's world. As of 2010, it is estimated that approximately 33,217 Petabytes of worldwide data are digitally

Table I. Relevant Tape Sample Information

Tape	Tape thickness (μm)	Substrate	Substrate thickness (μm)	Manufacturer
BaFe particle aramid tape	5.2	Aramid	3.6	Oracle/Sun: StorageTek T10000 T2
BaFe particle PEN tape	5.9	PEN	4.5	IBM: 3592 JC/JY

archived, and this is predicted to increase over 100 times before the end of the decade.[1] A study conducted by the Fleishman-Hillard group states that 68% of current "hard disk-only" users plan to start using tape for long-term archiving, and 58% plan to add tape for short-term data protection.[1] These simple data factors show that the magnetic tape industry is not in decline but in transition, transition from becoming one of the world's leading "backup" mediums to becoming a longer term archival medium.

Why magnetic tape for the "archival media" role over other types of media? The answer to this is surprisingly simple and widely agreed upon. The primary advantage of tape is both cost and longevity. From a cost point of view, magnetic tape cost per gigabyte is hard to compete with. In 2010, LTO-5 tape with a 1.5-TB native capacity costs $0.04/GB.[1] Larger capacity tapes that have come out since, have driven this cost down even further. Cost aside, tape is also considered largely reliable; because cartridges aren't spinning or vibrating all the time, they are not generating heat that needs to be cooled. When not in use, a tape can sit non-animatedly in reserve until the information needs to be drawn upon. The inherent energy consumption of magnetic tape systems is considered low, because they are only operated for controlled periods of time and don't need to be continuously active or volatile as many other systems do. Also, with the increased productivity of today's computer systems, tape is not susceptible to the lightning quick overwriting of data by being an external system. A good example of the benefit of having a non-volatile archival system is when Google experienced a bug in February of 2011 that infected several Gmail users' account. The disk based copies of the accounts were damaged beyond recovery. Google explained to its users, "To protect your information from these unusual bugs, we also back it up to tape. Because the tapes are offline, they're protected from such software bugs."[2]

Archival mediums share many of the same factors that have been of engineering significance for the more typical backup mediums. Therefore, these factors are still important and must still be thoroughly investigated. These factors include: media reliability, cost, projected life span of systems, and media limitations. However, the term "archival" opens up deeper seated values in the "long-term" characteristics and material behaviors. Most industrial applications are requesting thirty or more years of archival life for tapes that must retain their high transfer rates. In some industries and fields, such as the medical field, a longer archival life approaching 100 years is rapidly becoming more of interest. This means that tape characteristics need to be looked at: chemically, mechanically, and for magnetic signal degradation. And now these tapes are not only being created with increased storage capability in mind, but also increased media life.

Mechanical and viscoelastic properties/characteristics of two current advanced large storage tapes will be presented. Measurements and knowledge of these properties can help to define the pros and cons of the materials used under a set of given conditions. In the future, it can also be used to help predict the longevity of the given tape. Factors such as substrate materials, binders, temperature, humidity, strain and stresses need to be evaluated on a sample basis to help actively predict the tape's mechanical characteristics. Tape deformation directly affects the tape's reliability, which is the factor that needs to be clearly understood and defined. With the viscoelastic characteristics of the tape and its constituents defined, simulations and theory can be applied at a future date to help better predict the tape's effective lifespan.

Test Samples. Experiments were performed using samples from two commercially available magnetic tape cartridges: The Storagetek T10000-T2 tape cartridge produced by Sun/Oracle, and the 3592 JC/JY tape cartridge produced by IBM. (For a quick breakdown of relevant tape information refer to Table I.) Both tapes use barium ferrite magnetic particles, and the abbreviation BaFe is used for the chemical composition: $(Ba^{2+}(Fe^{3+})_2(O^{2-})_4$. The T10000-T2 tape uses an aromatic poly(amide) or aramid substrate, and the 3592 tape uses a poly(ethylene naphthalate) or PEN substrate. (These tapes will be referred to as the "aramid tape" and "PEN tape.") The aramid tape offers 5 TB of native data capacity at a data rate of 240 MB/sec, and the PEN tape offers 4 TB of native data capacity at a data rate of 250 MB/sec making them among the most advanced commercially available tapes at the time this paper was written. These cartridges are produced for Enterprise class tape systems, and use the most advanced, commercially available materials for tape products.

The aramid tape is one of the thinnest tapes currently on the market at 5.2 μm, and the aramid substrate is 3.6-μm thick. The front coat is made up of a magnetic layer that is approximately 0.1-μm thick and an under layer, or binder, that is 1.0-μm thick. This leaves 0.5 μm which makes up the protective back coat of the tape. The magnetic layer of the tape consists of BaFe particles, aiding in its small thickness and higher storage rate. Storagetek also advertises a thirty year archival life given ideal storage conditions. The cartridge also offers a locking hub

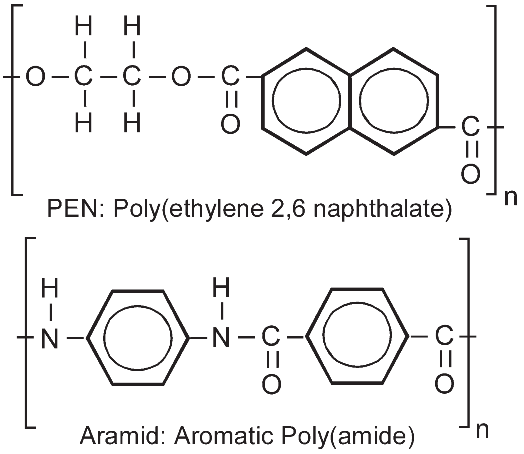


Figure 1. Chemical structures of PEN and aramid.

to help decrease damage to the tape due to long-term storage, and the 5 TB capacity tape has a total length of 1147 m.

