

## Thermal characterization of shape memory polymer blends for biomedical implantations <sup>☆</sup>

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### Abstract

Two solution-based shape memory polymers (SMPs) were investigated that undergo 50-fold changes in their elastic moduli as these polyurethanes are heated above their respective glass transition temperatures ( $T_g$ ) of 25 and 55°C. Because biomedical implantations require transformation temperatures that are nominally 37°C, such polymer solutions must be blended to achieve the correct  $T_g$ . After the temperature of solvent evaporation and the quantity of solvent present were measured by thermogravimetric analysis (TGA), a drop of each as-received solution and five blends were isothermally heated to +150°C for 5 min using differential scanning calorimetry (DSC). Thereafter, the mean  $T_g$ s were determined at the start, midpoint, and finish of the transition following two successive runs. Values of the complex modulus ( $E^*$ ) and loss tangent ( $\tan \delta$ ) were measured for each blend at 1.1, 11, and 110 Hz from –20 to +100°C by dynamic mechanical analysis (DMA). From the results we conclude that these SMPs do not deliver a reliable  $T_g$  in the temperature range of interest, a narrow temperature transformation, or an extended range of  $E^*$  values. Consequently, these SMPs do not support our present biomedical implantations that require “elasticity memory”.

*Keywords:* DMA; DSC; Polymer; PU; Shape memory; TGA

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### 1. Introduction

Since the first heat shrinkable tubing of polyethylene and thermoelastic alloy of nickel–titanium were introduced [1,2], many types of intelligent material systems

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and structures have been developed. Shape memory polymers (SMPs) are just one subcategory of smart materials, which have been engineered to operate from  $-30$  to  $+90^{\circ}\text{C}$ . The main design feature of SMPs is “elasticity memory” [3], that is, the capability of reversibly changing elastic modulus over orders of magnitude within a few degrees of the glass transition temperature ( $T_g$ ). Only about ten years ago, the first SMP was introduced based on polynorborene that had a  $T_g$  of  $35\text{--}40^{\circ}\text{C}$ . *trans*-Isopolyprylene and styrene–butadiene-based SMPs followed. In 1988, the fourth Japanese SMP was introduced that was based on polyurethanes with either ether or ester linkages, which were available in standard forms having  $T_g$ s that today can be varied  $\pm 50^{\circ}\text{C}$  from room temperature ( $21^{\circ}\text{C}$ ) [4]. These were processable by conventional means (injection, extrusion, and blow molding), could be colored, and were biocompatible. In this last case, these SMPs have been designed as medical devices for orthopedic braces, splints, and catheters [5].

Other than the manufacturers’ efforts, little has been reported by independent laboratories regarding the properties of SMPs. Recently, however, an injection molded SMP was studied in tension both  $20^{\circ}\text{C}$  below its  $T_g$  and  $10^{\circ}\text{C}$  above its  $T_g$  of  $45^{\circ}\text{C}$  [6,7]. As the  $T_g$  was transversed, Young’s modulus decreased two orders of magnitude above the  $T_g$ , and the strength decreased by 87.5%. Using an injection molded SMP and a solution of SMPs, composites were made with woven fiberglass (WFC) and chopped fiberglass (CFC), respectively. Below  $T_g$ , the WFCs were 20% stronger than the CFCs, and 37% greater than the unreinforced SMPs. In the same region, the modulus followed similar trends; that is, the WFCs were 45% stiffer than the CFCs and 75% greater than the unreinforced SMPs.

Recently, two SMPs have been offered in solution that reportedly undergo dramatic changes in elasticity memory as the materials are heated above their respective  $T_g$ s. Since biomedical devices often require that  $T_g = 37^{\circ}\text{C}$ , these solutions must be blended to achieve the correct  $T_g$ . By thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA), the thermal characteristics of SMP blends were obtained and assessed for use in biomedical implantations.

