A DMA Study of Heat-Shrinkable, Peelable Fluoropolymer Tubing, Part II: Application-Oriented Approach

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ABSTRACT

A study of peelable heat shrink tubing has been carried out using DMA techniques along with application-oriented testing to better predict performance in catheter manufacturing processes. Peelable and non-peelable heat shrink tubes were tested in both expanded and recovered states. For the expanded tubes, DMA tests were carried out at 1 Hz and a range of high temperatures to account for nonisothermal recovery during the reflow step. For the recovered tubes, DMA tests were carried out at multiple frequencies around room temperature to account for stick-slip tear propagation during the removal step. The results showed good general agreement with previously-reported studies for polymers, blends and composites up to failure. However, there was little correlation evident between DMA results and overall tear energy or observed length of tearing in the tube, which are important characteristics of peelable tubing formulations. In order to effectively characterize the performance of peelable heat shrink tubes after tear initiation, tearing tests would be required.

INTRODUCTION

Zeus Industrial Products, Inc., is a global manufacturer of fluoropolymer heat-shrink tubing [1]. A major application for this tubing is as a processing aid during catheter construction. In the catheter manufacturing process, a polymeric jacketing material such as PEBA block copolymer, is placed over a braided core and then allowed to reflow through the braids and into contact with the core at an elevated temperature as an encapsulating fluoropolymer heat-shrink tube recovers over the assembly. The heat shrink recovery force is such that the intimate contact of the jacketing material with the braid and liner material promotes a strong adhesion between the layers. To facilitate removal of the heat-shrink tube from the catheter at the end of the reflow process, the tube is typically scored at one of its ends and peeled away from the catheter assembly.

BACKGROUND

Peelability in fluoropolymer heat shrink tubing is achieved by blending immiscible or semi-miscible polymers together during extrusion in order to facilitate tearing after expansion and recovery. For peelable heat shrink tubing to be successful in its end use application, strength and toughness in the hoop direction during recovery must be balanced with easy, linear tearing in the longitudinal direction once recovery is completed and the tube is to be removed. The interplay of these requirements is quite complex and relies on

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mechanisms that are poorly understood. In Part I of this study, the authors examined criteria proposed in the literature for characterizing peelable heat shrink tubing performance. These current methods were found to have significant drawbacks and limitations [2].

In this paper, we examine using a more comprehensive approach to determine the desirable characteristics of peelable heat shrink tubing at conditions close to those encountered in the actual application. In this way, criteria that are meaningful for catheter manufacturing can be developed.

THEORETICAL

The performance of peelable heat shrink tubing is difficult to characterize because of the disparate requirements of the product in the catheter manufacturing application. During reflow at elevated temperature, the stretched heat shrink tube must recover quickly and evenly over the melting jacketing material. After cooling to room temperature, the heat shrink tube must tear readily along its entire length for ease of removal. The physical and mechanical requirements of the heat shrink tubing must be optimized in order to efficiently meet these very different criteria at two different temperature ranges.

Consider first the reflow step at temperatures above 200°C. The recovery characteristics of the stretched (or expanded) tube will depend on the physical properties of the polymer blend as well as on how the tube was stretched, and to what extent. Both material selection and stretching conditions will affect the degree of polymer orientation and the ability of the tube to recover during reflow. A further complication arises from the non-isothermal nature of many methods of reflowing the jacket onto the braided liner. The heat shrink tube will in fact recover over a range of temperatures depending on the fluoropolymer blend as it is heated up in an oven or laminator beyond the temperature at which it was stretched originally. The closer the recovery temperature to the melting range of the jacket material, the more efficient the reflow process will be. The degree to which the tube is stretched originally will influence the orientation imparted onto its constituent polymer chains. A high orientation of the polymer chains decreases the overall entropy of the tube and provides a high driving force for recovery [3].

