A DMA Study of Heat-Shrinkable, Peelable Fluoropolymer Tubing, Part I: An Analysis of the Existing Art

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ABSTRACT

A study of commercial peelable heat shrink tubing has been carried out using DMA techniques currently reported in the literature. The methods for evaluating the performance of peelable heat shrink were found to have either limited applicability or feature significant drawbacks as to their general applicability to the specific end use of catheter manufacturing. A more practical approach is needed to assess the peelable heat shrink tube at conditions as close as possible to the end use of the product.

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 this 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 process, the tube is typically scored at one of its ends and peeled away.

BACKGROUND

Peelability in fluoropolymer heat shrink tubing is achieved by blending 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. The interplay of these requirements is quite complex and relies on mechanisms that are poorly understood. A number of simple criteria have been proposed in the literature to date, but an overall fundamental process model is lacking.

Suzuki *et al.* [2] propose criteria based on a change in loss energy between 175° and 185°C, as well as a maximum storage modulus at 50°C as measured by dynamic mechanical analysis (DMA). Their technique has the advantage of being simple, but is

beset by a number of potential issues. First of all, the samples used to calculate the loss energy are plaques molded from heat-shrink tubes and not the tubes themselves.

The added heat history invariably results in test specimens having different molecular orientation and crystallinity thereby yielding dynamic mechanical properties that differ significantly from those of the original tube. Secondly, the two temperatures chosen for the calculation of the loss energy difference are arbitrary. They are lower than temperatures used to reflow PEBA copolymers onto a braided shaft, which typically exceed 200°C. Thirdly, the sinusoidal frequency chosen for the test, 0.033 Hz, is very low. Modern laminators can achieve reflow of the jacketing layer within seconds [3], so this frequency condition is not representative of the typical end use application.

Suzuki *et al.* [4] further propose a method based on determining the thickness of a "polymer entanglement unit" in the recovered tube which the authors correlate to an arbitrary measure of "tear straightness". This method has the advantage of testing the actual tube after recovery at 200°C, thus avoiding one of the flaws in their other work [2]. However, molecular entanglement of polymer chains is closely related to the loss and storage moduli of polymers [5], and is therefore a more complicated way of obtaining information that is readily measured by DMA. The authors, however, do not attempt to correlate "tear straightness" to any DMA-obtained parameters such as E', E" or tan δ.

Kikuchi *et al*. [6] propose a method of relating tear properties of a fluoropolymer heat-shrink tube containing virgin PTFE particles by evaluating the degree of fiberization of the particles using X-ray diffraction. These authors found a good correlation among tear strength, heat shrinkage rate and peel force with degree of fiberization. But these results are limited to the specific system discussed.

In this paper, we aim to examine in detail the method disclosed in Reference [2] for characterizing heat shrink performance since this method is claimed to be generally applicable for catheter manufacturing.

THEORETICAL

The correlation between dissipative energy measurements, such as E" or tan δ, and the tear properties of polymers has long been known [7]. Suzuki *et al.* [2] relate the change in dissipative or "loss" energy over a 10°C temperature range to the "tearability and heat shrinkability" of a fluoropolymer composite tube. In their analysis, loss energy is determined from DMA data by calculating the area of the hysteresis loop generated at each end of the temperature range at a specific oscillatory frequency for a specific sample geometry. When the difference in the values of loss energy at 175°C and 185°C is greater than 0.05 µJ, the tube performance is deemed to be good. The detailed procedure for obtaining a hysteresis loop under cyclic deformation of a sample has been described elsewhere [8, 9]. The loss energy can also be calculated from a DMA temperature sweep as described below.

In a typical DMA test procedure, force and displacement for an imposed amplitude and frequency are measured with respect to a temperature ramp [10, 11]. The measured force, F, and displacement, L, is used to calculate the complex stiffness, K*, which can be resolved into elastic and viscous components.

$$(K^*)^2 = (K')^2 + (K'')^2 \quad (1)$$

$$\tan \delta = K''/K' = F''/F' \quad (2)$$

So that, by substitution,

$$F'' = F \Big/ \sqrt{(1 + 1/\tan \delta^2)} \quad (3)$$

where: K' and K" are the storage and loss stiffnesses, respectively, before any geometry factors have been applied, F' and F" are the corresponding storage and loss components of the axial force, and δ is the phase angle.

