

## Analysis of Audio Magnetic Tapes with Sticky Shed Syndrome by ATR-FTIR

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**ABSTRACT:** Audio magnetic tapes that are difficult to play may be affected by a form of degradation called “sticky shed syndrome” (SSS). SSS exhibits physical symptoms during playing such as squealing, not packing tightly on the reel and possible tape material loss during playing. This research investigated attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to identify spectroscopic markers for SSS in audio magnetic tapes with poly(ester urethane) (PEU) binder layer. This article presents results for applying this technique to 50 audio magnetic tapes from the Library of Congress (LC) collections. This technique and analysis is intended to be used as a tool in identifying audio magnetic tapes with SSS from the mid 1970s through the 90s for improved preservation and to increase workflow in libraries and archives. This ATR-FTIR technique had a success rate of 71% for identifying SSS tapes and 86% for non-SSS tapes. The research also discusses spectral and chemical changes in the PEU binder layer between SSS tapes, non-SSS, and SSS tapes treated by baking including changes in hydrogen bonding of the carbonyl groups. The results support chemical/physical changes occurring in the soft segment of the PEU binder layer of SSS tapes. The absorption ratio of free to hydrogen bonded carbonyl groups was also correlated with SSS. © 2012 Wiley Periodicals, Inc.† J. Appl. Polym. Sci. 000: 000–000, 2012

**KEYWORDS:** degradation; polyesters; polyurethanes; properties and characterization; spectroscopy

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### INTRODUCTION

“Sticky shed syndrome” (SSS) is a phrase used to describe technical problems in playing an audio or audio-visual magnetic tape that are believed to be caused by the chemical and physical degradation of the tape. This research was undertaken to further develop a test method based on attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) initially proposed by Zelst<sup>1</sup> to identify SSS in audio tapes, better understand spectral changes that occur with SSS tapes and the changes during baking treatment of SSS tapes. Physical symptoms of SSS include squealing sounds from the tape during playing, deposition of tape residue on tape heads and rollers, the tape not being tightly packed on a reel (loose packing indicates possible SSS), and possible loss of high frequency sound during playing due to residue on tape heads. In addition, playing a SSS tape may cause further damage to the tape including loss of the binder layer. Because the binder layer contains the recorded information on the tape, loss of this layer may result in permanent loss of recorded information. SSS has been found to be specific to tapes with poly(ester urethane) (PEU) binders, mainly from the mid 1970s through the 1990s.<sup>1,2</sup>

SSS is generally difficult to observe without playing the tape. Developing a method to screen tapes for SSS should improve

workflow by allowing the identification of SSS tapes so they can be treated before playing. Treating an affected tape before playing minimizes the chances of damage to the tape during playing and subsequent loss of information, downtime in cleaning equipment, and time spent removing the tape from a winder before baking. If a SSS tape is played without treatment, the tape player normally needs to be stopped, the tape removed from the player and treated before playing is continued.

The preferred treatment method<sup>3</sup> at the Library of Congress (LC) Packard Campus is baking. Baking modifies the audiotapes so that the SSS is temporarily suppressed (no squealing, coating of the binder on tape heads) and tapes can be played without damage.<sup>1–3</sup> Present LC protocols usually involve baking the tape 5–8 h at ~130°F (54.4°C).<sup>3</sup>

The first goal of this research was to further develop a test based on ATR-FTIR that was initially proposed by Zelst<sup>1</sup> to screen tapes for SSS in audio magnetic tapes and to better understand the chemical nature of SSS and PEU binder layer degradation. Using ATR-FTIR as a test to identify tapes with SSS and treating these tapes before playing would improve workflow procedures by reducing damage to the tapes and loss of information, as well as time spent removing SSS tapes and



Figure 1. Audio magnetic tape cross section.

cleaning tape heads. The second goal was to investigate and better understand chemical changes that occur in SSS tapes after they are treated by baking.

### Audiotape Composition

Most audiotapes have a binder layer that is 2–4- $\mu\text{m}$  thick, composed of 20% binder PEU and 80% magnetic particles such as iron oxide ( $\text{Fe}_2\text{O}_3$ ) and chromium dioxide ( $\text{CrO}_2$ ).<sup>4–6</sup> The binder layer usually contains additional materials such as lubricants, dispersants, and stabilizers. Typical lubricants are fatty acid esters such as butyl tetradecanoate, butyl hexadecanoate, and/or octadecanoic acid. The base film is normally poly(ethylene terephthalate) (PET)<sup>1,2</sup> and is 6–36- $\mu\text{m}$  thick.<sup>6</sup> The base film gives the audio magnetic tape its mechanical properties.<sup>2,7</sup> Audiotapes also have a back coating that is  $\sim 1\text{-}\mu\text{m}$  thick, normally containing carbon particles (for static dissipation)<sup>2</sup> dispersed in the same polymer as in the binder layer.<sup>1,2</sup>

Figure 1 shows a schematic of a typical cross-section of an audiotape. The binder layer is phase separated into “hard” and “soft” segments (see Figure 2). The hard segments generally contain the polyurethane,<sup>1,2,4,8</sup> which are ordered but not necessarily crystalline and act as crosslinks.<sup>8</sup> The soft segments contain the higher molecular weight polyester, which can vary in composition and are responsible for the elastomeric properties of the binder layer.<sup>1,8,9</sup>

Because there are many formulations for audio tapes<sup>2,9–11</sup> and manufacturers can change components during production to achieve specific chemical and mechanical properties, the polyester soft segment may be composed of one of the following polymers: poly(ethylene adipate) (PEA), poly(1,4-butylene adipate) (PBA), poly(caprolactone) (PCL), or polycarbonate.<sup>1,9</sup> The polyurethane hard segment may be composed of one of the following monomers: *m*-xylene diisocyanate, toluene diisocyanate, 3,3'-tolidene-4,4'-diisocyanate (TODI), or 4,4'-methylene diphenyl diisocyanate (MDI)<sup>9</sup> The polyurethane hard segment also has a chain extender between isocyanate molecules such as butane-1,4-diol (BD) or hexane-1,6-diol (HD).<sup>9</sup> Figure 3 shows a typical PEU molecule with the hard segment (polyurethane and chain extender) and soft segment (polyester).<sup>9</sup> The soft segment in Figure 3 is PBA, and the hard segment shows MDI polymerized with BD chain extender.

Hydrogen bonding for the carbonyl group normally occurs in the hard segments between the oxygen in the carbonyl ( $\text{C}=\text{O}$ ) and hydrogen in the amine ( $\text{NH}$ ).<sup>8,12,13</sup> The polyester's carbonyl group in the soft segment does not form hydrogen bonds within the polyester itself,<sup>14,15</sup> but may form hydrogen bonds with the  $\text{NH}$  in the hard segment.<sup>12,13,15</sup> Most hydrogen bonds are within the hard segment but some may be attributed to the polyester carbonyl oxygen ( $\text{C}=\text{O}$ ) and the hydrogen in the hard segment's amide ( $\text{NH}$ ).<sup>13</sup> The ratio of hydrogen bonds in the hard segment to hydrogen bonds between the polyester carbonyl group and amide was measured by Lu<sup>13</sup> for PEU samples as 6.3 : 1 to 3.9 : 1 (hard : soft).

