

Dynamic Mechanical Analysis of Polymers in the Liquid State: Use of a Perforated Shim Stock Support

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Synopsis

This report summarizes some initial results on the use of a perforated brass shim stock support to extend the useful range of dynamic mechanical testing well over 100 degrees above the traditional limiting polymer softening points of T_g or T_m . Weak secondary relaxations were observed above T_g in both polyisobutylene (PIB) and polystyrene (PS) homopolymer, copolymer, and blend systems and above T_m in gutta percha (*trans*-polyisoprene). The DuPont 981 Dynamic Mechanical Analyzer (DMA)-990 Thermal Analyzer system was used to characterize these weak liquid state processes. The DMA instrument deforms the specimen in flexure, thus minimizing the shear component present in some other techniques. Specimen-coating weights are typically in the range 20–40 mg. The perforations are particularly useful for polymers having low inherent adhesion to metals or systems which are very brittle in the glassy state, e.g., low MW PS's and many methacrylates.

INTRODUCTION

For several years an ongoing program of research has been carried out at this Institute to elucidate weak secondary transitions above T_g in various polymer systems utilizing a variety of techniques: differential scanning calorimetry (DSC),¹ Fourier transform infrared (FTIR),² electron spin resonance (ESR),³ thermomechanical analysis (TMA),⁴ dynamic mechanical analysis (DMA),⁵ and dielectric.⁶ More recently, a program has been implemented using DSC to characterize transitions above T_m in semicrystalline systems.⁷

This communication describes the application of a new technique, utilizing DMA, to study polymers in the liquid state, i.e., $T > T_g$ in amorphous systems and $T > T_m$ in semicrystalline systems. The technique uses a piece of perforated shim stock to support the polymer sample well above the softening points of T_g or T_m . A discussion of the historical development of a number of support systems for dynamic mechanical testing follows.

Determination of dynamic mechanical properties of amorphous polymers in the liquid state above T_g and semicrystalline polymers above T_m tends to be difficult because of the sharp drop in modulus and strength, and the onset of flow above T_g or T_m . Various techniques have been developed to circumvent these problems. Schmieder and Wolf,⁸ using a hanging torsion pendulum, employed high molecular weight specimens of polyisobutylene (PIB) and *Hevea* rubber, and also vulcanization, to study the liquid state.

Ferry and his students, using the Fitzgerald apparatus, employed high molecular weight PIB,^{9,10} lightly vulcanized elastomers,¹¹ and PIB dispersed in butyl rubber which was then vulcanized.¹² Sidorovich et al.^{13–15} dispersed low molecular weight ($MW \leq 100,000$) *cis-trans*-vinyl polybutadiene (PBD) in high

MW (10⁶) PBD either unvulcanized or lightly vulcanized. These systems relied on physical entanglements or chemical crosslinks to maintain the integrity of the liquid polymer.

A parallel development involved the use of composite systems. A metal strip coated with the polymer to be studied was measured in flexure,¹⁶ with a theory for calculating the properties of the coating advanced several years later.¹⁷ The use of an interactive filler in poly(methyl methacrylate) (PMMA) permitted measurements well above its T_g .¹⁸ O'Malley et al. used a special specimen holder to apply shear with the Rheovibron.¹⁹ Gillham employed a multistrand glass braid impregnated with polymer to support the pendulum arm of a torsion pendulum.²⁰ This torsion braid apparatus (TBA) was used to measure the liquid state properties of polystyrene (PS) as a function of \bar{M}_n ,²¹ PS blends,²² and plasticized PS.²³ Cowie and McEwen employed impregnated filter paper with the Rheovibron on a variety of oligomers and polymers, reporting liquid state properties as a function of temperature and frequency.²⁴⁻²⁶

Still another technique is that of encapsulation, in which a low T_g material is dispersed as discrete particles in a high T_g polymer which forms the continuous phase. A history of various encapsulation techniques has been given and details of a specific method for the encapsulation of PIB in PS by solution blending and freeze drying was described.⁵ This composite molding was measured with the DuPont Dynamic Mechanical Analyzer (DMA). The loss behavior of PIB and some other polymers was studied always below the T_g of PS. The inherent weakness of this technique is that no more than 25-35 wt % of the dispersed phase can be used, thereby limiting sensitivity.