The storage and loss energies can be calculated as functions of temperature by multiplying the appropriate component of F, i.e. F' or F", by the measured displacement at each temperature. It should be noted that in this approach the sample geometry must be kept constant for all tests so that energies can be compared.

EXPERIMENTAL

In order to maintain a constant sample geometry, Suzuki *et al.* [2] conducted their testing on melt pressed plaques, not the actual heat-shrink tubes. A Carver Press set to 310°C was used to mold the sample tubes into plaques by leaving the sample under minimal pressure (<100 psi) for 2 minutes and then increasing the pressure to 500 psi and holding for a duration of 1 minute. The resulting plaque was then immediately removed from pressure and quenched in an ice water bath. Replicates from the pressed plaques were obtained by using a 5 x 50 mm rectangular die.

DMA temperature sweeps were carried out using tension clamps and the tests were conducted by imposing a negative preload force as described by Suzuki *et al.* [2]. Experiments were performed at frequencies of 0.1 Hz, 1Hz, and 10 Hz with amplitudes of 5 µm, 15 µm, and 25 µm with each individual experiment being conducted at a singular frequency and amplitude from -100°C to 230°C at a ramp of 5° C/min. The axial force, F, and tan δ were then used to calculate F'' using Equation (3). With F'' and the corresponding change in sample length, or ΔL, the loss energy at any temperature could be determined.

The plaques used in this study were pressed from the three commercial heat shrink tubes described in Table 1. Note that although these tubes have very different recovery ratios,

the combined effects of extrusion and expansion on the polymer morphology are erased during the molding of plaques.

Table 1. Sample Plaques Tested

Commercial Designation	Description of the Tube
HS1: Heat Shrink A	Exp. ID: 0.082”; Rec. ID: 0.051”; Rec. Ratio: 1.6:1
HS2: Heat Shrink B	Exp. ID: 0.163”; Rec. ID: 0.116”; Rec. Ratio: 1.4:1
HS3: FluoroPEELZ™	Exp. ID: 0.150”; Rec. ID: 0.075”; Rec. Ratio: 2:1

RESULTS

Figure 1 shows a typical graph obtained from a DMA temperature ramp. In this case, the specimen plaque was made from HS1 and tested at a frequency of 1 Hz with an amplitude of 15 µm.