The 4 TB capacity PEN tape has a total length of 880 m. It is capable of slightly faster data transmission than the Storagetek tape. The overall thickness of the tape is 5.9 μm, and the PEN substrate has a thickness of 4.5 μm. The magnetic layer of this tape also uses BaFe particles to help gain high GB/in^2 storage values while keeping the thickness down.

Aramid vs. PEN Substrates. A major difference between the test samples is the choice of substrate. Aramid, or aromatic poly(amide), is usually considered one of thinnest available substrates with great strength and viscoelastic properties. A molecular layout of an aramid structure can be seen in Figure 1. It has a rigid rod like structure that exhibits a high degree of orientation, with amide groups that assist with the formation of intermolecular hydrogen bonds. Aramid enables the formulation of high-strength, high modulus films that are important to the growth of the tape industry. It is manufactured using a solution casting process and then drawn slightly using a drawing process.[3] This process is slightly more expensive than the simpler PEN creation process, taking away from the attractiveness of aramid. Aramid has been used as a substrate since the mid 1990s, primarily by Sony. Sony initially used aramid as the substrate to its small Hi8 camcorder tapes, due to the benefit of its decreased thickness for smaller video cassettes. Sony continued to create tapes with an aramid substrate that crossed over into the more typical data storage realm under the Advanced Intelligent Tape or AIT name throughout the early to mid-2000s before discontinuing the tape. Although aramid was used intermittently since then, its popularity has never been mainstream primarily because of the increased manufacturing costs. With increased data storage demands, thin tape substrates are of ever increasing relevance as a solution. Aramid has become more attractive to manufacturers once again.

PEN film is made using a simpler, less expensive, biaxial drawing process. As seen in Figure 1, it is made up of a hydrocarbon backbone with a slightly rigid naphthalene ring that gives it an advantage over more traditional poly(ethylene terephthalate) or PET (not shown). PET was generally the most popular substrate for tape until early 2000, at which point PEN gradually became the industrial standard in the tape industry for the past 10–15 years.[3] PEN's advantage of being able to sustain its properties given decreased thickness has helped lead to many advances in the amount of storage capacity available per tape cartridge and helped to herald the rise of a more standardized tape format (LTO) recognized across the industry. An advantage PEN currently has over aramid, beyond cost, is the simple fact that it has been an active substrate long enough in the tape industry now to have more of its mechanical behaviors and properties well researched and understood. This information can be used to help recognize the characteristic behaviors to expect from a PEN based tape and see where improvements can be made not only in PEN but other substrates through comparison. Some of the properties of PEN are so well characterized that chemists have been able to correlate the causes of a portion of the permanent energy losses (deformation) to specific molecular changes or movement. When a material's behavior is understood at a molecular level, particularly a composite's or polymer's, then it allows for the design or recognition of the properties needed in the ideal material.

By studying BaFe PEN, a well understood material that is being used in what ranks currently as one of the industries most advanced tapes, a good comparison can be made against the less common but similarly advanced BaFe aramid tape. This comparison should allow a better understanding of the fundamental material properties, which both allow and limit today's storage capacities, life span, plus general operation and storage conditions.

Rationale for Research and Objectives. A custom-built dynamic mechanical analyzer capable of performing experiments at ultra-low frequencies was used to study the viscoelastic properties of the BaFe PEN and BaFe aramid tapes and their respective substrates. Rummel and Weick[4] describe the need for ULDMA due to transitions observed in magnetic tape materials at near-room temperature conditions. Weick[5] also observed these transitions in earlier work using commercial DMA equipment, and noted that such transitions could lead to problems with archival storage of magnetic tapes due to changes in stress-strain characteristics as the tape is stored in a roll. The investigation was therefore carried-out using temperatures in the 25–70°C range, and frequencies of 0.006–0.065 Hz within this temperature range. Representative peak elastic modulus curves could then be studied using raw data.[4] Next, using Fourier frequency analysis, data sets were broken-down into frequency content to enable the determination of coherence and time delays or phase angles between the stress and strain. This enabled storage and loss modulus data to be determined in addition to the loss tangent, which show relevant transitions for the tape materials. As a result, the viscoelastic characteristics of the tapes and substrates could be discussed and compared, which adds to our fundamental understanding of how these materials will perform during archival storage.

EXPERIMENTAL

ULDMA

Rummel and Weick[4] describe the ultra-low frequency dynamic mechanical analyzer (ULDMA) used in this study. Because of

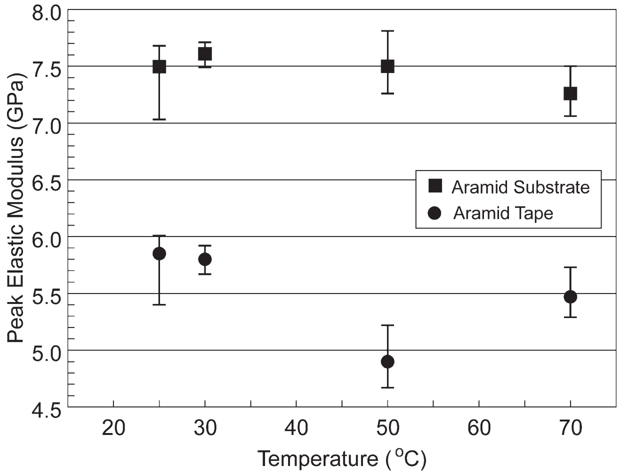


Figure 2. Sample average peak elastic modulus and range for aramid tape and substrate.