Consider next the heat shrink removal step at around room temperature. Propagation of a tear throughout the length of a polymeric tube is driven by complex mechanisms. The characteristic saw tooth nature of the stress-strain curve is indicative of this complexity, and is attributed to stick-slip behavior observed when polymers fracture resulting in variable local strain rates during crack propagation [4, 5]. Peelable heat shrink tubes are formulated with semi-miscible polymer blends in order to facilitate crack propagation by deliberately introducing a weaker interphase region into the matrix. The force required to propagate fractures in polymer blends and composites is widely believed to increase with tan δ, which represents the ability of a polymer matrix to dissipate energy [6]. Low values of tan δ are expected to allow a crack to propagate easily through the matrix. For an easy-to-tear peelable tube, there is a further constraint that the crack propagate linearly

down the entire length of the tube for easy removal from the catheter. This latter requirement is difficult to predict from simple measurements of mechanical properties.

Given the complexity of the interactions between the polymers, phase morphologies, tube extrusion and expansion conditions, as well as the end-use conditions encountered in catheter manufacturing, an integrated approach is required to effectively describe peelable heat shrink tubing tailored to these applications.

EXPERIMENTAL

In order to elucidate the numerous considerations involved in the design and manufacturing of peelable heat shrink tubing, the specimens listed in Table 1 were tested for comparison purposes.

Table 1. Tubes Tested in this Study

ID	Description of the Tube
HS	Heat Shrink, Exp. ID: 0.082"; Rec. ID: 0.051"; Rec. Ratio: 1.6:1
PHS1	FluoroPEELZ^{TM}, Exp. ID: 0.087"; Rec. ID: 0.054"; Rec. Ratio: 1.6:1
PHS2	Tearable HS, Exp. ID: 0.083"; Rec. ID: 0.051"; Rec. Ratio: 1.6:1

All specimens tested are commercial products. The standard heat shrink (HS) sample was produced by Zeus using a single fluoropolymer and expanded at a 1.6:1 ratio subsequent to extrusion. By design, specimen HS is not easily torn. Both peelable heat shrink tubes listed (PHS1, PHS2) have been manufactured using semi-miscible polymers giving them the capability to both recover when exposed to a heat and to tear easily under manual shearing forces. PHS1 is manufactured by Zeus, while PHS2 is a commercially-available peelable heat shrink product.

The peelable and non-peelable tubes were characterized by dynamic mechanical analysis (DMA) as well as by tear testing. All tubes were tested in their original expanded state in the DMA. DMA and mechanical testing was also performed on tubes that had been recovered for 10 minutes at 210°C in a laboratory oven.

Mechanical tear testing was performed using an Instron 5965 mechanical force tester equipped with 0.5 inch manual thumb grips. A 10-inch section was cut from each tube. A single end of each 10-inch section was sliced longitudinally along the centerline of the tube for a length of 1 inch using a slit block. Each half of the slit section was then placed in a T-peel orientation in the Instron, with one section placed in the stationary grip and the other section placed in the crosshead grip. The grips were then separated longitudinally at a rate of 1 inch/second until a load drop was realized. This occurred when the tube became completely separated. The mean tear force (lbf) and tear energy (J) were reported.

Thermo-mechanical testing was performed using a TA instruments model Q800 Dynamic Mechanical Analyzer (DMA) equipped with film tension grips. To mimic application conditions to which the material may be exposed, tubes were tested at both tear and recovery conditions.

For DMA tear characterization, recovered tubes were used. A 1-inch sample was removed from each recovered tube and sliced longitudinally along the centerline of the tube for a length of 0.5 inches. Each half of the slit section was then placed in the T-peel orientation in the DMA, with one section placed in the stationary grip and the other section placed in the movable grip. The software geometry was configured to the tube orientation with a test amplitude of 0.0006 inches. The wall thicknesses of the specimens were roughly equal and the sample lengths were around 0.32 inches. Individual samples were tested using this method at 0.1 Hz, 1 Hz, and 10 Hz from -50°C to 80°C. Tan δ and storage modulus at room temperature were reported.