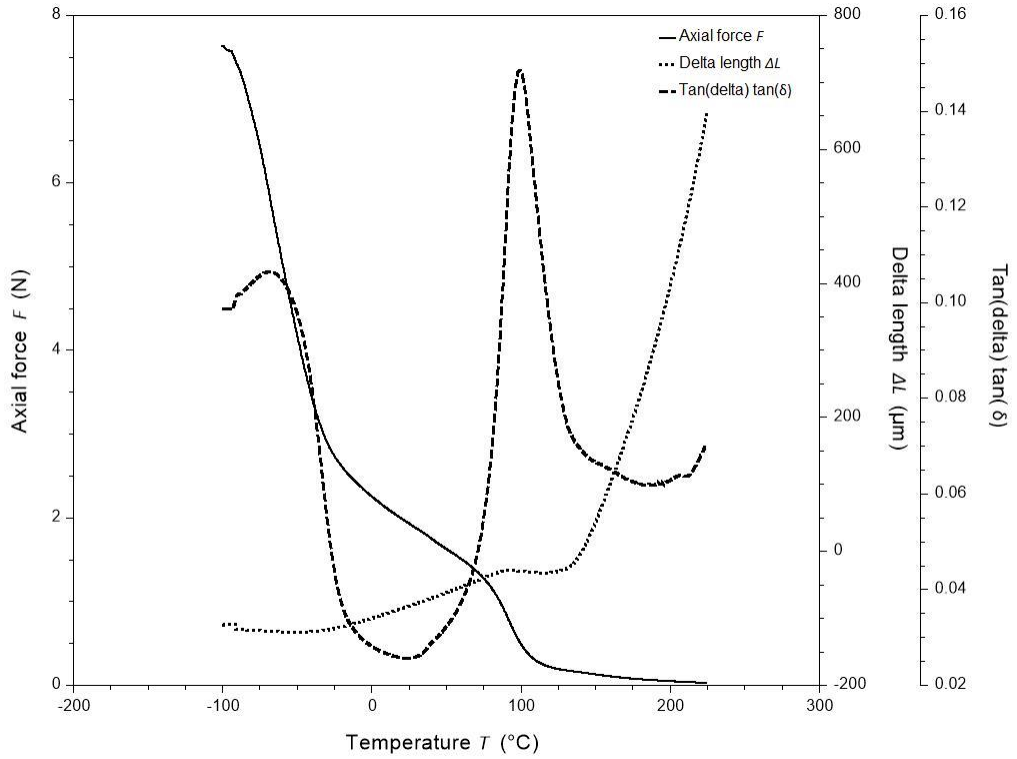

Figure 1: Temperature Ramp @ 1Hz Frequency and 15 µm Amplitude for HS1

Tan δ values for various temperatures, amplitudes and frequencies for plaques made from HS1, HS2 and HS3 are summarized in Table 2, Table 3, and Table 4, respectively.

Table 2. Summary of Tan δ for HS1

Frequency (Hz)	Amplitude (µm)	20°C	30°C	175°C	185°C	210°C	220°C
0.1	5	0.0362	0.0378	0.0972	0.1060	0.0964	0.0659
0.1	15	0.0610	0.0577	0.0849	0.0942	0.1084	0.1038
0.1	25	0.0390	0.0369	0.0900	0.0902	0.1008	0.0970
1.0	5	0.0275	0.0270	0.0547	0.0534	0.0527	0.0639
1.0	15	0.0257	0.0260	0.0625	0.0615	0.0650	0.0669
1.0	25	0.0453	0.0447	0.0534	0.0515	0.0517	0.0539
10.0	5	0.0298	0.0283	0.0372	0.0345	0.0290	0.0243
10.0	15	0.0313	0.0310	0.0391	0.0364	0.0318	0.0308
10.0	25	0.0451	0.0446	0.0384	0.0352	0.0305	0.0293

Table 3. Summary of Tan δ for HS2

Frequency (Hz)	Amplitude (µm)	20°C	30°C	175°C	185°C	210°C	220°C
0.1	5	0.0359	0.0372	0.1002	0.1005	0.0771	0.0581
0.1	15	0.0442	0.0442	0.0892	0.0898	0.0824	0.0744
0.1	25	0.0545	0.0551	0.0667	0.0793	0.0936	0.0939
1.0	5	0.0264	0.0263	0.0504	0.0490	0.0505	0.0524
1.0	15	0.0371	0.0361	0.0491	0.0475	0.0473	0.0488
1.0	25	0.0404	0.0389	0.0487	0.0473	0.0492	0.0473
10.0	5	0.0364	0.0340	0.0367	0.0340	0.0303	0.0309
10.0	15	0.0413	0.0390	0.0373	0.0354	0.0317	0.0315
10.0	25	0.0660	0.0652	0.0369	0.0343	0.0306	0.0303

Table 4. Summary of Tan δ for HS3

Frequency (Hz)	Amplitude (µm)	20°C	30°C	175°C	185°C	210°C	220°C
0.1	5	0.0501	0.0528	0.0934	0.1147	0.1354	0.1031
0.1	15	0.0418	0.0416	0.0867	0.0884	0.0764	0.0879
0.1	25	0.0483	0.0467	0.0922	0.0922	0.0820	0.0780
1.0	5	0.0264	0.0266	0.0502	0.0505	0.0562	0.0667
1.0	15	0.0328	0.0327	0.0499	0.0491	0.0564	0.0570
1.0	25	0.0458	0.0457	0.0523	0.0513	0.0531	0.0568
10.0	5	0.0271	0.0266	0.0360	0.0351	0.0346	0.0416
10.0	15	0.0302	0.0279	0.0374	0.0354	0.0328	0.0335
10.0	25	0.0376	0.0376	0.0394	0.0362	0.0313	0.0319

ΔE_{Loss} was calculated between 175°C and 185°C and is shown for HS1, HS2 and HS3 plaques in Figure 2, Figure 3, and Figure 4, respectively.