their viscoelastic characteristics, magnetic tapes demonstrate a phase lag between the applied strain, and measured stress.[5] The extent to which the stress signal lags behind the strain signal varies based on the viscoelastic properties of the sample, and experimental parameters, such as temperature and frequency. The phase lag, or phase angle shift, can be calculated by finding the amount of time the stress signal lags behind the strain signal, and multiplying that value by the frequency of the signal:

$$\delta = \omega \Delta t = (2\pi f)\Delta t, \tag{1}$$

where ω is the angular frequency in radians, f is the ordinary frequency in Hz, Δt is the time delay, and δ is the phase angle shift in radians. Once the phase angle shift is determined, important mechanical characteristics of the magnetic tapes can be determined using the equations listed below:

$$E' = \cos(\delta)\left[\frac{\sigma}{\varepsilon}\right], \tag{2}$$

$$E'' = \sin(\delta)\left[\frac{\sigma}{\varepsilon}\right], \tag{3}$$

$$\tan(\delta) = \frac{E''}{E'} \tag{4}$$

If the strain applied to the sample, the corresponding stress experienced by the sample, and the phase angle shift between the strain and stress signals are known, the storage modulus, E', loss modulus, E'', and loss tangent, $\tan(\delta)$, can be calculated.[5,6] Because of the viscoelasticity of magnetic tapes, the measured stress signal is composed of the in-phase stress, and out-of-phase stress. The in-phase component of the stress signal represents the elastically stored energy that is completely recoverable, known as the storage modulus, E'. The out-of-phase component of the stress signal is associated with the strain induced energy dissipation, or nonrecoverable energy that is lost to the system, referred to as the loss modulus, E''.[5,6]

Sample Preparation

Tape samples were cut to a length of approximately 150 mm from a reel. They were handled by the ends to be clamped into the test devices to avoid contamination, humidity, or unnecessary additional deformation of the sample. Scotch tape tabs were formed over the ends of the samples to enable handling. Substrate samples were prepared by placing them on a glass plate located in a fume hood. Using a procedure described by Weick,[7,8] methyl ethyl ketone was used to gently remove the front and back coats of the tape.

A Mitutoyo SJ-301 surface profilometer was used to calculate and verify the thickness of the tape and substrate material samples shown in Table I. The profilometer was accurate to the nearest 0.01 microns, and was used with a 2-μm tip installed.[9]

Experimental Procedure

Berry[9] and Rummel[10] describe the detailed procedure used to perform the ULDMA experiments using magnetic tape and substrate samples. Repeatability of the experimental apparatus and reproducibility of results are addressed in their work and in the article by Rummel and Weick.[4] Data sets were acquired using a National Instruments data acquisition board and LabView software. Specific virtual instruments (VI's) were developed using the LabView software for the samples tested. Experiments for the work presented herein were performed for approximately 2 h at 30, 50, and 70°C test temperatures and room temperature (nominally 25°C) consistent with past research.[4] Humidity within the small sleeve heater around the test samples could not be measured, but past research by Weick[5,8] has shown that relative humidity drops to less than 5% for 30°C experiments and less than 1% for 50 and 70°C experiments performed in larger heated test chambers used for viscoelastic testing of these types of samples. Four test frequencies were used at each temperature: 0.006, 0.010, 0.033, and 0.065 Hz.

RESULTS AND DISCUSSION

Average Peak Elastic Modulus Values and Ranges

Before examining the viscoelastic characteristics, it is useful to simply study the influence of temperature on the peak elastic modulus for the BaFe–aramid and BaFe–PEN tape and substrates. This is shown in Figures 2 and 3. The vertical bars represent the peak elastic modulus range measured at each temperature for the four frequencies used in the experiments,

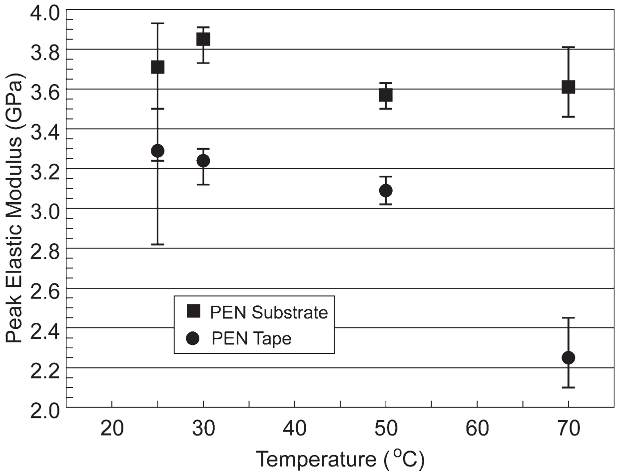


Figure 3. Sample average peak elastic modulus and range for PEN tape and substrate.

and should not necessarily be misconstrued as error bars. The influence of frequency on the peak elastic modulus is relatively small compared to the influence of temperature. (As discussed later, the influence of frequency becomes more prevalent when the time delays are used to determine the storage modulus, loss modulus, and loss tangent.)