All of the methods just enumerated have revealed one or more mechanical loss peaks in the liquid state. These peaks occur above T_g in loss-temperature plots,^{5,8,9,13,14,18-26} and below T_g in loss-frequency plots,^{10-12,15} where it is called the "slow process" by Ferry and his students,¹¹ with T_g being the "fast process."

Starting with the TBA method, the loss peak above T_g was referred to as a liquid-liquid transition or relaxation, designated T_{ll} ^{21-23,27}; further, both T_{ll} and $T_{ll}' > T_{ll}$ were observed in plasticized PS.²³ Nielsen immediately suggested that the observed $T > T_g$ loss peak might be an artifact arising from the viscous interaction of the molten polymer with the glass braid in shear deformation.²⁸ Nielsen did not deny the possible existence of a liquid state loss process but felt that it should be demonstrated by a technique other than TBA. Gillham and Boyer²⁷ responded by noting, *inter alia*, that T_{ll} by TBA depended on \bar{M}_n whereas Newtonian viscosity increases as \bar{M}_w , and secondly, that a transition above T_g in PS had been observed by a nonflow process, namely, thermal expansion. Neumann et al.²⁹ and Heijboer³⁰ subsequently supported the artifact source for T_{ll} .

Quite recently, Starkweather and Giri developed a coated metal strip technique specifically for the DuPont 981 DMA system.³¹ This is a resonant apparatus with two arms pivoted to vibrate in a horizontal plane; one arm is driven electrically while the second arm is passive. These authors replaced the traditional polymer specimen clamped to the two arms by a polymer coated metal strip, i.e., a piece of shim stock which had negligible losses in the temperature region of interest.

EQUIPMENT AND MATERIALS

The DuPont 981 Dynamic Mechanical Analyzer (DMA) and associated 990 Thermal Analyzer programmer/recorder unit was used in this study. A description of the DuPont DMA system may be obtained from the literature.³²⁻³⁴

The shim stock support material used was 10-mil brass sheet stock (Precision Brand Products, Inc., Downers Grove, Ill.). Small pieces of $\frac{1}{2}$ in. width and variable length ($\frac{3}{4}$, 1, or $1\frac{1}{4}$ in.; $\frac{3}{4}$ in. primarily) were cut out of the continuous roll of 6-in. width brass sheet stock. Shim stock supports may be of any rigid material but must be free of loss peaks with a modulus relatively insensitive to temperature, over the temperature range of interest.

Three polyisobutylene (PIB) samples of varying molecular weight were obtained from Polysciences, Inc. (Paul Valley Industrial Park, Warrington, Pa.). A sample of relatively high MW *trans*-polyisoprene in the form of a sample of the natural rubber, gutta percha, was secured through Prof. Edgar Andrews, Queen Mary College, London, England. Three polystyrene (PS) MW standards available from Pressure Chemical Co. (Pittsburgh, Pa.) also were used.

In addition, preliminary experiments have been carried out on two series of styrene copolymers. We report on one representative member of each series. The first series was a set of three random copolymers of styrene and ethyl acrylate (S/EA) prepared by Prof. P. L. Kumler (State University of New York, Fredonia, N.Y.). The second series encompasses a set of six styrene-acrylonitrile (SAN) copolymers made available to us through Dr. R. H. Stehl of the Dow Chemical Co., Midland, Mich. Table I lists the polymer samples studied in this report and offers some characterization and source data for each sample.

EXPERIMENTAL

Our use of a shim stock support differs in one key feature from other recent shim supported DMA work,³¹ namely, that our shim stock contains holes in a specific configuration. This system is called perforated shim stock, conveniently referred to by us as the "holey shim stock" technique. One reason for putting a series of holes in the shim support is to inhibit vertical and horizontal sample flow upon heating a polymer sample to a temperature far exceeding its usual T_g or T_m softening point, as the case may be. Another reason is to facilitate better adhesion of the sample to the metal surface; in effect, the holes allow the sample to pull itself together through the shim stock support.