### Prior Research on Degradation of Poly(ester urethane)

PEU may degrade by a number of mechanisms including slow thermal degradation, hydrolysis, oxidation, and ionization radiation.<sup>16,17</sup> Hydrolysis is a chemical reaction that is documented in the literature to occur at the polyester's ester group.<sup>1,9,18</sup> Salazar et al.<sup>16</sup> found the primary degradation mechanism for indoor storage of tapes manufactured with Estane<sup>®</sup>5703 (PEU from B.F. Goodrich) was hydrolysis. Hydrolysis of the ester bonds in the polymer soft segment is generally considered to be a significant contributor to chemical degradation of the tape's PEU binder layer (see Figure 4).<sup>18,19</sup> Hydrolysis yields an alcohol and carboxylic acid, causing a reduction in molecular weight<sup>1,9,18</sup> of the polymer backbone and may change the tape's mechanical/physical properties such as tensile and dynamic storage modulus.<sup>8</sup>

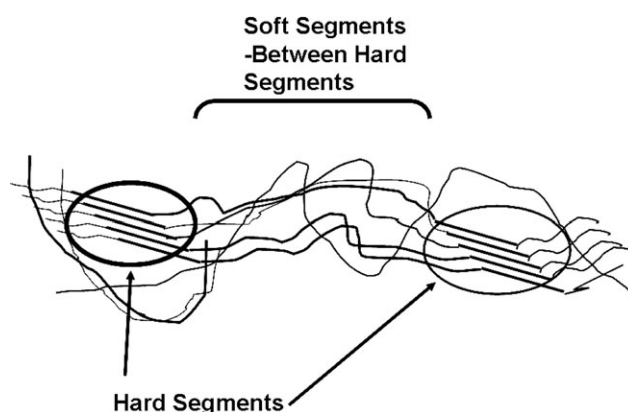


Figure 2. Soft and hard segments of the PEU in the binder layer.

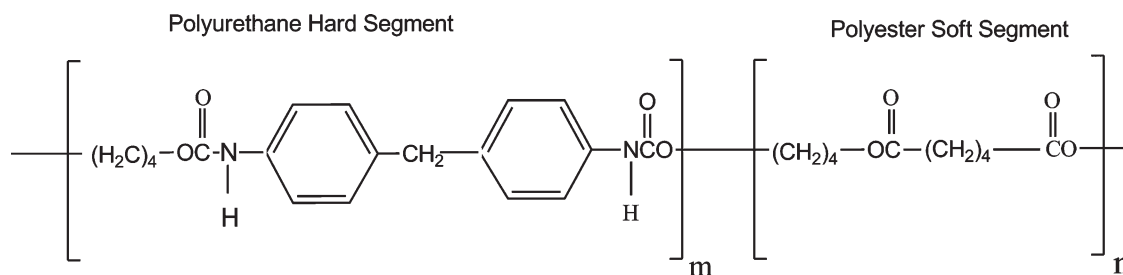


Figure 3. Example of a poly(ester urethane) in the binder layer.

Zelst<sup>1</sup> found a reduction of the molar mass of a non-SSS tape's PEU binder compared with SSS tapes PEU binder of the same formulation (from a weight average molecular weight of  $51$  to  $64 \times 10^3$  for non-SSS tapes to  $12$  to  $13 \times 10^3$  Da for SSS tapes) by size exclusion chromatography (SEC).<sup>1</sup> In addition, the SSS binder molecular mass to weight fraction distribution had a bimodal character with the higher molecular weight distribution being comparable with the non-SSS samples.<sup>1</sup> Cuddihy<sup>18,20</sup> measured the rate of hydrolysis by acetone-extractable material in the temperature range of  $36$ – $75^\circ\text{C}$  for the PEU binder and found it to increase with temperature and relative humidity (RH) for  $\text{RH} \geq 30\%$  in the air. For lower RH levels normally associated with baking ( $\text{RH} \leq 11\%$ ), greater temperatures have not been found to increase hydrolysis.<sup>18</sup> Brown et al.<sup>21</sup> found that the hydrolysis reaction rate constant for PEU also increased with temperature between  $35^\circ\text{C}$  and  $70^\circ\text{C}$  for  $100\%$  RH and a LC report<sup>22</sup> attributed binder hydrolysis as a factor in tapes with SSS. Hydrolysis has also been found to increase molecular chain mobility.<sup>8</sup> Other factors that may contribute to the breakdown of audio magnetic tapes include degradation of the back coating, oxidation, loss of lubricants, and mold.<sup>1,2,22</sup>

Previous researchers used FTIR spectroscopy to study SSS tapes.<sup>1,23</sup> Zelst<sup>1</sup> identified SSS tapes PEU binder layer peaks at  $1730$ ,  $1367$ ,  $1257$ ,  $1163$ , and  $950\text{ cm}^{-1}$  that increased in absorption when compared with a non-SSS tape of the identical product formulation. Zelst's work<sup>1</sup> was able to differentiate the ATR-FTIR spectra between SSS and non-SSS tapes of an identical formulation from the same manufacturer and was used as a starting point for this research effort. Edge et al.<sup>23</sup> also measured peaks at  $920\text{ cm}^{-1}$  and  $720\text{ cm}^{-1}$  that increased with accelerated aging at  $90^\circ\text{C}$  and  $100\%$  RH over 180 days for polyester based ferric-oxide home video tapes. Edge's work also supports the use of FTIR as a tool to distinguish SSS audio magnetic tapes from non-SSS tapes.

Zelst<sup>1</sup> also subtracted non-SSS FTIR spectra from SSS spectra for the same tape formulation and found the resulting spectrum that matched PBA. PBA is a polyester precursor for PEU in the binder layer.<sup>1</sup> Zelst's findings support a degradation reaction occurring on SSS tapes, such as hydrolysis.

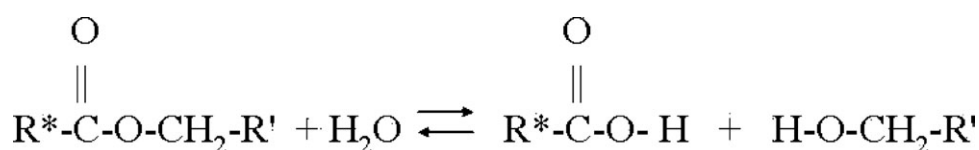


Figure 4. Hydrolysis reaction for polyester (Cuddihy<sup>18</sup>).

### Prior Research on Baking of Poly(ester urethane)

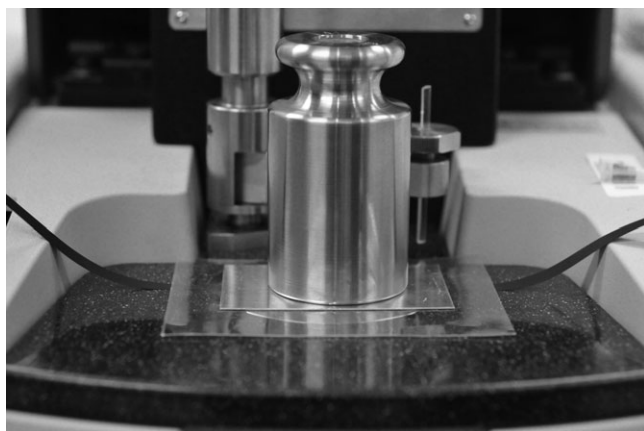
Baking temporarily suppresses the physical symptoms of SSS so that a SSS tape can be played. The physical symptoms of SSS will reappear after a certain period of time for baked tapes. Zelst<sup>1</sup> investigated molecular weight distributions of SSS and non-SSS tapes before and after baking ( $50^\circ\text{C}$ , overnight) with SEC experiments and did not notice a change in the PEU binder's number and weight average molecular averages or molar mass distribution to within experimental error. This is an indication that the forward or reverse reactions that could affect the molecular weight (hydrolysis) were not occurring during baking or the changes were within the measurement error of the instrument. Zelst baked the SSS tapes and showed the FTIR spectral peaks attributed to PBA were reduced in absorption and hypothesized that the PBA diffused away from the surface of the binder layer back into the center binder layer. Zelst also baked three SSS tapes PEU binder layer alone (room temperature to  $100^\circ\text{C}$ ) and found a weight loss of  $0.22$ ,  $0.16$ , and  $0.07$  wt % for the binder layer.<sup>1</sup>

Cuddihy<sup>18</sup> performed experiments that showed there was no chemical change with a PEU binder layer for magnetic recording tapes aged at  $16\%$  RH and  $61^\circ\text{C}$  and  $18\%$  RH and  $48^\circ\text{C}$  for 15 weeks as measured by acetone-extractable material. Cuddihy found that at RH values lower than  $16\%$  at  $61^\circ\text{C}$  and  $18\%$  RH at  $48^\circ\text{C}$  the PEU binder layer should not degrade by hydrolysis. Bajsic et al.<sup>24</sup> baked PEU at  $70^\circ\text{C}$  for 4 h and the PEU samples showed a degree of annealing with changes in the soft segment glass transition temperature and increased hard and soft segment phase separation.