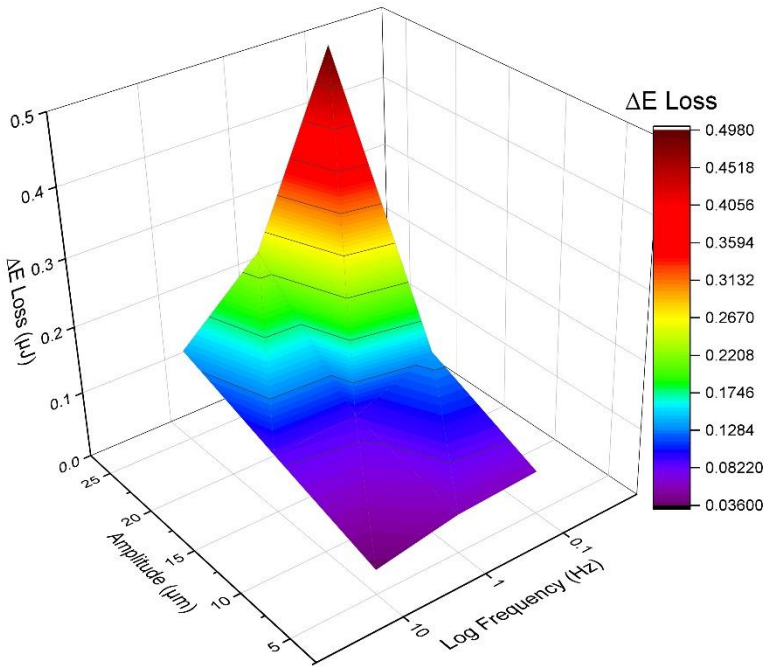

Figure 2: ΔE_{Loss} (175°C - 185°C) vs Amplitude and Frequency for HS1

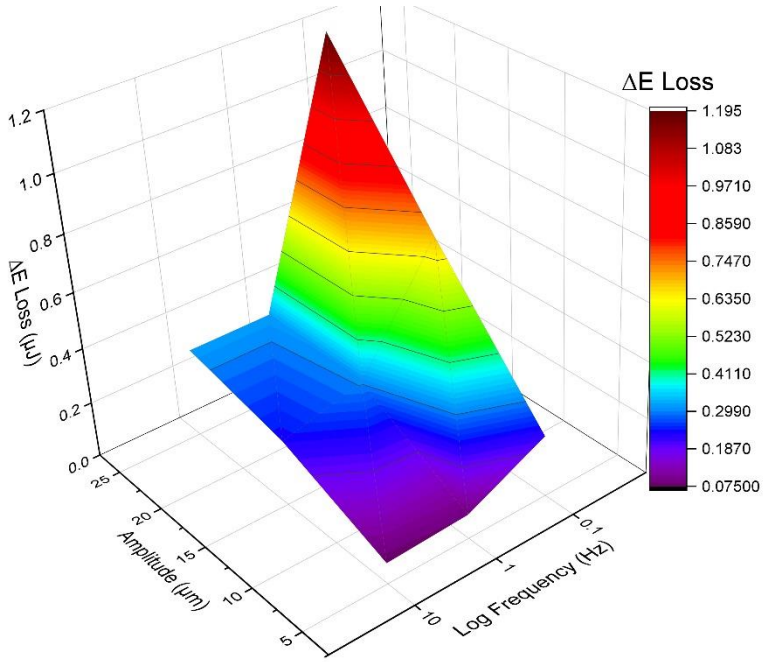

Figure 3: ΔE_{Loss} (175°C - 185°C) vs Amplitude and Frequency for HS2

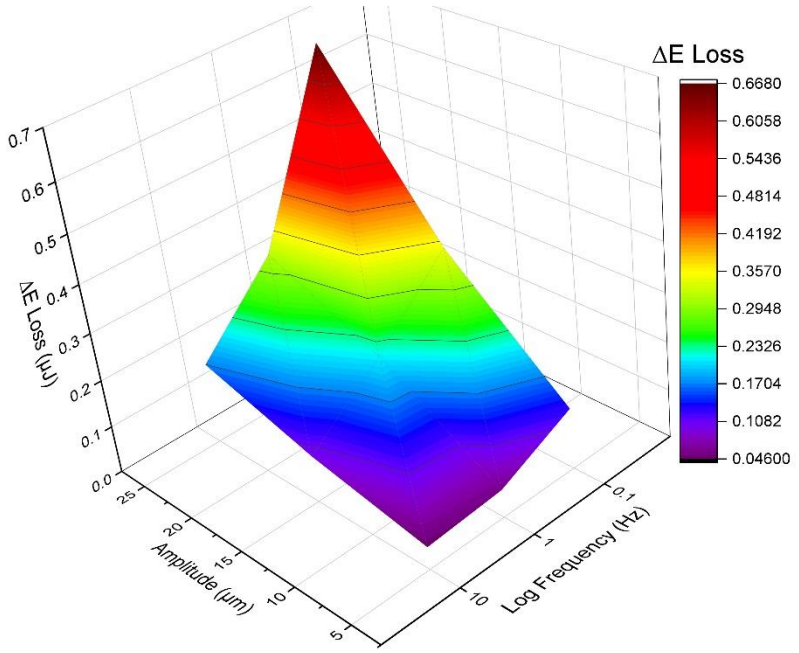

Figure 4: ΔE_{Loss} (175°C - 185°C) vs Amplitude and Frequency for HS3

The effect of different temperature intervals on ΔE_{Loss} is shown in Figure 5 (20°C to 30°C) and Figure 6 (210°C to 220°C) for HS3.