For DMA recovery characterization, a 0.2-inch rectangular section was cut radially from the expanded tube and placed in the tension grips. The software geometry was configured to the rectangular orientation with a test amplitude of 0.0006 inches. The sample wall thicknesses and lengths were as described above. Individual samples were tested at a frequency of 1 Hz from room temperature to 240°C. Tan δ and storage modulus at 180°C, 200°C, and 220°C were reported.

RESULTS AND DISCUSSION

Figures 1, 2, and 3 show results from tear tests for the recovered HS, PHS1, and PHS2 tubes, respectively. Features of interest include the peak and average forces required to sustain tearing, as well as the area under the force-extension curve which represents the overall tear energy. Whereas the HS tube exhibits a mean tear force in the area of 2.75 lbf, the PHS1 and PHS2 yield a mean tear force in the area of 1.3-1.45 lbf. Tear energies for the PHS1 and PHS2 tubes differ significantly from the HS tube, as expected. PHS1 and PHS2 show a much higher overall energy value which is consistent with sustained tearing of long lengths. The HS tube shows low overall energy which is consistent with material tearing off in chunks.

Figures 4, 5, and 6 show tan δ results for the recovered HS, PHS1, and PHS2 tubes, respectively, at 1.0 Hz frequency and 3°C temperature ramp rate. At around 23°C, both formulations exhibit minima in the tan δ curves, which would imply relative ease of tearing for both tubes around room temperature. The blend used in the PHS1 specimen further exhibits a pronounced shoulder between 40 and 60°C, but this increase in tan δ is well above room temperature.
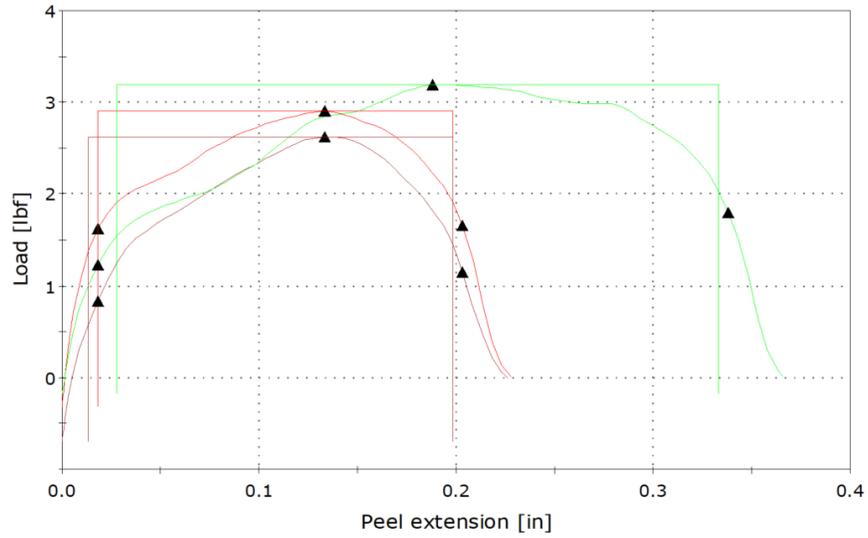
Figure 1. Load versus Extension for HS sample in tear tests at 23°C (three replicates).
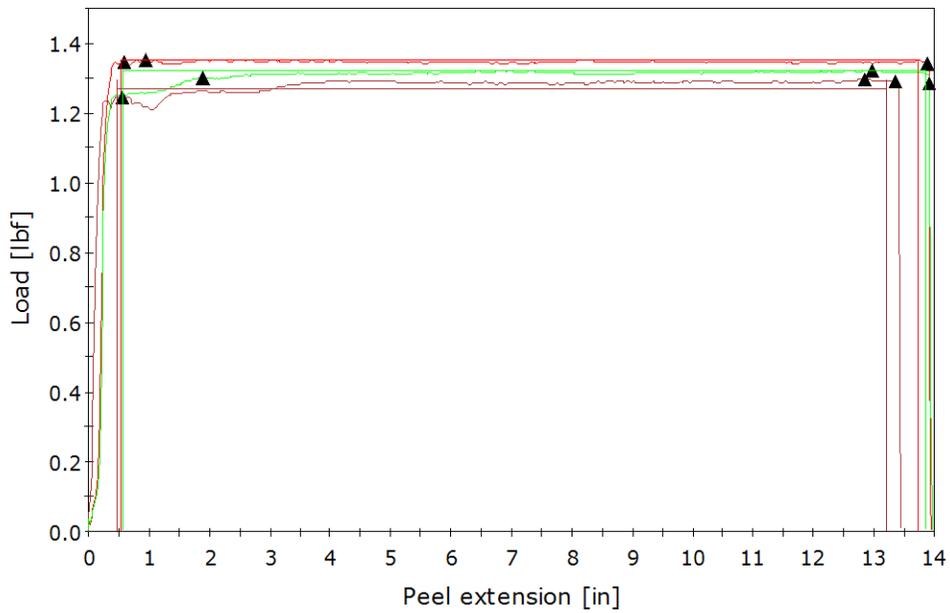