## 2. Experimental

### 2.1. Materials

Two polyurethanes were obtained from Mitsubishi Heavy Industries, through Memry Technologies: MS-2510 and MS-5510. The product literature indicates that these are ester-based polymers (MS-XX10) dissolved in *N,N*-dimethylformamide (DMF) having high elasticity in the rubbery range and nominal  $T_g$ s of  $25^{\circ}\text{C}$  (MS-25XX) and  $55^{\circ}\text{C}$  (MS-55XX) [8]. Although the details of the composition are proprietary, the Material Safety Data Sheet [9] states that the hard segments are comprised of 4,4'-diphenylmethanediisocyanate (MDI), and a Mitsubishi Technical Bulletin [3] infers that the soft segments and chain extenders may be comprised of low molecular weight polypropylene glycol (PPG: P-400) and bis(2-hydroxy-

ethyl)hydroquinone (Quiamine H). More generally the  $T_g$  is increased from subambient temperatures to the present regime by increasing the number of benzene rings in the diisocyanate molecule, decreasing the molecular weight of the polyol, and increasing the molar ratio of chain extender to diisocyanate. In addition to these as-received materials, blends were prepared having the following MS-2510/MS-5510 ratios: 3/1, 2/1, 1/1, 1/2, and 1/3.

## 2.2. Methods

To verify the solvent content of the solutions, the weight losses of the as-received samples (20 mg) were measured in air at a heating rate of  $10^\circ\text{C min}^{-1}$  from  $+20$  to  $+700^\circ\text{C}$  by TGA (TA Instruments). Based on the first plateau region of these spectra, the isothermal temperature required for solvent evaporation was adduced for all blends.

Using DSC (TA Instruments), one drop of each rather intractable solution (viscosity at  $25^\circ\text{C}$  was 80 000–120 000 cP [8]) was placed in an open DSC pan and ramped to this isothermal temperature under a blanket of  $\text{N}_2(\text{g})$  at a flow rate of  $100 \text{ ml min}^{-1}$  (Fig. 1). At the end of the perceived evaporation process (about 10 min), the time base plot was extended an additional 5 min prior to quenching the sample in  $\text{N}_2(\text{l})$ . Hereafter, each blend was heated two times at  $10^\circ\text{C min}^{-1}$  from  $-20$  to  $+80^\circ\text{C}$  under  $\text{N}_2(\text{g})$  and then quenched with  $\text{N}_2(\text{l})$ . The  $T_g$ s from these runs were determined at the “start” (S) and “finish” (F) by intersecting the extrapolated baselines with the tangent at the transition, and the respective mean values were obtained for the two final runs of each sample. In addition, the “midpoint” (M) was determined from the arithmetic average of all start and finish values for a given composition.

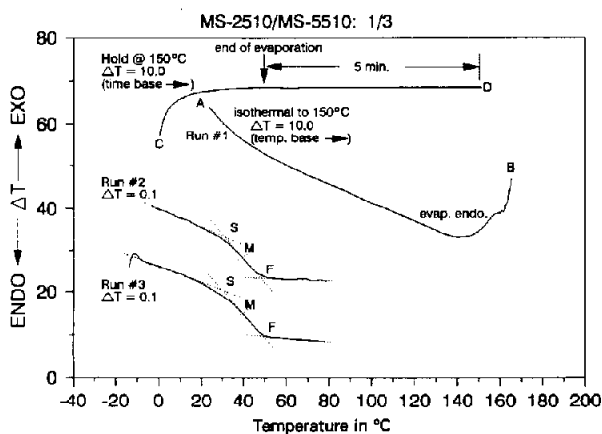


Fig. 1. DSC scan of a MS-2510/MS-5510 (1/3) blend. In the first run (A to B to C to D), the solvent was evaporated from the solution sample and then quenched in  $\text{N}_2(\text{l})$ . In runs # 2 and # 3, S, M, and F refer to the “start”, “midpoint”, and “finish”  $T_g$  values (see text).

For DMA ( $I$ -mass) measurements, large sheets ( $l \times w \times t = 8 \text{ cm} \times 6 \text{ cm} \times 0.02 \text{ cm}$ ) were processed from each solution blend by applying the solution to a low tack surface and evaporating the DMF in air at  $70^\circ\text{C}$  for 3 h and at  $110^\circ\text{C}$  for 15 h. After cooling, the sheets were annealed at  $150^\circ\text{C}$  for 1 h under a vacuum to insure the removal of all DMF and naturally cooled in the oven to room temperature ( $21^\circ\text{C}$ ). Three to seven samples, each nominally  $6.00 \text{ cm} \times 0.25 \text{ cm} \times 0.020 \text{ cm}$  ( $l \times w \times t$ ), were mounted in tension (18 g) and scanned at three frequencies (1.1, 11, and 110 Hz) from  $-20$  to  $+100^\circ\text{C}$  at a heating rate of about  $2^\circ\text{C min}^{-1}$  in air. From the loss tangent ( $\tan \delta$ ) and complex modulus ( $E^*$ ) data, the following information was adduced at 1.1 Hz: (1) the  $T_g$  value at the  $\alpha$  peak; (2) the magnitude of  $\tan \delta$  at  $T_g$ ; (3) the corresponding  $E^*$  at  $T_g$ ; (4) the  $E_{\text{min}}^*$  at ( $T_g + 30^\circ\text{C}$ ); and (5)  $E_{\text{max}}^*$  at ( $T_g - 30^\circ\text{C}$ ).