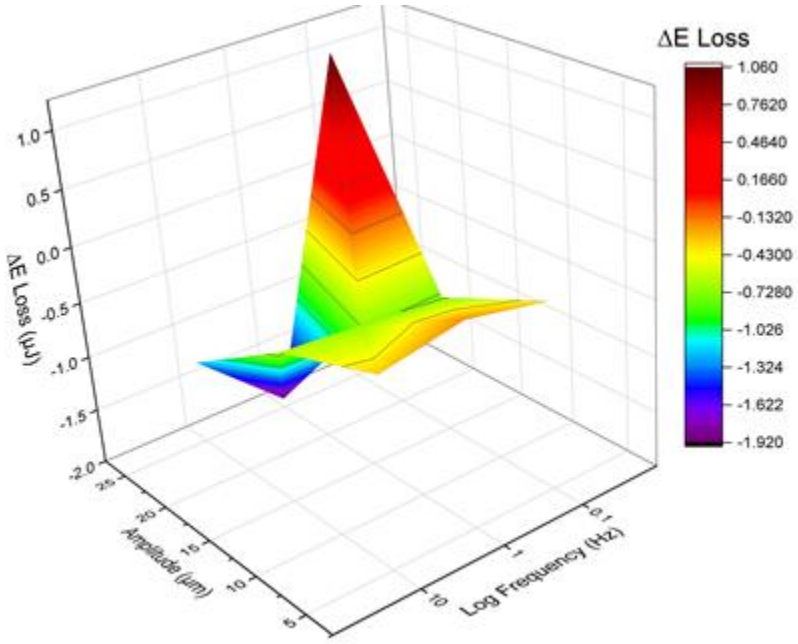

Figure 5: ΔE_{Loss} (20°C - 30°C) vs Amplitude and Frequency for HS3

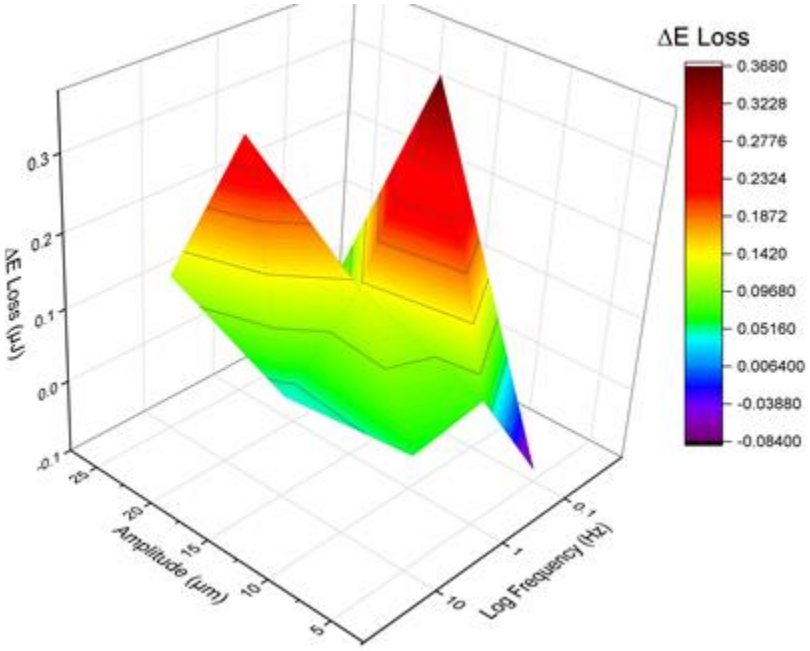

Figure 6: ΔE_{Loss} (210°C - 220°C) vs Amplitude and Frequency for HS3

DISCUSSION

It has long been known that DMA test frequency affects tan δ for semicrystalline polymers, and that test amplitude affects tan δ for polymer composites [12]. In fact, Tables 1, 2, 3 show that tan δ varies considerably with frequency, amplitude and temperature for all three specimens in this study. This is especially true when one considers temperatures typically associated with reflow processes in catheter manufacturing (above 200°C) or heat shrink removal processes by tearing the tube (around room temperature). Hence the selection of the appropriate test conditions can be expected to have a significant impact on the loss energy, which is strongly related to tan δ.

Suzuki *et al.* [2] claim that the value of loss energy for plaques over a ten degree temperature differential can predict heat shrink tube performance during catheter manufacturing. In their method, loss energies are calculated at low frequency and amplitude. If one considers the effects of frequency and amplitude over a range of conditions that are more typical of the application, the drawbacks of this approach become apparent.

Heat shrink tubing can recover as much as 40% or more during the reflow step of the catheter manufacturing process. The recovery rates would also be much greater than the 0.033 Hz specified in Reference [2]. Modern laminators can operate at frequencies of 1 Hz or higher. In the removal step, similarly high rates of deformation would be expected during tearing of the heat shrink tube. Figures 2, 3 and 4 show that the effect of frequency and amplitude on ΔE_{Loss} over more reasonable ranges of amplitude and

frequency can cause large variations in that quantity for test plaques pressed from three commercial heat shrink tubes. Low frequency and low amplitude deformations are clearly not representative of the loss energy differential over a range consistent with the intended application of the heat shrink tube.