The baking experiments performed by Zelst<sup>1</sup>, Bajsic et al.,<sup>24</sup> and Cuddihy<sup>18</sup> are comparable with the baking conditions used in this research.

### EXPERIMENTAL

The tapes studied were one-quarter inch wide audiotapes from the LC collections that showed signs of being affected by SSS (as described above), and tapes that did not demonstrate signs of SSS. The tapes were believed to have been manufactured and



**Figure 5.** ATR-FTIR measurement technique with tape, PET, backing plate, and weight (photograph taken by R. Herbert, LC).

recorded from the 1970 s to 2003 based upon information associated with the tape, but specific dates were not confirmed. The SSS tapes studied were selected randomly from a group of ~10,000 tapes that were thought to be ~90% SSS. Twenty of the non-SSS tapes studied were selected randomly from a group

**Table I.** Audio Magnetic Tapes Analyzed that did not Demonstrate Sticky Shed Syndrome

Tape identification	Location from tape's leading edge for FTIR measurement (inches)	Instrument
Tape A406	36, 108, 180, 252	Nicolet 670
Tape Q406	36, 108, 216, 288	Nicolet 670
LWO 9607A	36, 108, 180, 252	Nicolet 670
RAA 53062	36, 108, 180, 252	Nicolet 670
RAA 09432	36, 72	Multiple
RAA 16250	36, 72	Multiple
RWE 7193	36, 72	Multiple
RWA 120	36, 72	Nicolet 670
RWA 1310	36, 108, 180, 252	Nicolet 670
RWA 3048	36, 72	Nicolet 670
RWA 3110	36, 108, 180, 252	Nicolet 670
RWA 4926	36, 72	Nicolet 670
RWA 5211	36, 108, 180, 252	Nicolet 670
RWA 5256	36, 108, 180, 252	Nicolet 670
RWB 7789	36, 72	Multiple
RWB 8777	72, 180	Nicolet 670
RWC 5279	36, 72	Nicolet 670
RWE 5269	36, 72	Multiple
RWE 5419	36, 72	Multiple
RWE 5270	36, 72	Multiple
RWE 5271	36, 72	Multiple
RWE 6903	36, 108, 180, 252	Nicolet 670

Multiple: Bruker Alpha measurements were made at 36 inches and Nicolet at 72 inches from the leading edge of the tape with 64 scans.

**Table II.** Audio Magnetic Tapes Analyzed that did Demonstrate Sticky Shed Syndrome

Tape identification	Location from tape's leading edge for FTIR measurement (inches)	Instrument
Tape 209 <sup>a</sup>	108, 180, 252	Nicolet 670
Tape 227 <sup>a</sup>	36, 108, 180, 252	Nicolet 670
RAA 07711	36, 72	Nicolet 670
RAA 09431	36, 72	Multiple
RAA 10114	36, 72	Multiple
RAA 13469	36, 72	Multiple
RAA 13809	36, 72	Multiple
RAA 14503	36, 72	Multiple
RAA 15167	36, 72	Multiple
RAA 15168	36, 72	Multiple
RAA 15967	36, 72	Multiple
RAA 16248	36, 72	Multiple
RAA 16249	36, 72	Multiple
RAA 16259	36, 72	Multiple
RWA 6020	36, 72	Nicolet 670
RWB 4685 <sup>b</sup>	1, 1.25, 30, 92, 200, 236	Nicolet 670
RWB 6146	36, 72	Multiple
RWB 6181 <sup>b</sup>	0.7, 1, 236, 364, 485	Nicolet 670
RWB 6268	36, 72	Multiple
RWB 6280 <sup>b</sup>	0.7, 1, 364	Nicolet 670
RWB 6319 <sup>b</sup>	0.7, 1, 3, 34, 128	Nicolet 670
RWB 6494 <sup>a</sup>	144, 216, 288	Nicolet 670
RWB 6895 <sup>a</sup>	12, 36, 48, 60	Nicolet 670
RWB 7788	36, 72	Multiple
RWB 7790	36, 72	Multiple
RWB 7817 <sup>a</sup>	36, 48, 60	Nicolet 670
RWB 8356 <sup>a</sup>	12, 72, 81, 134	Nicolet 670
RWB 8778	36, 72	Multiple

Multiple: Bruker Alpha measurements were made at 36 inches and Nicolet 670 at 72 inches from the leading edge of the tape with 64 scans.

<sup>a</sup>SSS tapes were baked after initial FTIR measurements and measurements repeated at locations indicated.

<sup>b</sup>SSS tapes were baked after the initial FTIR measurements and measurements repeated only at the first two locations.

of ~10,000 tapes that were thought to be mostly non-SSS tapes and two of the non-SSS tapes were selected from a scientific collection at LC. The LC Packard campus then played 48 of the tapes on a Scully model 280 tape player and two tapes from the LC scientific collection were played on a Sony model APR-5003 tape player to determine if they had physical evidence of SSS. There were nine product numbers and three manufacturers associated with 62% of the tapes studied but product numbers and manufacturers were not confirmed except for two tapes.

The tapes were then analyzed by measuring the absorption of infrared (IR) electromagnetic energy in the binder layer with ATR-FTIR instruments at laboratory conditions (~23°C and

**Table III.** Assignments for FTIR Peaks in the PEU Binder Layer

Peak wavenumber (cm <sup>-1</sup> )	Wavenumber refractive index correction ( $n = 1.55$ ) (cm <sup>-1</sup> ) <sup>a</sup>	Measured peak strength <sup>b</sup>	Literature molecular assignment <sup>c</sup>	Literature assigned segment model <sup>c</sup>
1725	2.5	VS	$\nu$ (C=O) free	Both <sup>8,15</sup>
1701	2.0	VS	$\nu$ (C=O), hydrogen bonded	Polyurethane <sup>15</sup>
1594	0.8	S	$\delta$ (C=C) Aromatic ring	Polyurethane <sup>8,15</sup>
1527 <sup>d</sup>	1.9	S	$\delta$ (N-H) + $\nu$ (C-N)	Polyurethane <sup>8,15</sup>
1476, 1463, 1436, 1458 <sup>e</sup>	0.6	W	$\delta$ (CH <sub>2</sub> )	Polyester <sup>15,26</sup>
1411	0.6	S	$\nu$ (C-C) primarily phenyl ring	Polyurethane <sup>8,15</sup>
1392, 1371, 1364	0.6	W	w (CH <sub>2</sub> )	Polyester <sup>15,27</sup>
1308	0.8	S	$\delta$ (N-H) + $\nu$ (C-N)	Polyurethane <sup>8,15</sup>
1252	0.6	Inflection, VW-M	$\nu$ (C-O-C), w (CH <sub>2</sub> )	Polyester <sup>8,15</sup>
1219	2.2	S	$\delta$ (N-H) + $\nu$ (C-N)	Polyurethane <sup>8,15</sup>
1169	3.1	S	$\nu$ (C-O-C)	Polyester <sup>15,26</sup>
1138	1.6	M	$\nu$ (C=O) + $\nu$ (O-CH <sub>2</sub> )	Both <sup>8,27</sup>

<sup>a</sup>Add correction to peak wavenumber, <sup>b</sup>VS, very strong; S, strong; M, medium; W, weak; V, stretch;  $\delta$ , bend; w, wagging, <sup>c</sup>Both—polyester and polyurethane model, <sup>d</sup>In addition to the 1527 cm<sup>-1</sup> peak, a peak at 1507 cm<sup>-1</sup> is sometimes present, <sup>e</sup>Peak represents a combination of overlapping peaks at different wavenumbers such as 1476, 1463, and 1436 cm<sup>-1</sup>.