### 3. Results

TGA scans showed that 68.7 and 69.8 w/w% of the as-received MS-2510 and MS-5510 solutions, respectively, were DMF and that the residual mass remained rather invariant over a temperature range from  $+150$  to  $+300^\circ\text{C}$ . Thereafter, there was nearly a linear loss of mass until nothing remained by  $+700^\circ\text{C}$  (Fig. 2). From these scans the isothermal temperature of  $+150^\circ\text{C}$  was selected for succeeding DSC runs and for the annealing temperature for DMA samples.

From DSC scans such as those for MS-2510/MS-5510 at a ratio of 1/3 (Fig. 1), values of the start and finish  $T_g$ s after two successive DSC runs suggested a linear increase ( $p < 0.001$ ) with changing composition (Fig. 3). Midpoint values (the triangles) for the as-received MS-2510 and MS-5510 equaled  $22.8$  versus  $25 \pm 1^\circ\text{C}$  and  $50.8$  versus  $55 \pm 1^\circ\text{C}$ , respectively. Differences between start and finish  $T_g$  data at a given composition ranged from a high of  $+24^\circ\text{C}$  (MS-2510) to a low of  $+11^\circ\text{C}$  (MS-5510).

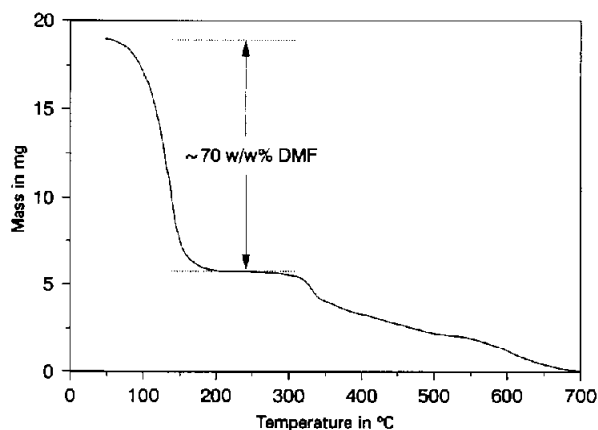


Fig. 2. TGA scan of MS-5510 (20 mg) that was tested in air at  $10^\circ\text{C min}^{-1}$  from  $+20$  to  $+700^\circ\text{C}$ .

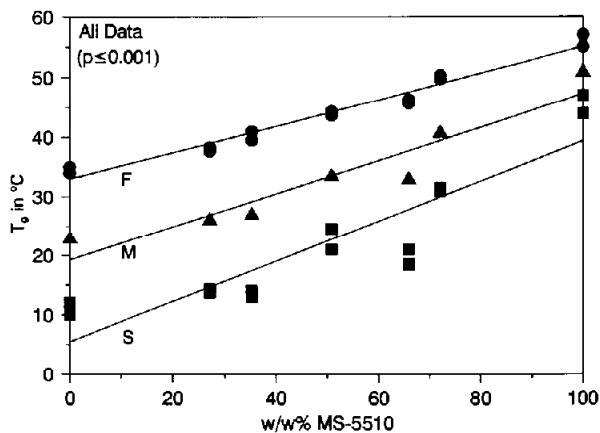


Fig. 3.  $T_g$  measurements of all data that were determined by DSC for blends of MS-2510 and MS-5510 (see Fig. 1 for connotations of S, M, and F).

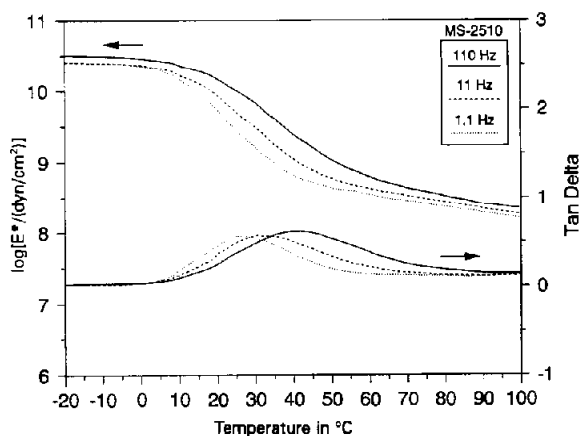


Fig. 4. DMA scan of MS-2510 at three frequencies.