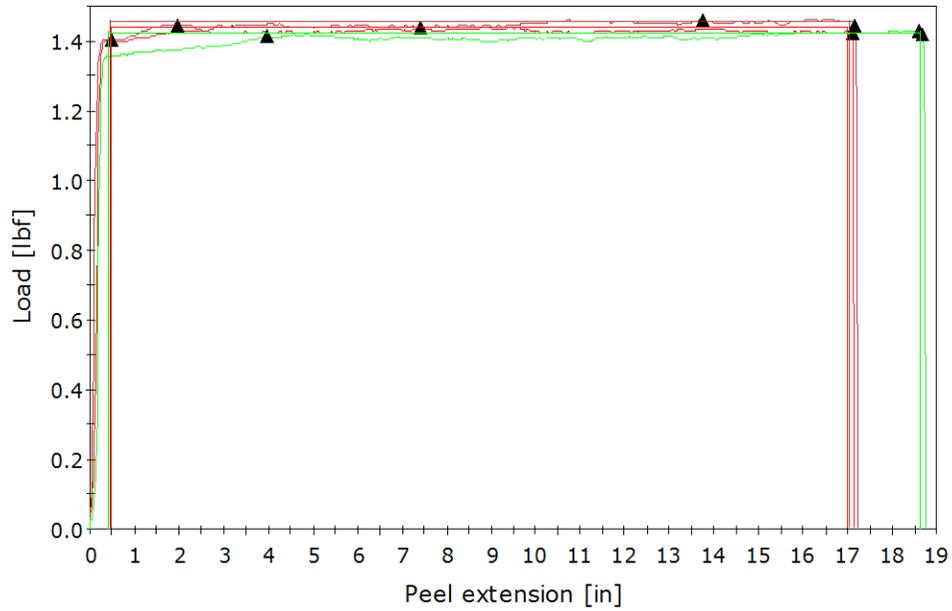Figure 2. Load versus Extension for PHS1 sample in tear tests at 23°C (three replicates).

Figure 3. Load versus Extension for PHS2 sample in tear tests at 23°C (three replicates).
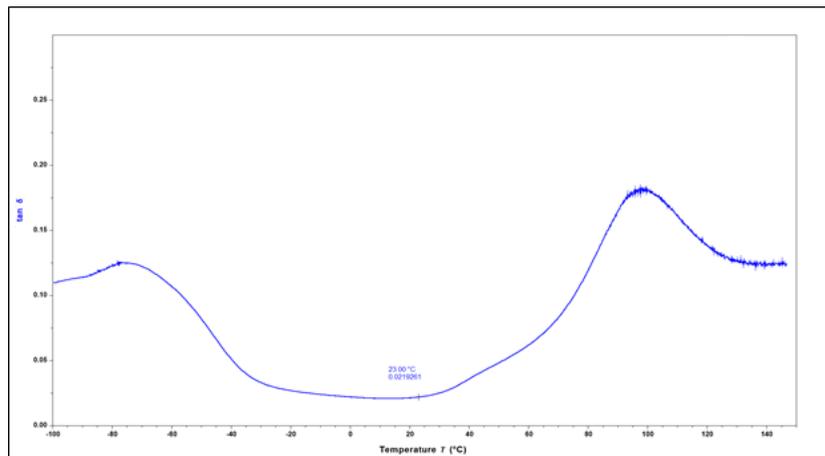