35–45% relative humidity). The instruments used were (1) a Nicolet 670 FTIR with an ATR durascope and a KRS-5 focusing crystal and 1-mm diameter diamond element for spectral measurement or a (2) Bruker Alpha FTIR with a 1 mm × 1 mm diamond element. The PEU binder side of the magnetic tape was placed face down on the diamond cell and a separate sample of PET was placed over the tape's back coating. An aluminum or steel backing plate was often times placed on the PET. A brass or stainless steel weight was then placed on the backing plate or sometimes the weight was placed directly over the PET. The weight was to provide the minimal contact pressure between the tape and diamond cell to obtain suitable spectra (0.26–0.63 N/cm<sup>2</sup> for the Nicolet 670 and between 0.26 and 3.9 N/cm<sup>2</sup> for the Bruker Alpha), and this technique is further illustrated in Figure 5. This ATR-FTIR technique in about half the tapes measured left a small mark or indentation in the binder layer where the outside circumference of the diamond cell made contact with the tape (few measurements: ~20  $\mu$ m wide or less and 0.7–2.4 mm in length).

The Nicolet 670 averaged 256 scans, through a range of 4000 to 400 cm<sup>-1</sup> wavenumbers at a resolution of 4 cm<sup>-1</sup>. The number of scans was later reduced when it was determined that 64 scans were satisfactory for distinguishing SSS tapes from non-SSS tapes and the number of data points per tape was also reduced from 4 to 2. The Bruker Alpha spectral measurements were made in the same manner as the Nicolet 670. The details of the measurements and tapes are shown in Tables I and II.

A baseline correction with the Omnic 8.0 software was applied to the spectra to correct for localized variations in scattering, diffraction and refraction in samples. The spectra below 800 cm<sup>-1</sup> had significant increase in absorption attributed to the iron oxide magnetic particles<sup>25</sup> in the PEU binder layer, and this part of the spectrum was not used in the analysis. The

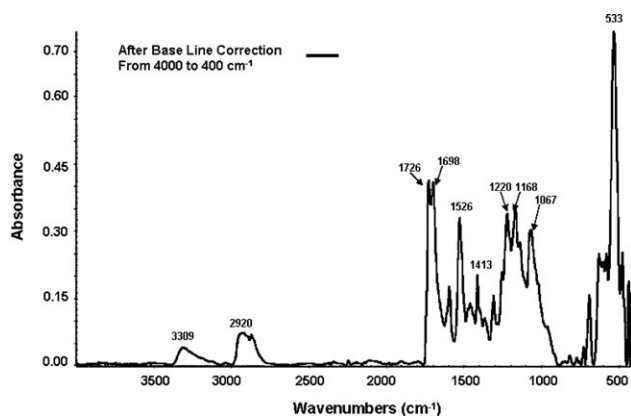
Omic 8.0 software was used for ATR corrections ( $n = 1.55$ ) and a summary of the ATR corrections results are shown in Table III. As a check on the ATR corrections, Estane 5778 was dissolved in acetone and applied to a KBr pellet, and the pellet was measured in transmission mode followed by ATR mode. The absolute value of the difference in the peak wavenumbers between the corrected ATR and transmission mode was 0.1 cm<sup>-1</sup> to 5.6 cm<sup>-1</sup>, with an average value of 1.75 cm<sup>-1</sup> between 1730 and 1017 cm<sup>-1</sup>.

After the baseline correction, the peak absorptions was divided by the peak absorption of the aromatic carbon-carbon single bond absorption (1412 cm<sup>-1</sup>) to calculate the absorption ratios and to minimize differences caused by changes in contact pressure and area. The 1412 cm<sup>-1</sup> peak was also used by other investigations to calculate absorption ratios.<sup>28,29</sup> Mean absorption ratios are reported in Tables IV, VI, VIII, and IX.

Ten SSS tapes were baked after the initial FTIR measurements on the Nicolet 670 at 130°F (54.4°C) for 5 h in a laboratory convention oven and FTIR measurements repeated on the Nicolet 670 ( $\pm 1/8$  inch, all 10 tapes were measured within 2–24 h after baking to allow time for the tape to cool, and at the same contact pressure).

## RESULTS AND DISCUSSION

Typical FTIR spectra for the binder layer of audio magnetic tapes studied are shown in Figures 6–8, and peak assignments are given in Table III. The FTIR spectra in Figures 6–8 and discussed in this report have been identified as PEU through the Hummel Polymer and Additives FTIR Library and references.<sup>1,8,15</sup> Table III also contains the mean peak wavenumbers and ATR correction values ( $n = 1.55$ , 45 degree, single bounce). The 1.55 refractive index value was selected because it



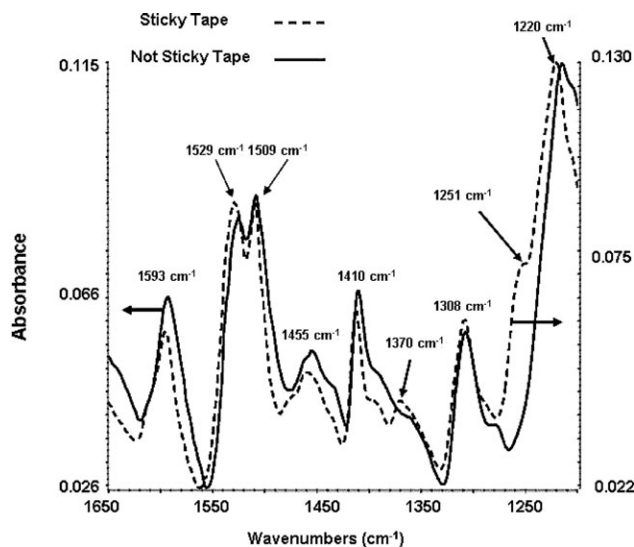
**Figure 6.** Example of the PEU binder layer spectrum of an audio magnetic tape from 4000 to 400  $\text{cm}^{-1}$ .

was an average value for the PEU binder based on literature references.<sup>30,31</sup> The ATR corrections in Table III are for comparisons between ATR measurements found in this research and non-ATR transmission measurements in the literature.<sup>8,15,27</sup> All other FTIR-ATR spectra in this article are reported as uncorrected wavenumbers. Figure 6 shows the overall spectrum between 4000 and 400  $\text{cm}^{-1}$ , Figure 7 between 1650 and 1200  $\text{cm}^{-1}$ , and Figure 8 the carbon-oxygen bond region from 1200 to 900  $\text{cm}^{-1}$ , respectively.