DMA scans for the 32 samples varied most between MS-2510 (Fig. 4) and MS-5510 (Fig. 5) for the  $E^*$  and  $\tan \delta$  properties. Given identical axes several characteristics of both as-received materials displayed onset, endpoint, and peak values that were similar in magnitude, however. The most notable changes were associated with a shift in temperature as the product or the frequency was changed. The latter was typical of the  $7^\circ\text{C}$  increase reported for every decade increase in frequency [10].

When  $T_g$ s were determined from the  $\alpha$  peak of DMA runs at 1.1 Hz (Table 1), values of MS-2510 equaled  $23.9 \pm 3.0^\circ\text{C}$  for eleven samples with corresponding  $\tan \delta$  and  $E^*$  values of  $0.492 \pm 0.048$  and  $2.45 \pm 0.38 \text{ Gdyn cm}^{-2}$ , respectively. The

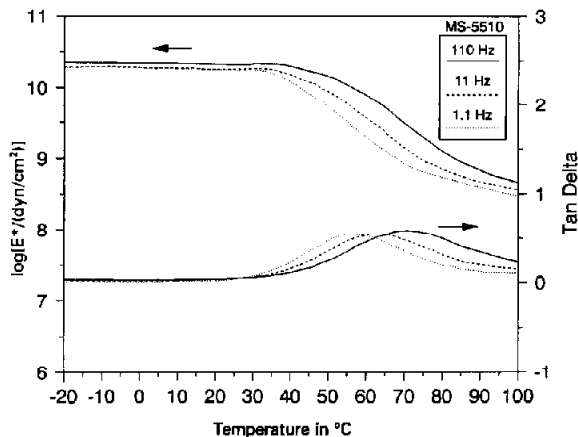


Fig. 5. DMA scan of MS-5510 at three frequencies.

$E_{\min}^*$  and  $E_{\max}^*$  values at  $(T_g \pm 30^\circ\text{C})$  equaled  $0.361 \pm 0.088$  and  $20.5 \pm 1.8$  Gdyn  $\text{cm}^{-2}$ . When the other as-received material was evaluated, the  $T_g$  equaled  $55.1 \pm 1.3^\circ\text{C}$  for three samples with corresponding  $\tan \delta$  and  $E^*$  values of  $0.534 \pm 0.016$  and  $2.90 \pm 0.40$  Gdyn  $\text{cm}^{-2}$ . The  $E_{\min}^*$  and  $E_{\max}^*$  equaled  $0.429 \pm 0.047$  and  $14.0 \pm 2.8$  Gdyn  $\text{cm}^{-2}$ . Overall, the DMA measurements followed a linear relationship ( $p < 0.001$ ; Fig. 6, solid line).

#### 4. Discussion

The TGA measurements confirmed that the solvent composition of both as-received polymers equaled the manufacturer's claim of 70 w/w% (Fig. 2). This was quite important, since a tacit assumption was made that weights of as-received polymers could be readily used to calculate the intermediate compositions, if the solvent compositions were equivalent. In contrast, neither the  $T_g$  values nor the  $E^*$  values were consistent with our expectations.

As Fig. 3 shows, the  $T_g$ s did not occur over a narrow temperature range of  $6^\circ\text{C}$  [5] even though the present DSC samples were heated at  $10^\circ\text{C min}^{-1}$  versus the manufacturer's value of  $20^\circ\text{C min}^{-1}$  [3]. Moreover the  $T_g$  values that were measured by DMA were only comparable with the DSC results when the finish  $T_g$  values were selected as the basis for the comparison (see Fig. 6). This shift from the midpoint is consistent with a  $5\text{--}15^\circ\text{C}$  difference proposed for  $T_g$  values determined by either dilatometry or differential thermal analysis versus those determined from  $\tan \delta$  peaks at 1.0 Hz [10]. A deviation from linearity appears, when the MS-2510/MS-5510 ratio was more than 3/1 (i.e.  $< 25$  w/w% MS-5510). From the viewpoint of designing biomedical implants, this outcome is a point of contention because the composition required to achieve a  $T_g = 37^\circ\text{C}$  occurs in this vicinity.