Shim supports were prepared in the following manner. One-half inch by three-quarters inch, ten mil shim blanks were cut out of brass roll stock. A series of 11 holes ($\#55$, 0.052 in., 0.13208 cm) were drilled in the central third of the shim. (See the inset of Fig. 1 for the drill hole pattern.) Preliminary work on longer shims (1 in. and $1\frac{1}{4}$ in.) incorporated more holes in a similar pattern. Drill hole burrs were roughed smooth, and the entire shim surface was scratched rough with a piece of 150-grade garnet sandpaper. We note that the sanding process introduces better polymer-metal adhesion by creating greater surface area and a more irregularly textured surface.

Polymer coatings were most readily applied by a solution casting process.

TABLE I
 Polymer Sample Characterization

Sample	\bar{M}_n	\bar{M}_w	Source	Notes
PIB-2814 ^a	7100 ^b	81,800 ^b	Polysciences	—
PIB-6084 ^a	859,000 ^b	2,818,000 ^b	Polysciences	—
PIB-6085 ^a	691,000 ^b	2,342,000 ^b	Polysciences	—
Gutta percha	—	220,000 ^c	^d	$T_m = 63^\circ\text{C}^e$
PS-37,000	36,300 ^{f,g}	32,600 ^{f,h}	Pressure Chem. Co.	lot 7b
PS-110,000	111,000 ^{f,g}	111,000 ^{f,h}	Pressure Chem. Co.	lot 4b
PS-2,000,000	1,990,000 ^{f,i}	2,050,000 ^{f,h}	Pressure Chem. Co.	lot 14b
S/EA-58/42	—	j	^k	—
SAN-70/30	36,000 ^l	91,000 ^l	^m	45.7 mol % AN

^a PIB sample designations refer to their Polysciences catalog number.

^b GPC molecular weight characterization obtained from Ref. 35.

^c Viscosity average molecular weight \bar{M}_v , from dilute solution viscosity measurement, benzene, 32°C.

^d Prof. Edgar Andrews, Queen Mary College, London, England.

^e Melting point by DSC at 10 K/min.

^f Molecular weight characterization provided by Pressure Chemical Co., Pittsburgh, Pa.

^g Membrane osmometry.

^h Light scattering.

ⁱ Fractionation.

^j Viscosity measurements of samples having compositions on either side of this sample indicate an \bar{M}_v greater than 100,000.

^k Prof. Philip L. Kumler, State University of New York, Fredonia, N.Y.

^l GPC characterization provided by the Dow Chemical Co., Midland, Mich.

^m Dr. Rudolph H. Stehl, Dow Chemical Co., Midland, Mich.

Typically, a sample is dissolved in a quite concentrated mixture with a good solvent and "painted" onto the central perforated region of a shim with a glass stirring rod. (See the inset of Fig. 1 for the polymer coated central perforated region of the shim.) Following solution coating, the samples are dried for an extended period of time at elevated temperatures to remove residual solvent.

In the present study, all three polymer types—PIB, gutta percha, and various PS's—were dissolved in chloroform. Drying times and temperatures ranged from several hours at 100°C for PIB to a couple of days at 185°C for gutta percha and the polystyrenes. Drying was always done in a vacuum oven to preclude oxidation at the elevated temperatures. The rate of temperature increase for drying the glassy styrene polymers had to be somewhat slow as they were prone to form bubbles. Once exceeding the glass transition temperature range (approx. $T_g + 50^\circ\text{C}$), bubbled samples would "melt down" onto the perforated region of the shim to form quite smooth coatings. Final dried polymer sample coatings weighing 20–40 mg were found to give satisfactory damping loss displays on the DMA instrument (990) recorder.

The 981 DMA was operated at a scan speed of 5°C/min for all heating and cooling runs. Temperature calibration using a PMMA standard was checked for the heating mode. The 990 programmer/recorder was set in a cycle mode so that typically both heating and cooling traces were obtained on all samples run. Some temperature variation (up to 20°C) between heating and cooling loss peak transition temperatures arises from simple thermal lag of the massive DMA heating block and sample clamp assembly.