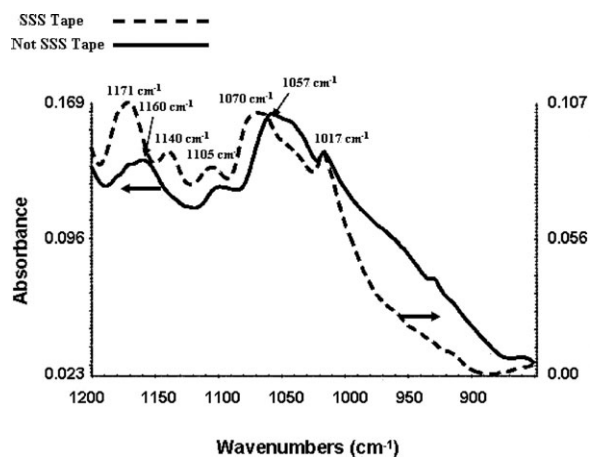
Because formulations and components of the audio magnetic tapes<sup>2,10,11</sup> changed over time with the manufacturing of the tapes; the infrared spectra for all audiotapes would not be expected to be identical. Therefore, this study was limited to tapes with similar PEU binder layer spectra as shown in Figures 6–8.

### Qualitative Test for SSS Tapes

A qualitative test was developed with ATR-FTIR for SSS with a PEU binder layer by analyzing spectral differences between SSS and non-SSS audio magnetic tapes. The spectral differences



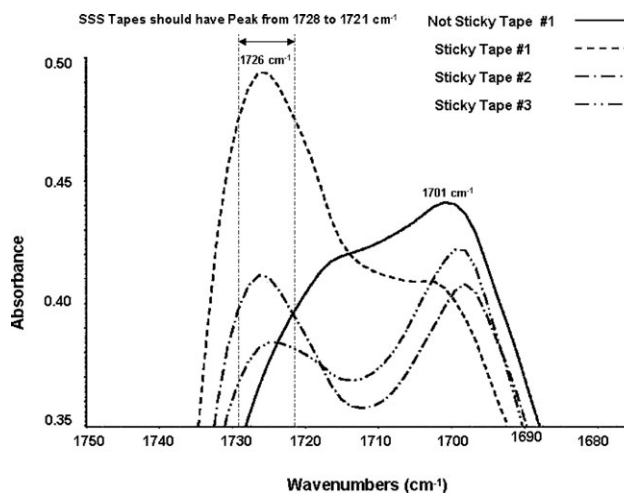
**Figure 7.** The PEU binder layer region between 1650 and 1200  $\text{cm}^{-1}$ .



**Figure 8.** The PEU binder layer region between 1200 and 900  $\text{cm}^{-1}$ .

found include the shape of the carbonyl peak (1730 to 1693  $\text{cm}^{-1}$ ), the presence of a peak at 1364  $\text{cm}^{-1}$ , the presence of a peak, shoulder, or inflection at 1252  $\text{cm}^{-1}$ , and the presence of a peak at 1138  $\text{cm}^{-1}$ .

The carbonyl bond showed noticeable differences between the SSS tapes and non-SSS tapes. SSS tapes spectra (71%) had a pronounced free carbonyl peak at  $\sim 1725 \text{ cm}^{-1}$  (peak may occur in the range 1728 to 1721  $\text{cm}^{-1}$ ) and a shoulder or peak for the hydrogen bonded carbonyl at 1701  $\text{cm}^{-1}$  (range 1713 and 1689  $\text{cm}^{-1}$ ; see Figure 9). In comparison, most non-SSS tapes (82%) had a lower wavenumber peak (1716 to 1693  $\text{cm}^{-1}$ ) and often times a shoulder at 1722  $\text{cm}^{-1}$  (1727 to 1715  $\text{cm}^{-1}$ ). The difference in the carbonyl peak between the SSS tapes and non-SSS tapes correlated with the carbonyl group's hydrogen bonding, with the SSS tapes having greater concentration of free carbonyl groups as compared with non-SSS tapes. Table IV shows the carbonyl peak absorption ratio ( $A_{1725}/A_{1701}$ ) for the tapes analyzed. Tables IV, VI, and VII also have results of a not paired two tailed, *t*-test between non-SSS tapes and SSS tapes. Differences in the mean value between non-SSS tapes and SSS tapes with *P* values less than 0.05 were considered statistically



**Figure 9.** Carbonyl peaks.

**Table IV.** Carbonyl Peak Absorption Ratio ( $A_{1725}/A_{1701}$ ) for Non-SSS and SSS Tapes

Tape type	Mean carbonyl peak absorption ratio ( $A_{1725}/A_{1701}$ ) $\pm$ standard deviation	<i>P</i> value for carbonyl absorption ratio <sup>a</sup>
Non-SSS tapes	0.88 $\pm$ 0.09	0.00
SSS tapes	1.03 $\pm$ 0.19	

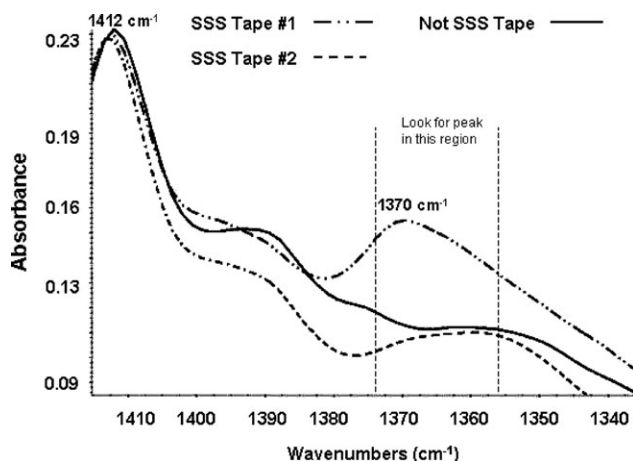
<sup>a</sup>t-Test, two tailed, not paired, unequal variance.

significant (for 95% confidence level) and *P* values greater than 0.05 were too small to be considered statistically significant (no change between non-SSS tape and SSS tape).

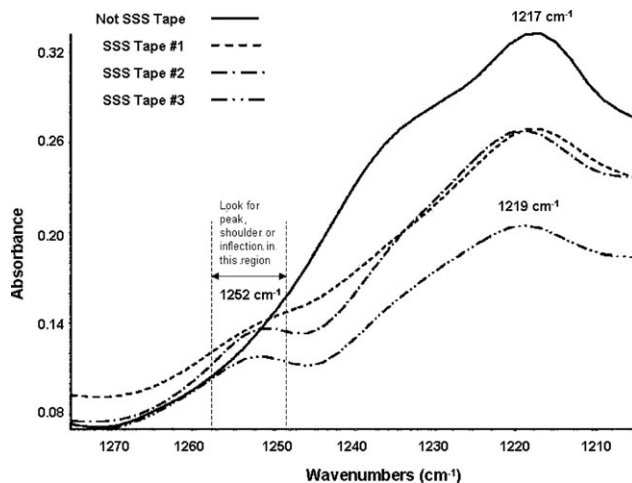
The second spectral difference is the presence of a weak to medium peak with an average value of 1364  $\text{cm}^{-1}$  (range of 1373 to 1356  $\text{cm}^{-1}$ , see Figure 10). This peak had increased absorption for the CH<sub>2</sub> wag with SSS tapes. This increased absorption may be related to a number of factors including degradation products being close to the PEU tape surface,<sup>1</sup> differences in the molecular weight and chemical composition of the polyester (PEA, PBA, and PCL), and/or a changes in molecular orientation of the CH<sub>2</sub> group in the polyester soft segment.<sup>32</sup> This peak was present in 96% of the SSS tapes and was also present in non-SSS tapes, but less frequently (50%).

The third spectral difference is the peak, shoulder, or inflection point at or near 1252  $\text{cm}^{-1}$ , which was present in 96% of the SSS tapes. It was not present in 86% of the non-SSS tapes (see Figure 11). This peak, shoulder, or inflection may be an indication that the tape is degraded and additional carbon-oxygen bonds are being formed, possibly by hydrolysis.