Table 1  
Dynamic mechanical properties of SMP blends at 1.1 Hz<sup>a</sup>

MS-2510/ MS-5510 ratio	$T_g$ at $\alpha$ peak in °C	$\tan \delta$ at $T_g$	$E^*$ at $T_g$ in Gdyn cm <sup>-2</sup>	$E_{\min}^*$ at ( $T_g + 30^\circ\text{C}$ ) in Gdyn cm <sup>-2</sup>	$E_{\max}^*$ at ( $T_g - 30^\circ\text{C}$ ) in Gdyn cm <sup>-2</sup>
1/0	19.5	0.426	3.27	0.440	19.4
	21.0	0.490	2.56	0.368	18.2
	21.1	0.481	2.84	0.432	21.3
	22.7	0.480	2.03	– <sup>b</sup>	19.1
	27.3	0.495	2.15	0.143	19.3
	22.8	0.456	2.23	0.396	21.4
	23.1	0.450	2.15	0.405	18.3
	28.1	0.560	2.53	0.361	22.9
	28.2	0.569	2.38	0.349	21.5
	24.8	0.548	2.68	0.384	23.5
23.8	0.457	2.10	– <sup>b</sup>	20.8	
3/1	33.8	0.611	1.91	0.275	19.9
	36.8	0.553	1.98	0.266	11.7
	37.0	0.901	1.36	– <sup>b</sup>	18.9
	35.3	0.502	1.36	– <sup>b</sup>	15.4
	37.6	0.549	1.79	0.271	15.0
2/1	38.0	0.576	1.46	0.298	20.3
	38.8	0.623	1.25	0.308	12.9
	35.7	0.595	1.65	0.261	17.1
1/1	38.8	0.441	1.72	0.363	15.0
	40.8	0.416	1.59	0.370	12.3
	42.8	0.457	1.41	0.237	16.5
1/2	46.6	0.551	1.39	– <sup>b</sup>	11.6
	46.9	0.523	2.08	0.344	11.4
	47.2	0.488	1.76	0.382	17.0
	45.0	0.541	1.98	0.373	18.7
1/3	48.7	0.674	1.75	0.279	12.1
	52.3	0.657	1.56	0.246	13.1
	49.4	0.486	2.04	0.354	11.6
0/1	54.2	0.537	3.31	0.457	17.1
	56.5	0.516	2.51	0.375	16.2
	54.5	0.548	2.88	0.456	11.6

<sup>a</sup> Samples nominally 6.00 cm × 0.25 cm × 0.02 cm ( $l \times w \times t$ ) were mounted in tension (18 g) and scanned at about 2°C min<sup>-1</sup> for three frequencies (1.1, 11, and 110 Hz). <sup>b</sup> Data was not available, because the scan was terminated prior to ( $T_g + 30^\circ\text{C}$ ).

With one exception, the  $\tan \delta$  values were consistently independent of composition (Table 1, column 2 and Fig. 7) and averaged 0.536. This value was comparable to the  $\tan \delta = 0.5$  reported by Liang et al. in their review article [7]. By contrast, the  $E^*$  values at  $T_g$ ,  $E_{\min}^*$  values at ( $T_g + 30^\circ\text{C}$ ) and  $E_{\max}^*$  values at ( $T_g - 30^\circ\text{C}$ ) differed considerably in magnitude and functionality (Table 1, columns 4–6). The mean

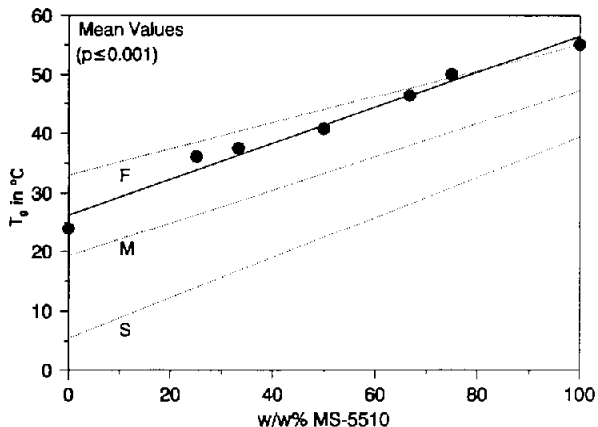


Fig. 6. Mean values of  $T_g$  measurements that were determined by DMA (data and solid line) superposed over the results from DSC (shown here as dotted lines from Fig. 3).