It has been noted previously that the interval selected by Suzuki *et al.* for evaluating ΔE_{Loss}, namely 175°C to 185°C, is somewhat arbitrary. Typically, reflow is conducted at temperatures above 200°C, while removal of the shrink tube is performed around room temperature. In order to examine the predicted performance of the tubes at more realistic temperature intervals, ΔE_{Loss} was calculated over the ranges 20 – 30°C (corresponding to removal conditions) and 210 – 220 °C (corresponding to reflow conditions). Figures 5 and 6 show the difficulties encountered in using this same approach over these more reasonable temperature intervals. In Figure 5, the change in ΔE_{Loss} is negative over much of the response surface, which would indicate poor heat shrink performance according to the criterion of Suzuki *et al.* that ΔE_{Loss} should be greater than 0.05 µJ. Similarly, there are regions of Figure 6 that are also negative in ΔE_{Loss}. Both Figure 5 and Figure 6 depict highly complex response surfaces which make it difficult to draw any general conclusions as to the utility of the quantity ΔE_{Loss} in these experimental spaces. It is therefore not surprising that the authors selected the non-representative temperature range of 175°C to 185°C where, notwithstanding its lack of significance to the catheter manufacturing process, the surfaces are at least smoother.

CONCLUSIONS

Many of the methods currently available in the literature to characterize the performance of peelable heat shrink tubing have either limited applicability or feature significant drawbacks as to their general applicability. The method of Suzuki *et al.* [2] was examined in detail, and is seen to fall into the latter category. In this method, the heat shrink tubes are molded into plaques prior to testing their dynamic mechanical response. The molding process provides a secondary heat history which eliminates the initial processing (extrusion) and secondary processing (expansion) history of the original tube, thereby altering polymer blend characteristics such as crystallinity and morphology. Moreover, the molded sample is then tested under conditions of amplitude, frequency and temperature that do not correspond to end use conditions. The quantity measured in these tests, ΔE_{Loss}, has been shown to vary considerably over the space of interest to catheter manufacturing.

Current methods of evaluating the performance of peelable heat shrink tubing lack applicability to the specific end use of catheter manufacturing. A more practical approach would be to assess the tube itself at conditions as close as possible to the end use of the product. Future studies will focus on the behavior of the tube in the heat shrink application.

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