Overall, the peak elastic modulus values for the aramid tape and substrate shown in Figure 2 are higher than the values for the PEN tape and substrate in Figure 3. This is consistent with past observations for these materials.[7,11] Aramid is known to have a higher elastic modulus than PEN because of its rigid aromatic structure compared to the more aliphatic structure of PEN. Furthermore, the peak elastic modulus measured for each substrate is higher than what was measured for their respective tape. This is also consistent with past observations for magnetic tape materials, and is due to the application of the front coat and back coat to make the tape. Although the front coat has relatively high modulus BaFe particles, they are held in what is typically a urethane-elastomer binder with a lower elastic modulus.

An increase in temperature tends to lower the elastic modulus of the tape and substrate for both the aramid and PEN samples. The peak modulus data measured for the aramid substrate at 30, 50, and 70°C follow this general trend and the data measured for the PEN tape at these temperatures. One would expect this decrease for polymers in temperature ranges where primary "glass" transitions or secondary transitions do not occur, and this is the case for the aramid samples. However, secondary transitions are known to occur in PEN samples in this temperature range,[5] and even primary glass transitions are being approached for PEN in this range. This can be observed in the peak elastic modulus data for the PEN substrate at 50 and 70°C. The average peak elastic modulus for the PEN substrate at 50°C is approximately the same as the average measured for the PEN tape at 70°C. The viscoelastic analysis to determine the time delay and thus the storage modulus, loss modulus, and loss tangent sheds some light on this observation in the next section.

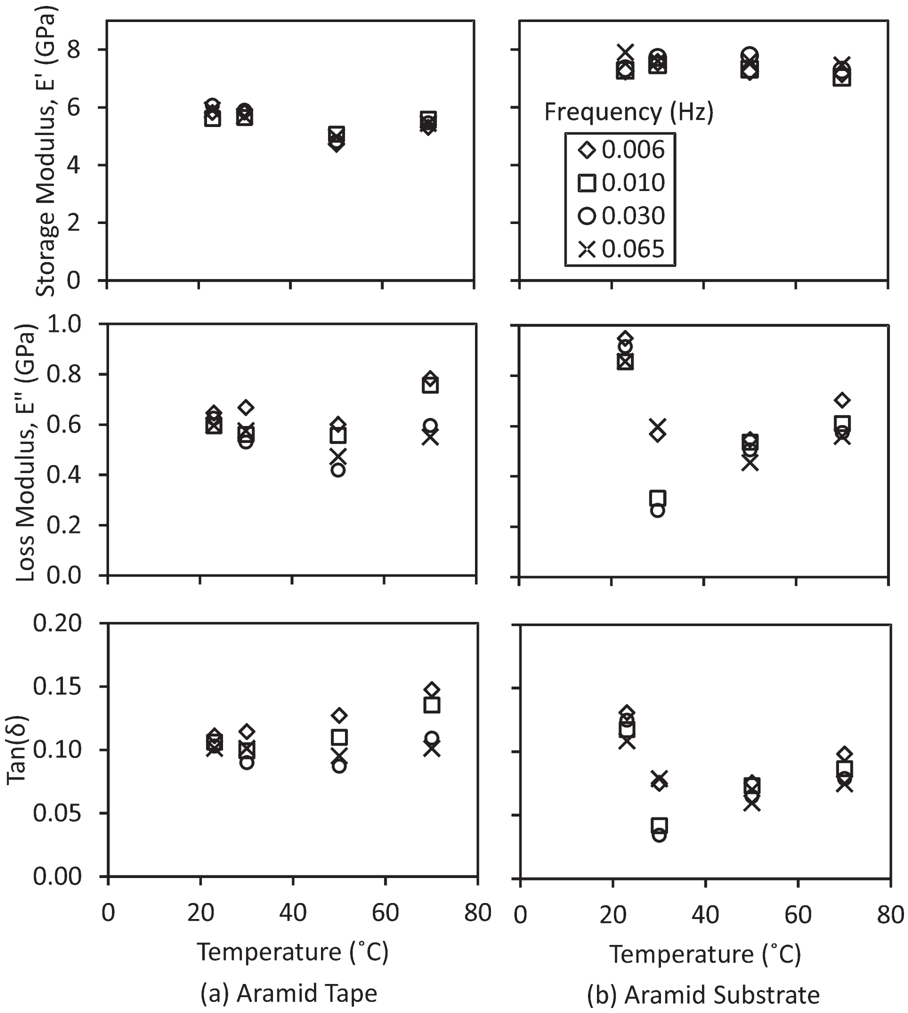
Despite the expected influence of temperature on peak elastic modulus noted above, there are some exceptions because of uncontrolled humidity and equipment anomalies. First, although the peak modulus values measured at the nominal 25°C room temperature are expected to be higher than what was measured at 30°C, this was not always the case due to the influence of humidity. The room temperature data actually reflects a temperature range of 22–27°C, and the experiments were performed without the heater shroud around the samples causing them to be exposed to changes in humidity in the room, which were measured to be 37–45%. The wider range of peak elastic modulus values measured at the nominal 25°C temperature is also influenced by this humidity range. Secondly, the relatively large decrease in peak elastic modulus measured for the aramid tape at 50°C is believed to be lower than it should be (~15–20%) due to the possibility that the tape was buckling at these lower strain points. Initial pre-strain was slightly higher in other experiments to avoid this problem.[9]