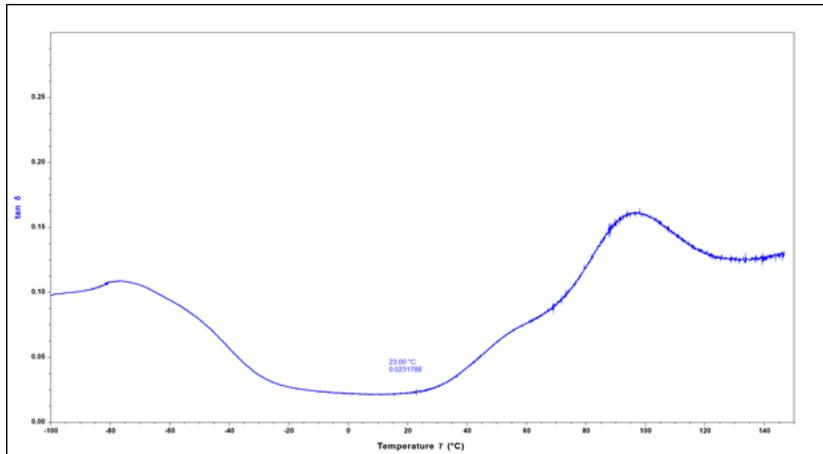Figure 4. Tan δ for recovered HS as a function of temperature.

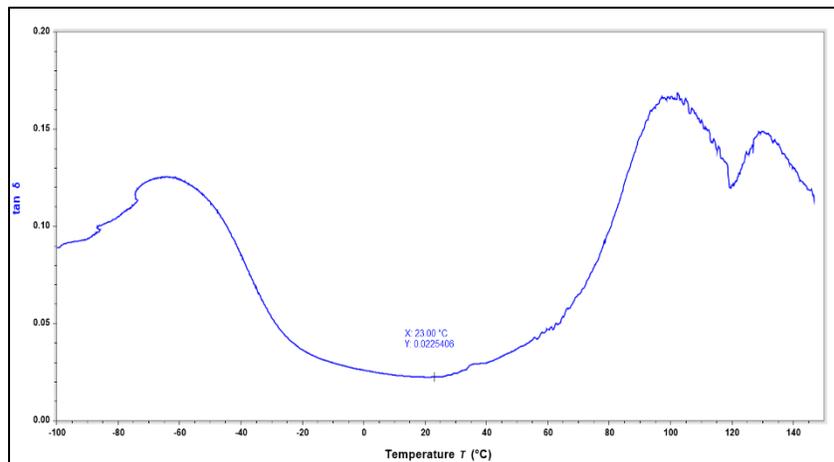Figure 5. Tan δ for recovered PHS1 as a function of temperature.

Figure 6. Tan δ for recovered PHS2 as a function of temperature.

Table 2 presents summaries of DMA data at room temperature, along with Mean Load and Overall Energy values from the tear tests. The results are shown for different test frequencies since rate of tearing is not always the same as crack tip propagation rate due to the stick-slip phenomenon noted earlier. It is interesting to note that tan δ shows a monotonic decrease with frequency for both formulations, indicating that ease of tearing increases with frequency. This result makes intuitive sense since the ability of the matrix to dissipate energy would decrease as the rate of deformation increases.