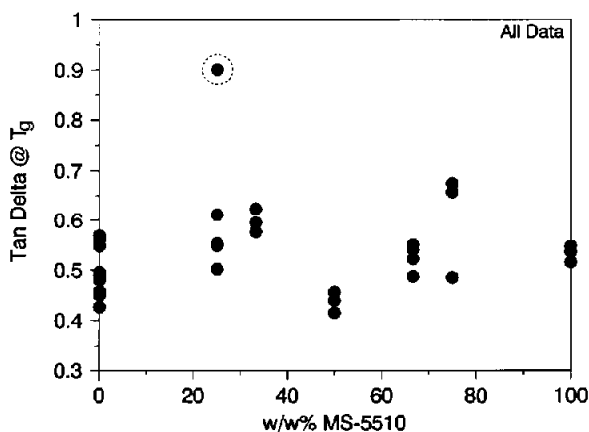


Fig. 7.  $\tan \delta$  values for all data as a function of composition. The circled datum point is an outlier.

values of  $E_{\max}^*$  at  $(T_g - 30^\circ\text{C})$  decreased monotonically with w/w% MS-5510 ( $p \leq 0.02$ ) from about 19.0 to 12.5 Gdyn  $\text{cm}^{-2}$  (Fig. 8). In contrast,  $E^*$  at  $T_g$  appeared parabolic (Fig. 9), the mean values at 100 w/w% MS-2510 and MS-5510 being nearly equivalent at 2.5 and 2.9 Gdyn  $\text{cm}^{-2}$ , respectively. Finally, at  $(T_g + 30^\circ\text{C})$  the  $E^*$  decreased some 50-fold as a consequence of the transition (cf. Fig. 10 versus Fig. 8) and appeared independent of composition within the range from 0.3 to 0.4 Gdyn  $\text{cm}^{-2}$ . This factor of 50 was less than the reported factors that ranged from 100 [3,5] to as much as 500 [7]. Our expectations that 1.1 Hz would represent the static measurements, such as those conducted on JIS dumb-bell No. 2 test pieces [3], was apparently inadequate. Even increasing the window of comparison from  $(T_g \pm 10^\circ\text{C})$  to  $(T_g \pm 30^\circ\text{C})$  proved ineffectual. From typical scans



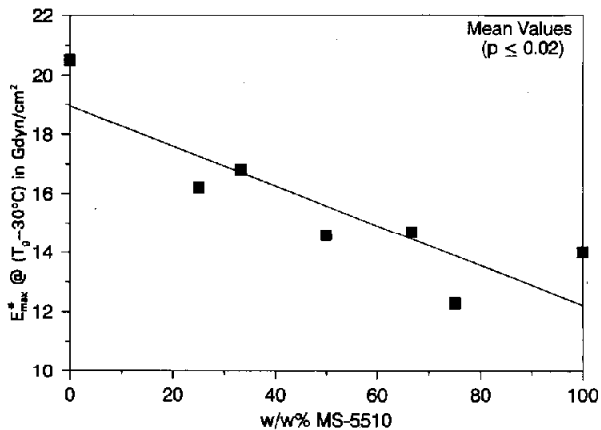


Fig. 8. Mean values of the maximum complex moduli  $E_{\max}^*$  at  $(T_g - 30^\circ\text{C})$  as a function of composition.

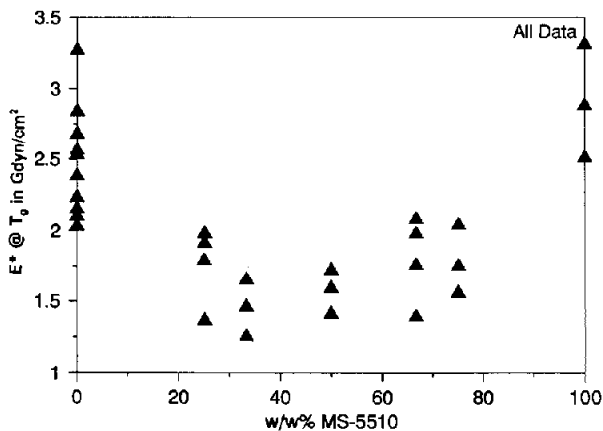


Fig. 9.  $E^*$  at  $T_g$  for all data as a function of composition.