Viscoelastic Data–Storage Modulus, Loss Modulus, and Loss Tangent

BaFe–Aramid Magnetic Tape and Aramid Substrate Samples. Figure 4 shows the viscoelastic characteristics for the BaFe–aramid tape and aramid substrate samples. The storage modulus, E', is understood to represent the elastic characteristic of the material, whereas the loss modulus, E'', represents the viscous characteristic of the material, and the loss tangent, $\tan(\delta)$, is the ratio E''/E'. The storage modulus for the aramid tape stays fairly flat across the entire temperature range with only a slight decline as temperature rises. Keep in mind the 50°C tape sample results are between 15 and 20% lower than they should be, as explained previously. With this taken into account the storage modulus for the aramid tape could be described as having a slightly decreasing trend, and therefore maintains its relatively high modulus at higher temperatures. This decreasing trend can also be observed in the storage modulus results for the aramid substrate sample. However, the substrate behaves more elastically because it has a higher storage modulus than that measured for the aramid tape. The presence of the lower modulus front and back layers of the aramid tape effectively decrease the overall storage modulus of the aramid tape when compared to the aramid substrate itself.

The viscous loss modulus, E'', proves to have some of the most interesting data for aramid. Results for the aramid tape show a slightly parabolic general trend with slightly higher loss modulus values at the lowest and highest temperatures. This trend is believed to be due to the error in the 50°C elastic modulus discussed previously that anomalously decreased the modulus a little when experiments were initially performed at this temperature. If this error were taken into account, the viscous loss modulus would likely appear as a fanning spread from room temperature on up, with a more linear trend rather than parabolic. Furthermore, for the aramid tape the low frequencies generally correspond with a high viscous loss modulus, and in contrast high frequencies generally tend to correspond with a low viscous loss modulus. This trend is more pronounced at higher temperatures. Therefore, it seems that the frequency takes over as the primary factor when considering viscous loss, particularly as temperature increases to 50 and 70°C.

When observing the aramid substrate by itself some additional anomalies appear. The room temperature viscous loss appears to be much higher than the rest of the temperatures. The best possible explanation for this phenomenon comes from reviewing the experimental process for any factor that might play a role. The room temperature experiments take place without the heat shield surrounding and controlling the environment around the test sample during the experiment. When the heat shield is in place and operating, it would greatly reduce the humidity around the sample. Otherwise, the sample was exposed to the average humidity level of the room, which ranged anywhere from 37 to 45%. When looking at the molecular layout of aramid in Figure 1 some nitrogen and hydrogen groups can be observed that would probably make this material more hygroscopic and sensitive to water. This effect would be greatly reduced on the tape because the hygroscopic aramid substrate is protected by the other layers. This effect could have



(a) Aramid Tape

(b) Aramid Substrate

Figure 4. Dynamic viscoelastic characteristics of (a) aramid tape, and (b) aramid substrate as a function of temperature and frequency.

also played some role in the disparity of the 30°C results for the substrate, which anomalously shows the highest viscous loss at the highest 0.065 Hz frequency even through the other experiments at 30°C for the aramid substrate follow the expected trend of lower frequencies corresponding with higher viscous loss.[9] At the higher 50 and 70°C temperatures this effect disappears and the viscous loss modulus increases, as expected. Note that the expected trend of the lower frequencies having a higher viscous loss modulus continues at these temperatures.

The loss tangent or tan(δ) graphs are shown at the bottom of Figure 4. With relatively low viscous loss modulus values in comparison to the high elastic storage modulus values, the magnitude of the loss tangent values is small. This graph re-emphasizes the role that low frequency plays in raising the loss or more correctly the dissipation of energy in both the aramid tape and substrate, particularly at the higher temperatures because there's an increasing trend that corresponds with lower frequency tests. Furthermore, at the higher temperatures the loss tangent increased, which corresponds with the tape and substrate behaving less like an amorphous solid, and more like a viscous fluid-like material. Finally, from the nominal 25°C experiments, the influence of humidity can once again be observed.

BaFe–PEN Magnetic Tape and PEN Substrate Samples. Viscoelastic properties are shown graphically in Figure 5 for the BaFe–PEN tape and PEN substrate samples. Observing the storage modulus, E', of the PEN tape, a noticeable decline is visible as the temperature increases. The frequency effects on the storage modulus appear to be inconsequential, because the grouping is so tight. The gradual decline matches the expected decay of the material under these conditions based on past experiments.[4,5,10] The decline is not as extreme for the PEN substrate. Once again this can be attributed to presence of the front coat and back coat for the magnetic tape.

The viscous loss modulus, E'', shows some interesting results. The room temperature samples for the PEN tape seem to experience high loss or dissipation of energy. This effect is most likely the result of humidity effects on the tape because the loss drops back down in the 30°C sample set. It is also interesting that the loss for the room temperature tape samples at low frequency is much higher than the high frequency samples. This