Heating traces at 5°C/min are accurate and calibrated to the correct temperature. Cooling trace temperatures lag an average 15°C and thus appear consistently low. In all cases, we observe essentially duplicate transition loss processes on heating and on cooling. All polymer damping plots shown following are presented in terms of relative damping vs. temperature. The inherent design of coating polymer only in the central perforated region of the shim support, the existence of holes connecting both polymer coated surfaces, and the often uneven coating thickness, make precise calculations of absolute modulus or $\tan \delta$ values untenable.

The DuPont DMA apparatus is a constant amplitude, variable frequency test method. Samples were deformed in flexure with a horizontal peak-to-peak displacement of 0.2 mm. The resonant frequency of the system decreases with temperature because it is dependent on the modulus of the specimen. Since the polymer coatings were a small portion of the total composite specimen and because the modulus of the brass shim is rather insensitive to temperature over wide temperature ranges, the frequencies observed on any coated shim sample reported herein ranged from 10 to 20 Hz.

Perforated shim supports may be reused a number of times. When reusing a support, most of the previously coated sample is removed by dissolving it away in a good solvent (usually the original coating solvent). Next, the perforations are redrilled (to the same size) and the shim surfaces are re-etched with sand paper to restore a fresh irregularly textured surface. Repeated reuse and sanding of the brass shim stock does reduce its thickness, resulting in a lower background modulus for the support. We have recycled several pieces of perforated shim stock up to five or six times without difficulty.

RESULTS

The damping profile of an 11-hole brass shim of dimensions $\frac{1}{2}$ in. by $\frac{3}{4}$ in., without a polymer coating, is shown in Figure 1. Over the temperature range of interest (-100–250°C) there are no damping processes that would interfere with a polymer transition. A very broad and weak damping maximum is detectable at maximum recorder sensitivity, centered around 50°C. Above 200°C the damping magnitude of the brass shim stock becomes temperature-dependent, progressively increasing with temperature. The remaining figures in this report attest to the fact that the magnitude of the perforated shim background damping is insignificant when superimposed polymer transitions are present.

The inset in Figure 1 shows the regions of polymer coating and clamp areas. Note the gaps between the polymer coated region and the clamp regions. This gap is an important consideration in being able to obtain reproducible and consistent results and will be discussed in more detail later.

Figure 2 shows a composite plot of heating and cooling traces for three different samples of polyisobutylene varying in molecular weight. In each case, a strong T_g process around -50°C and a somewhat weaker damping process around -10°C is observed on heating. The high temperature transition corresponds to T_{II} and its relative strength with respect to the T_g seems to vary directly with molecular weight.

A frequency dependent dynamic mechanical loss peak above T_g in a PIB sample of $\bar{M}_v = 1.35 \times 10^6$ was reported by Fitzgerald, Grandine, and Ferry⁹ using

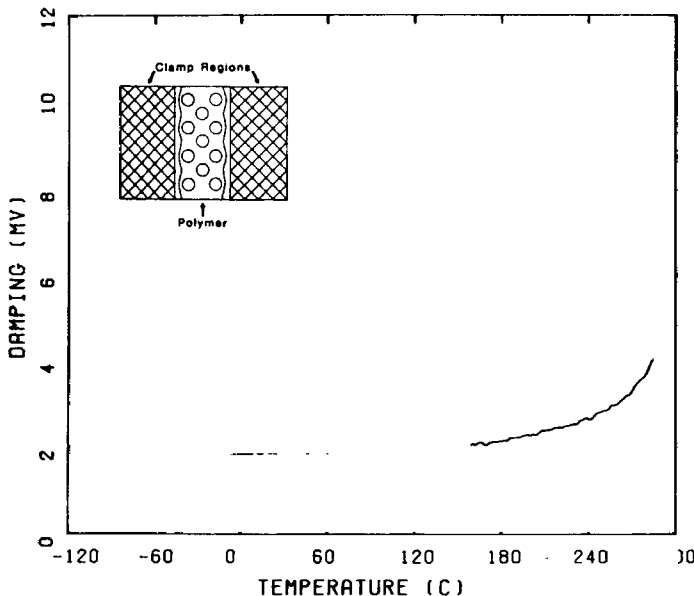


Fig. 1. Damping profile of a $\frac{1}{2} \times \frac{3}{4}$ in., 10 mil, 11-hole brass shim stock support over the temperature range -100 – 285°C . The ordinate of this and all other plots is relative damping, given by the voltage required to maintain a constant amplitude oscillation of 0.2 mm peak-to-peak. The inset depicts the geometry of the perforated shim support and the locations of the clamp regions, polymer-coated region, and uncoated gaps between those regions.