The fourth spectral difference observed was the peak or strong shoulder near 1138  $\text{cm}^{-1}$ , which was present in 96% of the SSS tapes (see Figure 12). It was not present in 55% of the non-SSS spectra. Tape formulations with a chemical group represented by the 1138  $\text{cm}^{-1}$  peak (carbonyl bonds and O—CH<sub>2</sub> bonds in the polyester component) may be more susceptible to hydrolysis



**Figure 10.** Spectra for PEU binder layer showing peaks between 1373 and 1356  $\text{cm}^{-1}$ .

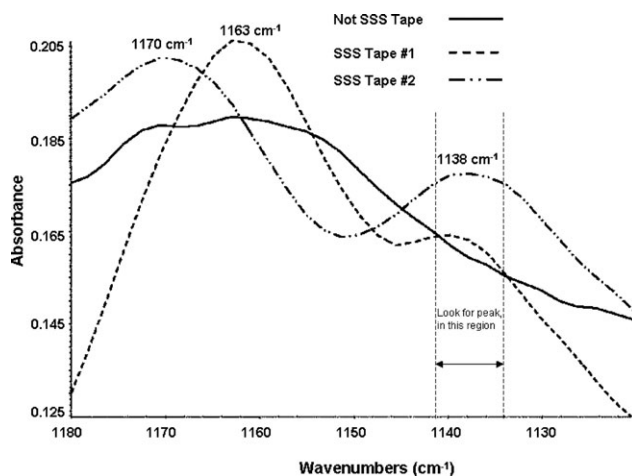


**Figure 11.** Spectra of the PEU binder layer showing peak at 1252  $\text{cm}^{-1}$ .

because these groups are believed to be involved with the hydrolysis reaction (see Figure 4).

### Discussion of Qualitative Test for SSS Tapes

The absorption peaks for this qualitative test are further displayed in Table V and should be used on audio magnetic tapes with a PEU binder layer manufactured from the mid 1970s to 1990s. This test was applied to the spectra from tapes in Table II and identified 71% of the SSS tapes. If the tape did not meet all the SSS criteria in Table V, it was considered a non-SSS tape. Non-SSS tapes (86%) in Table I were correctly identified. The three non-SSS tapes that were incorrectly identified had a carbonyl peak 1725  $\text{cm}^{-1}$  along with the other SSS features (1364, 1252, and 1138  $\text{cm}^{-1}$ ). The causes of SSS may vary (loss of lubricant, oxidation, and other chemical or physical degradation),<sup>1,2</sup> and this qualitative test does not address every degradation mechanism that could lead to SSS. In addition, the manufacturers and specific brands of the PEU collection tapes used in this research have not been identified and were randomly selected from a large sample population. In applying the test for SSS tapes outlined above, differences in chemical structure associated with different tape formulations may cause differences in



**Figure 12.** Binder layer peak at 1138  $\text{cm}^{-1}$  for SSS tape.

**Table V.** Peaks Assignments and Absorption Strength for the PEU Binder Layer of Audio Magnetic Tapes with SSS (Information Intended for Tapes Manufactured from 1975 to 1999)

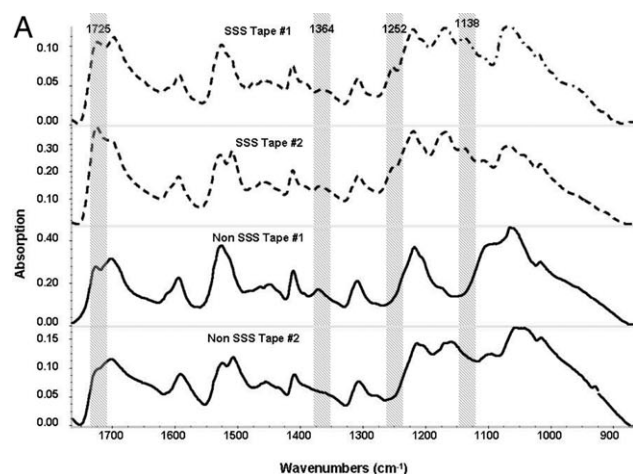
Mean peak wavenumber (cm <sup>-1</sup> )	Peak wavenumber range (cm <sup>-1</sup> )	Peak strength, shoulder, inflection
1725	1728-1721	VS
1701	1713-1689	VS peak or shoulder
1594	1596-1591	S
1527	1529-1522	S
1458	1462-1453	W
1412	1413-1409	S
1364	1373-1356	W-M
1308	1311-1305	S
1252	1257-1249	I-M—see Figures 7 and 11
1219	1220-1213	S
1169	1173-1156	S
1138	1141-1134	M to strong peak or shoulder—see Figure 12
1065	1073-1060 <sup>a</sup>	S-M
1017	1020-1015	S-W

VS, very strong; S, strong; M, medium; W, weak; I, inflection.

<sup>a</sup>One SSS tape analyzed had a peak at 1039 cm<sup>-1</sup>.

the FTIR spectra and partially explain why 29% of the SSS tapes and 14% of the non-SSS tapes were not correctly characterized. In addition, there is a possibility that some non-SSS tapes were in transition to SSS tapes.

It was noted the ATR left a small mark or indentation in about half the tapes measured. This mark or indentation was small compared with the tape's total length (normally 2500 feet) but was still undesirable, which is why minimal contact pressure was applied. This measurement may also be made in a portion

**Table VI.** Mean Absorption Ratios for Amide Peaks at 1527, 1308, and 1219 cm<sup>-1</sup> for Non-SSS and SSS Tapes

Type	Mean absorption ratio at 1527, 1308, and 1219 cm <sup>-1</sup> compared with 1412 cm <sup>-1</sup> ± standard deviation		
	$A_{1527}/A_{1412}$	$A_{1308}/A_{1412}$	$A_{1219}/A_{1412}$
Non-SSS	1.35 ± 0.24	0.93 ± 0.12	1.84 ± 0.27
SSS	1.43 ± 0.19	0.90 ± 0.13	1.79 ± 0.24
<i>P</i> value*	0.03	0.14	0.27

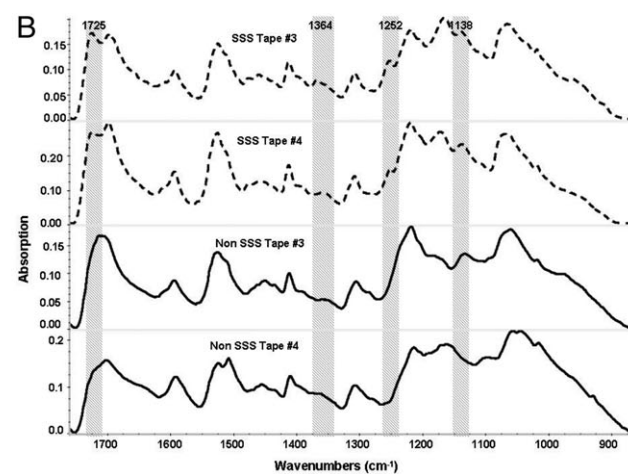
\*t-Test, two tailed, not paired, unequal variance.

of the tape without recorded information (often times at the start of the tape) to minimize/eliminate any impact on the fidelity of the tape.

Figure 13(A, B) shows four SSS tapes that met the criteria in Table V (and hence were correctly identified) and four non-SSS tapes that did not meet these criteria (and were also correctly identified as non-SSS tapes). The reasons why the non-SSS did not meet the criteria for SSS are the following: Non-SSS Tape #2, #3, and #4 did not have a peak at 1725 cm<sup>-1</sup>, non-SSS Tape #2 did not have a peak at 1364 cm<sup>-1</sup>, all four non-SSS tapes did not have a peak, shoulder, or inflection point at 1252 cm<sup>-1</sup> and non-SSS tapes #1, #2, and #4 did not have a peak or shoulder at 1138 cm<sup>-1</sup>.