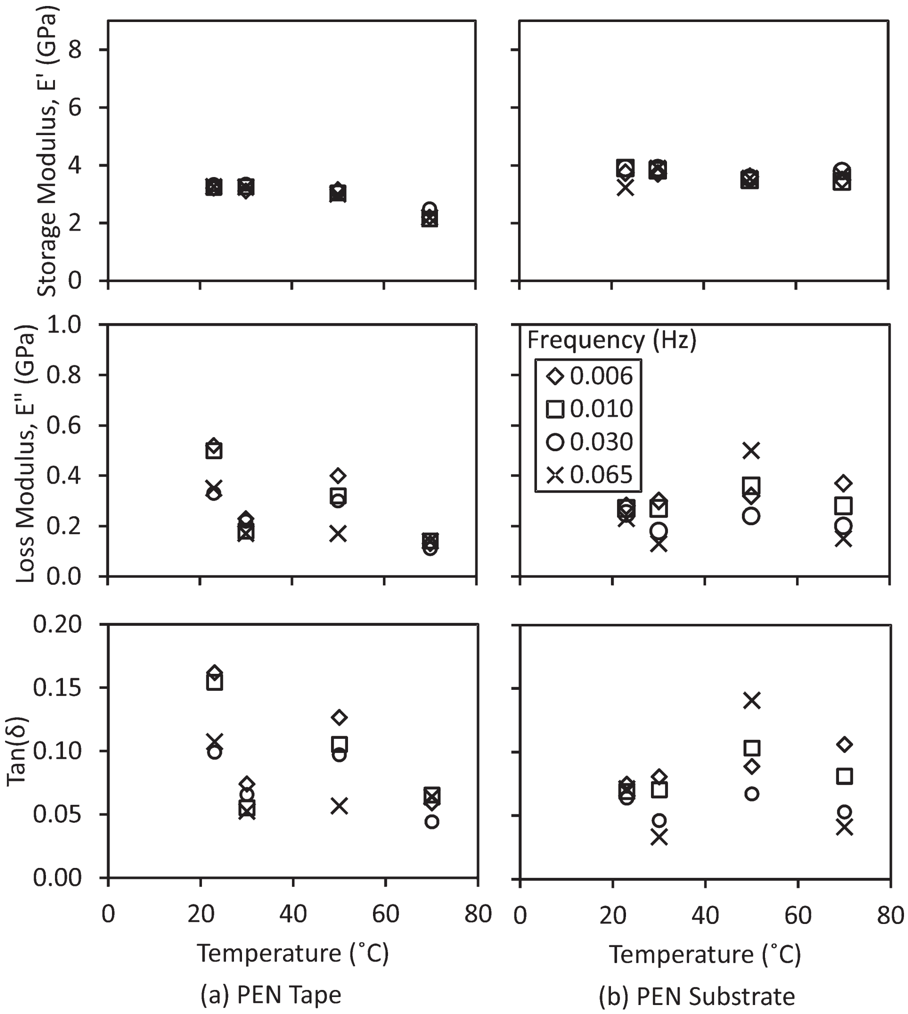


Figure 5. Dynamic viscoelastic characteristics of (a) PEN tape, and (b) PEN substrate as a function of temperature and frequency.

effect is not as prevalent for the 30°C samples, in which frequency appears to have less of an effect. Although the viscous loss for the PEN substrate samples at room temperature might also be experiencing the effects of uncontrolled humidity, this effect does not appear to be as prevalent as in the PEN tape samples. When looking at the 30°C samples for the PEN substrate, it appears that the lower frequency samples have more viscous loss than the high frequency samples, as expected.

The 50°C results see a significant increase in the viscous loss modulus for both the tape and the substrate samples when compared to the 30 or 70°C data. The loss modulus for both the PEN tape and the substrate also appear to be dependent on the frequency. However, frequency has a greater influence on the viscous loss modulus measured at 50°C for the PEN tape than it does at either 30 or 70°C. The observed trend for the PEN tape sample at 50°C shows the lowest frequency has the highest loss, although each subsequent frequency has a decreasing amount of loss, as expected. A similar general trend can be observed for the substrate at 50°C, except the highest frequency appears to have the highest loss instead of the lowest. This could be due to some experimental error as described when examining the peak elastic modulus; the frequency is much higher than expected, and the moving platform holding one end of the sample may not have operated as it should have.[9] However, past DMA experiments with PEN samples have shown these types of reversals in frequency dependence in the 50°C temperature range, and the observed peak at 50°C lines-up well with where the β^* secondary transition occurs in previous experiments.[5,8] The β^* transition in PEN is believed to be due to the motion of the naphthalene group in the molecular structure that leads to more viscoelastic energy dissipation in the material.

The 70°C loss modulus data for the PEN tape and substrate samples appear to show reduction in the modulus when compared to the 50°C β^* peak. When looking at the tape samples, the loss modulus results all seem to drop down to a small range of modulus values, regardless of frequency. Although the substrate shows a broader range of viscous loss values that are higher with correspondingly low frequency, but still reduced from the 50°C results. The low frequency data show the highest loss modulus at 70°C with a decreasing trend as frequency increases, which is expected.

Table II. Complex Modulus, E^*, and Complex Loss, E''/E^*, for Aramid and PEN Tapes and Substrates at Nominal Temperatures and Frequencies

Temperature (°C)	21-25		30		50		70	
Frequency (Hz)	E^* (GPa)	E''/E^* (%)	E^* (GPa)	E''/E^* (%)	E^* (GPa)	E''/E^* (%)	E^* (GPa)	E''/E^* (%)
Aramid tape								
0.006	5.86	11.04	5.87	11.37	4.76	12.63	5.36	14.61
0.010	5.65	10.55	5.68	9.89	5.10	10.94	5.64	13.42
0.030	6.11	10.24	5.93	8.96	4.83	8.67	5.49	10.87
0.065	5.94	10.06	5.72	10.07	5.00	9.48	5.47	10.06
PEN tape								
0.006	3.25	16.09	3.11	7.34	3.19	12.44	2.20	5.83
0.010	3.28	15.07	3.26	5.60	3.05	10.57	2.14	6.33
0.030	3.35	9.98	3.36	6.41	3.11	9.78	2.49	4.27
0.065	3.28	10.77	3.24	5.19	3.00	5.81	2.19	6.41
Aramid substrate								
0.006	7.31	12.97	7.58	7.48	7.26	7.53	7.19	9.77
0.010	7.32	11.68	7.48	4.18	7.34	7.31	7.06	8.64
0.030	7.39	12.39	7.73	3.43	7.81	6.48	7.31	7.86
0.065	7.95	10.78	7.62	7.84	7.62	5.97	7.49	7.46
PEN substrate								
0.006	3.76	7.32	3.73	8.08	3.63	8.73	3.51	10.55
0.010	3.92	6.98	3.84	7.12	3.50	10.28	3.46	8.23
0.030	3.92	6.49	3.91	4.53	3.58	6.76	3.81	5.24
0.065	3.24	6.97	3.90	3.30	3.59	13.88	3.68	3.96