the Fitzgerald resonant shear apparatus. It was also reported by Schmieder and Wolf⁸ with a hanging torsion pendulum. More recently, Wei and Gillham studied the same PIB samples we report on here, by the method of torsional braid analysis (TBA).³⁵ They reported two loss peaks, $T_u > T_g$ and $T_{u'} > T_u$, and the same type of MW character we observe.

Heating and cooling runs for a high molecular weight sample of *trans*-polyisoprene in the form of the natural polymer, gutta percha, are shown in Figure 3. Transition processes from low to high temperature include the T_g at -38°C , T_{ac} at 43°C , T_m at 62°C , and T_u at 130°C . T_{ac} is ascribed to a crystal-crystal premelting transition.

T_u refers to a $T > T_m$ transition first reported by Krüger et al.³⁶ in several crystalline polymers by Brillouin scattering and ascribed to the breakup of smectic structures. T_u has been observed in various *n*-alkanes and crystalline polymers in this laboratory by DSC.³⁷ Gutta percha is unique in showing a strong T_u by dynamic mechanical loss.

Interestingly, the T_u upon cooling appears stronger, relative to the T_g and T_m , than on heating; the reason for this is not apparent at this time. The most important feature we wish to convey is that we have successfully observed a semi-crystalline polymer sample in the melt state at a temperature far in excess of its T_m softening point using the perforated shim stock method.

Composite heating and cooling traces of two polystyrene MW standards (PS-37,000 and PS-110,000) are shown in Figure 4. T_g damping peaks are observed around 120°C with a higher temperature process ascribed as T_u appearing at 170°C .

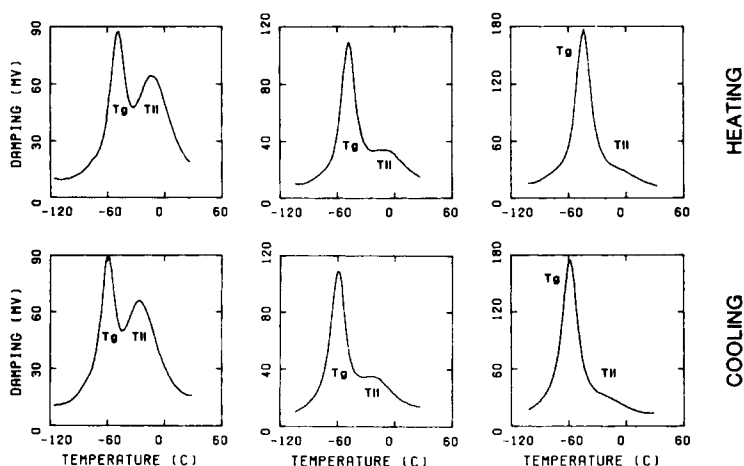


Fig. 2. Effect of molecular weight on the intensity of T_{II} in polyisobutylene for both heating (top) and cooling (bottom) runs. Molecular weights range from $\bar{M}_n = 7,100$, $\bar{M}_w = 81,800$ for PIB-2814 (left), to $\bar{M}_n = 859,000$, $\bar{M}_w = 2,818,000$ for PIB-6084 (center), to $\bar{M}_n = 691,000$, $\bar{M}_w = 2,342,000$ for PIB-6085 (right). Relative damping peak temperatures ($^{\circ}\text{C}$) and corresponding resonant frequency values (Hz) are given. PIB-2814 heating: $T_g = -49$, $f = 17.5$; $T_{II} = -13$, $f = 15.5$. PIB-2814 cooling: $T_g = -60$, $f = 18.0$; $T_{II} = -26$, $f = 15.5$. PIB-6084 heating: $T_g = -48$, $f = 16.0$; $T_{II} = -10$, $f = 14.0$. PIB-6084 cooling: $T_g = -59$, $f = 16.0$; $T_{II} = -25$, $f = 14.0$. PIB-6085 heating: $T_g = -44$, $f = 17.3$; $T_{II} = -8$, $f = 15.4$. PIB-6085 cooling: $T_g = -22$, $f = 18.1$; $T_{II} = -22$, $f = 15.4$.