The effect of test frequency on storage modulus is more complex, with E' showing no clear trend with frequency among the samples. Tear strength has been found to correlate well with E' in some instances [7], but the lack of a clear frequency dependence makes interpretation of the effect difficult in a situation where local strain rates can vary significantly within each specimen.

Table 2. DMA and Tear Data at 23°C

Specimen	E', MPa			Tan δ			Mean Load	Energy
	0.1 Hz	1.0 Hz	10 Hz	0.1 Hz	1.0 Hz	10 Hz	lbf	J
HS	2.64	4.57	3.64	0.0296	0.0219	0.0171	2.9	0.07
PHS1	1.87	1.83	2.70	0.0313	0.0206	0.0200	1.3	2.01
PHS2	2.07	2.39	2.84	0.0291	0.0222	0.0235	1.4	2.82

 Table 3 shows DMA data for the expanded tubes at temperatures above 180°C at a frequency of 1 Hz. The expanded tube will start to recover non-isothermally over a wide temperature range as the catheter assembly is heated up in an oven or laminator. E' drops monotonically in all cases reflecting the softening of the polymer matrix with temperature, as expected. The tan δ values for HS and PHS1 are fairly stable up to 220°C. For PHS2, there is a 13.5% drop in tan δ from 180°C to 220 °C. There are no discernable trends evident to differentiate the peelable and non-peelable formulations in the DMA data.

Table 3. High Temperature DMA Data at 1 Hz

Example	E', MPa			Tan δ		
	180°C	200°C	220°C	180°C	200°C	220°C
HS	5.82	4.47	3.39	0.0440	0.0423	0.0478
PHS1	7.98	6.02	3.77	0.0513	0.0496	0.0559
PHS2	5.89	4.80	3.61	0.0801	0.0737	0.0693

CONCLUSIONS

DMA analysis of heat shrink tubes was carried out at conditions reflecting the actual application conditions for catheter manufacturing. For the expanded tubes, DMA tests were carried out at 1Hz and high temperatures to account for nonisothermal recovery during the reflow step. For the recovered tubes, DMA tests were carried out at multiple frequencies around room temperature to account for stick-slip tear propagation during the removal step. The results showed general agreement with some previously-reported studies for polymers, blends and composites. However, there was little correlation evident between DMA results and overall tear energy or observed length of tearing in the tubes, which are major differentiators between standard and peelable tubing formulations. It can be concluded that while DMA may well be a good predictor of polymer behavior up to the failure point, it is inadequate for predicting what occurs beyond the failure point when tear propagation along the length of the tube becomes important for peelable formulations. Tearing tests are required to further characterize the peelable heat shrink tubes in such instances.

REFERENCES

1. https://www.zeusinc.com/products/heat-shrinkable-tubing/, 2020.
2. J.R. Campanelli, C. Hunter, "A DMA Study of Heat-Shrinkable, Peelable Fluoropolymer Tubing, Part I"
3. T. Xie, "Recent Advances in Polymer Shape Memory", *Polymer*, **52**, 4985-5000, 2011.
4. P.R.R. Maddala, "Investigation of Polymer Packaging Films Behavior Subjected to Tension and Tearing", Master's Thesis, Blekinge Institute of Technology, Karlskrona, Sweden, 48-54, 2017.
5. E. Andreasson, N. Mehmood, S. Kao-Walter, "Trouser Tear Tests of Two Thin Polymer Films", 13th International Conference on Fracture, Beijing, China, 2013.
6. R. Artiaga, A. Garcia, "Fundamentals of DMA" in 'Thermal analysis. Fundamentals and applications to material characterization' (ed.: Artiaga R.) Publicationes de la Universidade da Coruna, A Coruña, Spain, 183–206, 2005.
7. S. Araby, Q. Meng, L. Zhang, H. Kang, P. Majewski, Y. Tang, J. Ma, *Polymer*, **55**, 201-210, 2014.