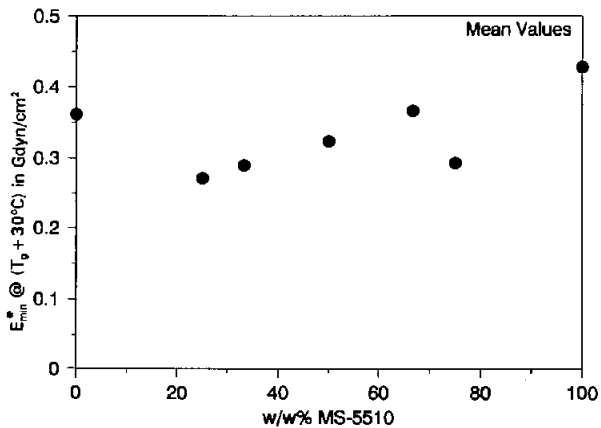


Fig. 10. Mean values of  $E_{\min}^*$  at  $(T_g + 30^\circ\text{C})$  as a function of composition.

such as Figs. 4 and 5, the transition clearly occurred over a temperature range of at least 50°C.

Although the discrepancy among the manufacturer's literature [3,4,5,8], the few independent studies, and the present work is apparent, the cause is less obvious. Gross differences in the character of the thermal scans suggest that the solution grades (MS-XXXX) are not comparable to the extrusion or injection molding grades (MM-XXXX), the later of which are exclusively quoted in the present literature. In other words, MS-2510 is not equivalent to MM-2510, despite the fact that both have  $T_g$ s equal to 25°C and are ester-based polymers having high elasticity in the rubbery region. For example, for MM-4500 [8], MM-4510 [4], MM-4520 [4], and MM-5520 [7] in the glassy state all moduli equal  $10^9$  Pa at ( $T_g - 10^\circ\text{C}$ ). At ( $T_g + 10^\circ\text{C}$ ), these moduli universally decrease to values that appear quite similar and range from  $10^6$  to  $10^7$  Pa. These changes are seemingly independent of the  $T_g$ s (45XX versus 55XX) and the ether-ester linkages or low-high elasticities in the rubbery regions (XX00 versus XX10 versus XX20) and suggest that the big differences are related to the form of the product.

Hayashi et al. [4] adopted an explanation for the high and low elastic moduli, respectively, as being "... due to energy elasticity of a crystal and a glass state noncrystal ..." at  $T < T_g$  and the "entropy elasticity based upon the micro-Brownian motion of a soft segment in the molecular chain ..." at  $T > T_g$ . Based upon the well-documented fundamental differences between crystalline and amorphous polymers [11], a hypothesis is advanced that the evaporation, annealing, and cooling processes, which are associated with solution polymers, permit the increased crystallization of segments at the expense of increased microphase separation. Relative to a more amorphous structure, this increase in crystallinity raises the moduli somewhat at  $T < T_g$  and by orders of magnitude at  $T > T_g$ , while broadening the region over which the  $T_g$  occurs. Moreover, if the crystalline regions in the otherwise more amorphous structure mimic a lightly crosslinked structure, the precipitous drop to the rubbery or viscous flow regions will be somewhat delayed, and a large rubbery plateau region will persist to higher temperatures. All of the past and present information suggests that the former may better represent the present MS-XXXX grade polymer, and the latter may better represent the MM-XXXX grade polymer. Consequently, the present hypothesis could serve as the basis for future experiments using not only the present thermal analysis methodologies but also specific spectroscopies (IR, Raman, and NMR), microscopies (electron and polarized light), scattering (SALS, SAXS, and WAXS), and mechanical tests (UTS and tensile stress hysteresis) [12,13].

## 5. Conclusions

Current blends based on MS-XX10 SMPs do not deliver a reliable  $T_g$  in the temperature range of interest, a narrow temperature transformation, or a range of values of  $E^*$  required to support our present biomedical implantations. Nonetheless, the  $T_g$  values appear to follow a rule of mixtures relationship, in which the

DSC and DMA measurements generally correlate. For both  $\tan \delta$  and  $E^*$  values the behavior is quite varied and complex, only once suggesting a linear relationship with composition ( $p \leq 0.02$ ) and more often suggesting unusual behavior for the MS-2510 and MS-5510 rich blends. Careful comparison of all results suggest that materials referenced in past work may have been functioning as lightly crosslinked amorphous structures, while samples in the present work may be functioning as more organized crystalline structures.

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