#### Analysis of Amide Groups Spectra between SSS and Non-SSS Tapes

Amide groups in the hard segment of the PEU binder were studied to analyze spectral differences between SSS tapes and non-SSS tapes. Table VI shows the mean absorption ratios for the amide peaks at 1527, 1308, and 1219 cm<sup>-1</sup> for SSS tapes and non-SSS tapes did not change significantly (to within one standard deviation). The mean wavenumbers of the amide peaks (see Table VII) were similar to within two standard deviations. The lack of change in amide absorption ratios and mean wavenumbers peaks for the amide peaks indicates that the chemical

**Figure 13.** ATR-FTIR spectra of the PEU binder layer in four SSS tapes and four non-SSS tapes.



**Table VII.** Mean Wavenumbers for Amide Peaks at 1527, 1308, and 1219  $\text{cm}^{-1}$  for Non-SSS and SSS Tapes

Type	Mean amide peak wavenumber $\pm$ standard deviation ( $\text{cm}^{-1}$ )		
Non-SSS	1525.2 $\pm$ 1.5	1306.7 $\pm$ 1.2	1214.9 $\pm$ 2.9
SSS	1526.6 $\pm$ 1.7	1307.8 $\pm$ 1.0	1218.6 $\pm$ 1.6
<i>P</i> value <sup>a</sup>	0.00	0.00	0.00

<sup>a</sup>t-Test, two tailed, not paired, unequal variance.

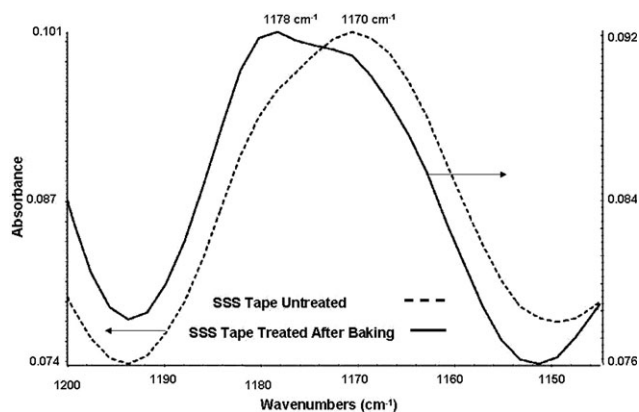
changes in the SSS tapes were not occurring in the polyurethane's amide group and the PEUs hard segment.

### Analysis of Spectra Differences between SSS and Non-SSS Tapes

The lack of change in the amide absorption ratios (see Table VI) combined with a change in the shape of the carbonyl peak (peak at 1725  $\text{cm}^{-1}$ ) points toward a chemical change in the soft segment (polyester) such as hydrolysis. The change in spectra at 1252  $\text{cm}^{-1}$  also supports hydrolysis playing a role in SSS formation because the carbon-oxygen bonds in the soft segment would be broken and reformed with hydrolysis. The 1364  $\text{cm}^{-1}$  peak could also be from smaller molecular molecules such as a lubricant diffusing to the tape surface or degradation product such as PBA, PEA, and PCL (Zelst research found spectral evidence of PBA),<sup>1</sup> differences in the molecular weight and chemical composition of the polyester (PEA, PBA, and PCL), and/or a changes in molecular orientation of the  $\text{CH}_2$  group in the polyester soft segment.<sup>32</sup>

The 1138  $\text{cm}^{-1}$  peak is hypothesized to represent a carbonyl and carbon-oxygen bond in the soft segment that is more likely to undergo a degradation reaction such as hydrolysis because the 1138  $\text{cm}^{-1}$  peak was more prevalent in SSS tapes than in non-SSS tapes.

As indicated in Table IV, the absorption ratio of carbonyl groups ( $A_{1725}/A_{1701}$ ) changed from 0.88 for non-SSS tapes to



**Figure 14.** The PEU binder layer 1169  $\text{cm}^{-1}$  peak before and after baking treatment.

1.03 for SSS tapes. This increase in the absorption ratio to 1.03 shows an overall decrease in hydrogen bonded versus free carbonyl group. Because hydrogen bonding is directly correlated with intermolecular attractive forces, a decrease in this ratio correlates with empirical observations for tape material coming off SSS tapes onto tape heads and the intermolecular forces not being great enough to hold the tape material onto the binder layer.

In addition, hydrolysis of the polyester urethane's has been reported to increase the hydrogen bonded carbonyl groups absorption (1701  $\text{cm}^{-1}$ ) and decrease the free carbonyl absorption (1725  $\text{cm}^{-1}$ ).<sup>8</sup> Because this was not observed for the SSS tapes in this study, the greater concentration of free carbonyl groups at 1725  $\text{cm}^{-1}$  may be an indication that SSS tapes do not fit into one known specific degradation mechanism such as hydrolysis.

The four peaks that are changing (1725, 1364, 1252, and 1138  $\text{cm}^{-1}$ , all are associated with the soft segment) indicate that SSS is a chemical reaction occurring in the soft segment of the PEU binder. In addition, this current research could support both

**Table VIII.** Shift in Peak Wavenumber and Absorption Ratio after Baking Treatment

Peak wavenumber ( $\text{cm}^{-1}$ )	Mean wavenumber shift <sup>a</sup> $\pm$ standard deviation ( $\text{cm}^{-1}$ )	<i>P</i> value for mean wavenumber shift <sup>b</sup>	Mean change in absorption ratio <sup>a</sup> $\pm$ standard deviation ( $A_{\text{peak}}/A_{1412}$ )	<i>P</i> value for mean change in absorption ratio <sup>b</sup>
1725	-1.6 $\pm$ 1.5	0.00	-0.20 $\pm$ 0.27	0.00
1701	1.0 $\pm$ 2.0	0.01	-0.06 $\pm$ 0.17	0.07
1594	-0.1 $\pm$ 0.9	0.53	-0.02 $\pm$ 0.12	0.33
1527	-0.9 $\pm$ 1.2	0.00	-0.06 $\pm$ 0.18	0.09
1458	0.1 $\pm$ 2.4	0.82	-0.01 $\pm$ 0.07	0.62
1412	-0.3 $\pm$ 0.5	0.00	-	-
1308	-0.2 $\pm$ 0.5	0.05	-0.03 $\pm$ 0.14	0.27
1219	-0.6 $\pm$ 1.1	0.01	-0.03 $\pm$ 0.18	0.47
1169	4.1 $\pm$ 3.3	0.00	-0.15 $\pm$ 0.25	0.00
1138	-0.9 $\pm$ 0.9	0.00	-0.06 $\pm$ 0.24	0.19
1065	-3.6 $\pm$ 3.7	0.00	0.06 $\pm$ 0.22	0.15

<sup>a</sup>Baked SSS tape—SSS before baking, measured at the same location, <sup>b</sup>t-Test, two tailed, paired.

**Table IX.** Carbonyl Peak Absorption Ratio ( $A_{1725}/A_{1701}$ ) for SSS Tapes before and after Baking

Tape type	Mean carbonyl peak absorption ratio ( $A_{1725}/A_{1701}$ ) $\pm$ standard deviation	<i>P</i> value for carbonyl absorption ratio <sup>a</sup>
Baked tapes	1.03 $\pm$ 0.12	0.00
Before baking	1.11 $\pm$ 0.17	

<sup>a</sup>*t*-Test, two tailed, not paired, unequal variance.