As observed for the aramid samples, the loss tangent values for the PEN samples are still relatively low because of the low E'' values in the numerator compared to the high E' values in the denominator. When looking at the loss tangent there are two major points that stand out. First, both samples show huge loss jumps in the 50°C region. This region almost certainly represents the β*secondary transition for the PEN material. The loss tangent also does a great job of reemphasizing the large room temperature loss in the tape sample, which as stated previously is probably due to humidity, although the highest loss tangent corresponds with the lowest frequency. There's a possibility that the binder material or even the back coat material is more hygroscopic, which causes the PEN tape to be more susceptible to humidity than the PEN substrate.

Comparison of BaFe–Aramid and BaFe–PEN Results. A full analysis of each material, aramid and PEN, in both their substrate and tape form has yielded some interesting and definitive results. If a material is well defined through dynamic mechanical analysis, the material's viscoelastic properties can be derived for any condition simply by knowing the temperature and frequency it is subject to. A good understanding of how a magnetic storage tape material reacts can be partially verified, and better understood, from the direct comparison of the tape's viscoelastic properties to the substrate's viscoelastic properties. Material choice for a given application is most often based on the knowledge of that materials performance under the specified conditions involved. Because the two magnetic tapes in this experiment both serve a similar purpose, looking at both sets of data and comparing them might be relevant to future material choice and design.

To compare the materials more accurately it was determined that two factors could be used to more easily see the viscoelastic conditions given any of the tested scenarios. The first factor is the material's complex modulus, which is the magnitude of the combined elastic storage modulus and viscous loss modulus shown in eq. (5). (For simplicity, E^* is used instead of $|E^*|$ for the complex modulus magnitude.) Results for both the aramid and PEN materials can be seen in Table II.

$$E^* = \sqrt{(E')^2+(E'')^2} \tag{5}$$

The complex modulus can be useful in determining the relative stiffness of the material. A higher complex modulus corresponds with having a higher elastic modulus. The complex loss percentage is the viscous loss modulus divided by the complex modulus then converted from a ratio to a percent value as shown in eq. (6).

$$\frac{E''}{E^*}\times 100\% = \text{Complex Loss Percentage} \tag{6}$$

For any magnetic tape to be successful, especially for long-term stability, the loss modulus should be relatively low. This means that the lower the complex loss percentage, the better the long-term stability of the material. Between the complex modulus and the complex loss percentage, more information can be gained about the viscoelastic material's overall performance.

First, it is important to recognize that there are now five viscoelastic properties, or derivations of properties that have been explored: the elastic storage modulus, E', the viscous loss modulus, E'', the loss tangent, tan δ, the complex modulus E^*, and the complex loss percentage. From any two of these five values the other three can be analytically derived. These values are all primarily dictated by the conditions they were tested at, so they would all use the same control variables of frequency and temperature. To more easily analyze the data and compare the viscoelastic properties of different materials, it would seem more practical to use just two of the five potential determined characteristics. Because the overall stiffness of the materials would usually be referenced through the peak elastic modulus, a value that correlates with it would be important when comparing materials. The complex modulus, as shown previously, should have this high correlation to the peak elastic modulus values making it well suited as a comparative value. The second consideration being made when selecting a strong, long lasting, advanced magnetic tape material or component is how much of that total stiffness might be dissipated over time or under given conditions. This would be dictated by the viscous loss modulus, E'', which is specific to the material as well. For quicker comparison, it would be easier to think of the viscous loss modulus as a percentage of the overall complex modulus, or the complex loss percentage shown previously. Using a table made up entirely of associated complex modulus values and complex loss percentages under a set of controlled parameters, it becomes much quicker to compare different materials. Ideally, a high complex modulus would be maintained while having a small complex loss percentage under any given parameters.

Table II offers a lot of information about the viscoelastic properties of the materials that can be understood more readily. It offers four distinct variables that should hold primary importance to the researcher. The frequency and temperature of the material are listed as experimentally controlled parameters, whereas the complex modulus and the complex loss percentage are the resulting measured characteristics of interest for the material.

Comparing the aramid tape results in Table II to the PEN tape results leads to some interesting findings. It is obvious that the aramid tape maintains a higher complex modulus, E^*, than the PEN tape throughout all the frequency and temperature sets. On average the aramid tape has a 2–3 GPa greater complex modulus in comparison to the PEN tape, although the aramid tape's 50°C s complex modulus values are around 18% lower than it should be, due to previously discussed experimental error. In general, the aramid tape seems to maintain a 10% complex loss, E''/E^*, that will rise up to about 14% at high temperatures and lower frequencies. In comparison, the PEN tape seems to experience high complex loss percentages at room temperature, this is probably due to humidity effects as discussed earlier. Otherwise the PEN tape seems to have low complex loss percentages in the 30 and 70°C sets at around 6–7%. However, PEN sees a significant spike in the complex loss percentages in the 50°C area. This phenomenon is due to the previously discussed molecular movement with the β^* secondary transition. Although PEN generally maintains lower complex loss percentages, the difference in complex modulus is still so great that the aramid tape would seem to have a higher resistance to overall deformation.

Looking at the aramid and PEN substrates comparatively, it is clear that the aramid substrate is much stiffer than the PEN substrate, with an almost 3–4 GPa difference in complex modulus values. Both samples share the expected general trend of a lower complex modulus at lower frequencies with some variation, as expected from previous results.

One of the more interesting observations made when looking at the substrate complex loss percentages compared to the tape complex loss percentages is every substrate complex loss percentage value is smaller than its corresponding tape value, with the exception of the room temperature values. This confirms that the front coat and back coat layers of the tape are affecting the overall viscoelastic performance of the tape. If we were to focus on comparing the room temperature substrate complex loss percentages, it is interesting to see that humidity does not affect the PEN substrate samples as much as the PEN tape samples. Transversely, it would appear that the aramid substrate is more affected by humidity than the aramid tape based on complex loss percentage. This could mean that the composition of the front coat and the back coat used by each tape are not necessarily the same, and their contribution to the influence of humidity on the viscoelastic deformation of the whole tape may be significant.

SUMMARY AND CONCLUSIONS

The ULDMA was used to evaluate BaFe–aramid and BaFe–PEN advanced digital magnetic tapes tested at four different frequencies: 0.006, 0.010, 0.033, and 0.065 Hz. Each frequency setting was further tested under a range of temperatures: 25 (room temperature), 30, 50, and 70°C. To better analyze the results from these tests the same experiments were also performed on the carefully prepared substrate material of the same advanced magnetic tapes.

The experimental data sets were put through a Fourier transform program that evaluated the data for the associated time delay and phase angle at each fundamental test frequency. To check the data thoroughly and further validate it, the program also checked the stress and strain data sets for coherence and intrinsically checked the frequency the experiment was performed at. From the phase angle determined from the Fourier transform program, the elastic storage modulus, E', viscous loss modulus, E'', and loss tangent, tan(δ) were calculated. These properties were used to evaluate the viscoelastic characteristics of the tape and substrate samples under each set of experimental parameters.

From the experiments and Fourier analysis it was determined that the aramid tape and substrate performed with a much higher peak elastic modulus, elastic storage modulus, and complex modulus. The PEN material performed similarly to past work, with a comparatively low storage elastic modulus and complex modulus, but was more sensitive to temperature with a β^* secondary transition peak at around 50°C. Typically, PEN tape performed with a lower complex loss percentage than aramid tape, the exception to this phenomenon being at PEN's β^* peak (around 50°C) and during the room temperature tests possibly due to the influence of humidity on the front and/or back coats of the PEN tape. This difference in complex loss percentage was also observed for the PEN substrate versus aramid substrate data, with humidity showing some influence on the aramid substrate at room temperature. From a viscoelastic point of view the material with the highest complex modulus while maintaining a minimal complex loss percentage would be preferable. However, definitive decisions about material choice cannot be made based on tests at specific temperatures or frequencies. Conditions or specifications relevant to the use and storage of the tape material in a reel in its cartridge need to be considered to predict the lifetime stability of the material. Data acquired using the low frequencies in this study can assist with such decisions, and are important to understand the fundamental viscoelastic characteristics of both the PEN and aramid based advanced magnetic tapes as the ideal life expectancy of these materials increases. Tape deformation as a result of viscoelastic creep or stress relaxation phenomena during storage occurs over long time periods, and the use of the low frequencies in these dynamic mechanical analysis studies helps us to both understand and better predict the storage limitations of magnetic tapes.

ACKNOWLEDGMENTS

The authors thank the TAPE Program members of the Information Storage Industry Consortium for their support of this research.

REFERENCES

1. International Magnetic Tape Storage Roadmap. Information Storage Industry Consortium: San Jose, CA, **2011**.
2. "Lost Emails" Restored to Life - IEEE Spectrum. Available at: http://spectrum.ieee.org/riskfactor/telecom/internet/google-gmail-lost-emails-restored-to-life, accessed on April 8, 2012.
3. Ma, T.; Bhushan, B. *J. Appl. Polym. Sci.* **2003**, *89*, 3052.
4. Rummel, N. J.; Weick, B. *J. Appl. Polym. Sci.* **2013**, *127*, 3124.
5. Weick, B. *J. Appl. Polym. Sci.* **2011**, *120*, 226.
6. Bhushan, B. Mechanics and Reliability of Flexible Magnetic Media, 2nd ed.; Springer-Verlag: New York, **2000**.
7. Weick, B.; Bhuhan, B. *J. Info. Stor Proc. Syst.* **2000**, *2*, 207.
8. Weick, B. *J. Appl. Polym. Sci.* **2009**, *111*, 899.
9. Berry, R. Dynamic Viscoelastic Properties of Advanced Magnetic Tapes. University of the Pacific, **2013**.
10. Rummel, N. Dynamic Mechanical Analysis of Magnetic Tapes at Ultra-Low Frequencies. University of the Pacific, **2011**.
11. Bhushan, B.; Ma, T.; Higashioji, T. *J. Appl. Polym. Sci.* **2002**, *83*, 2225.