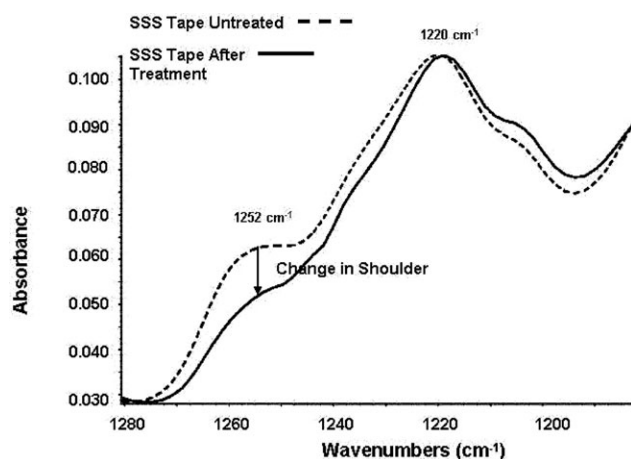
hydrolysis in combination with other degradation mechanisms including loss of lubricant from SSS tapes, occurring in the soft segment of the PEU binder. The results indicate the hard segments are not playing a significant role with the formation of SSS (no change at 1527, 1308, and 1219  $\text{cm}^{-1}$ ).

### Spectra Changes between SSS Tapes and Same Tapes Treated by Baking

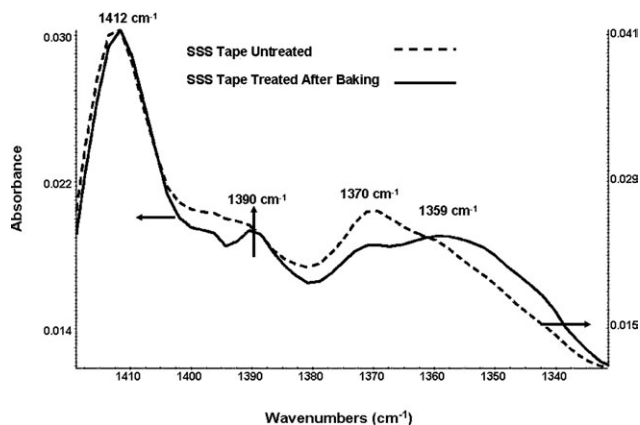
Tapes that were baked showed spectral changes in the polyester (soft) segments. Table VIII shows the results for changes in wavenumber and absorption ratios for the PEU binder layer of SSS tapes compared with baked tapes. The results of a paired two tailed, *t*-test are also presented in Table VIII. Differences between SSS tapes and baked tapes with *P* values less than 0.05 are considered statistically significant (for 95% confidence level) and *P* values greater than 0.05 were too small to be considered statistically significant (no change between SSS tape and baked tape).

The following spectral changes were observed:

- The peak wavenumber for the 1169  $\text{cm}^{-1}$  peak increased an average of 4.1  $\text{cm}^{-1}$  for the 9 out of 10 tapes analyzed after treatment (see Figure 14). In addition, the absorption ratio ( $A_{1169}/A_{1412}$ ) decreased by 0.15. The wavenumber and absorption changes indicate that the baking treatment may have had an affect carbon-oxygen on the PEU soft segment (C—O—C stretch).
- The carbonyl peak absorption ratio ( $A_{1725}/A_{1412}$ ) decreased by 0.20. This was the largest absorption ratio change



**Figure 15.** Change in the shoulder of the 1252  $\text{cm}^{-1}$  peak before and after baking treatment.



**Figure 16.** Change in 1390  $\text{cm}^{-1}$  peak before and after baking treatment.

between SSS tapes and baked tapes (see Table VIII). The 1725  $\text{cm}^{-1}$  peak is the free carbonyl bond associated with the PEU soft segment and points toward changes with the polyester carbonyl group. There was no change noted for the hard segment carbonyl bond at 1701  $\text{cm}^{-1}$  (therefore no noted change in the hydrogen bonding in the hard segment). Table IX shows the change in the carbonyl peak absorption ratio for baked versus prebaked tapes.

- The 1252  $\text{cm}^{-1}$  peak decreased for 6 out of 10 tapes (see Figure 15). The decrease of this peak may be an indication that a smaller molecule, such as soft segment degradation products diffused back into the center of the PEU binder layer.
- The shoulder of 1412  $\text{cm}^{-1}$  peak changed shape after treatment with an absorption increase from 1395 to 1390  $\text{cm}^{-1}$  and peak shifts and/or relative absorption changes from 1375 to 1355  $\text{cm}^{-1}$ ; the changes in the 1375 to 1355  $\text{cm}^{-1}$  region did not fit a specific pattern. The infrared absorption in this region is attributed to wagging of  $\text{CH}_2$  groups and may be an indication that smaller molecules are diffusing to/from the tape surface (hence decreased absorption peaks as these molecules penetrate deeper into the binder layer) and changes in the polyester molecule such as molecular weight and orientation of the C—H bonds. Figure 16 shows an example of these changes that occurred for 7 out of 10 tapes.

### Analysis of Spectra Changes between SSS Tapes and Same Tapes Treated by Baking

Three points are evident from the spectral results with the baking treatment. First, there was not a significant change in the PEU hard segment amide peaks as evident by lack of changes in the wavenumbers associated with the amide group (1527, 1308, and 1219  $\text{cm}^{-1}$ ), hydrogen bonding in the hard segment (1701  $\text{cm}^{-1}$ ), and the aromatic carbon-carbon bond (1594  $\text{cm}^{-1}$ ). Second, baking did not change the basic structure of the PEU polymer backbone as is evident by lack of larger changes in Table VIII (same covalent bonds were present before and after baking). Third, spectral changes at 1725, 1395 to 1390, 1375 to 1355, 1252, and 1169  $\text{cm}^{-1}$  support chemical changes in the PEU soft segment. These wavenumbers involve the carbon-oxygen single and double bonds (carbonyl groups) and carbon-hydrogen bonds of the polyester. The changes to the soft segment can be explained by changes in thermal energy causing molecular

thermal expansion, loss of water, diffusion of smaller molecules, and molecular reorientation of the polyester in the soft segment (1395 to 1390, 1375 to 1355, and 1252  $\text{cm}^{-1}$ ). In addition, the absorption ratio of free to hydrogen bonded carbonyl groups decreased with baking (1.11 to 1.03). This decrease in the carbonyl peak absorption ratio ( $A_{1725}/A_{1701}$ ) with baking shows an overall increase in carbonyl group hydrogen bonding per free carbonyl group. This carbonyl ratio result points toward the soft segments molecules after baking being more tightly adhered in the binder layer (assuming other intermolecular forces remain the same), and hence, tape can be played and SSS is temporarily suppressed. The baking results for the carbonyl ratio are similar to the SSS tapes when compared to non-SSS tapes (as shown in Table IV) and further indicate that hydrogen bonding is a factor in SSS.

## SUMMARY

This research was conducted to investigate an ATR-FTIR as a method to identify audio magnetic tapes in collections with SSS and to better understand the chemical changes that occur in the tape's binder layer as a result of SSS. This ATR-FTIR test was successful in identifying 71% of the SSS tapes and 86% of the non-SSS tapes. Archives are often digitizing collections and having a method to screen tapes for SSS may serve as a workflow improvement in addition to preventing damage to tapes in the collections. The ATR-FTIR spectral changes between SSS tapes and non-SSS tapes partially support hydrolysis occurring in the soft segment of the PEU layer; however, changes cannot be fully explained by hydrolysis and that other degradation mechanisms may be occurring. The ATR-FTIR results between tapes with SSS and the same tapes treated by baking show an annealing effect associated with the soft segment of the PEU but baking did not change the basic structure of the PEU polymer backbone as is evident by lack of larger changes. An increase in the free versus hydrogen bonded carbonyl groups absorption ratio ( $A_{1725}/A_{1701}$ ) correlated with SSS; with SSS tapes having a relative increase in the free carbonyl absorption compared with non-SSS tapes and baked tapes.

Further work at LC involving the analysis of SSS and non-SSS tapes involving multivariate statistics is on-going.<sup>33</sup> In addition, the affect of baking on the tape's fidelity and mass spectral surface analysis of SSS tapes may be topics of future research.

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