The T_g values appear to be high, which may be the result of a frequency effect or an effect of the rigid metal substrate. Hedvat³⁸ has presented conclusions showing that the T_g of a composite specimen may be lowered if the ratio, modulus of support to modulus of polymer sample, is high. Hence, we are inclined to

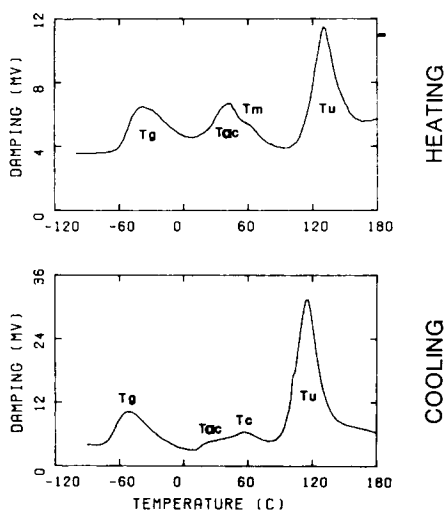


Fig. 3. Heating (top) and cooling (bottom) scans of *trans*-polyisoprene (gutta percha) showing mechanical relaxations of both amorphous (T_g) and crystalline (T_{acc} , T_m , T_c , and T_u) components. Relative damping peak temperatures ($^{\circ}\text{C}$) and corresponding resonant frequency values (Hz) are given. Heating: $T_g = -38$, $f = 15.4$; $T_{acc} = 43$, $f = 14.7$; $T_m = 62$, $f = 14.6$; $T_u = 130$, $f = 14.0$. Cooling: $T_g = -51$, $f = 15.9$; $T_{acc} = 26$, $f = 15.5$; $T_c = 56$, $f = 15.4$; $T_u = 115$, $f = 14.3$.

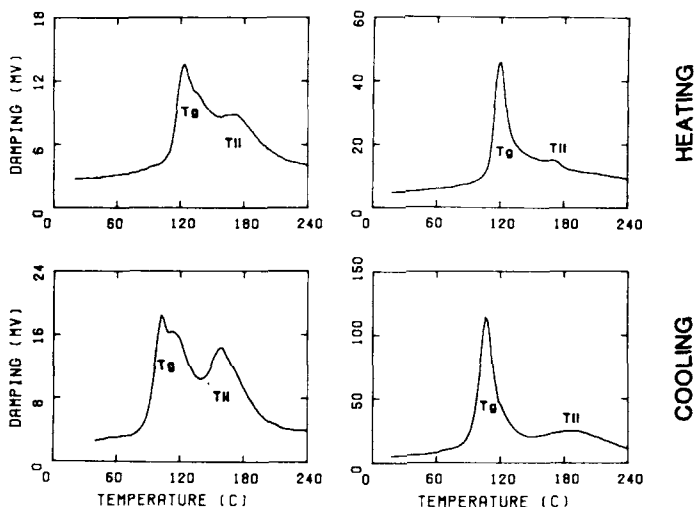


Fig. 4. DMA loss peaks for two PS molecular weight standards. T_g and T_{II} are evident in both heating (top) and cooling (bottom) thermograms for PS-37,000 (left) and PS-110,000 (right). The intensity of T_{II} diminishes as MW increases. (Compare Fig. 2 for the MW effect on the T_{II} of PIB.) Relative damping peak temperatures ($^{\circ}\text{C}$) and corresponding resonant frequency values (Hz) are given. PS-37,000 heating: $T_g = 123, f = 13.6$; $T_{II} = 171, f = 13.3$. PS-37,000 cooling: $T_g = 102, f = 14.2$; $T_{II} = 158, f = 13.5$. PS-110,000 heating: $T_g = 119, f = 15.3$; $T_{II} = 170, f = 14.1$. PS-110,000 cooling: $T_g = 106, f = 16.3$; $T_{II} = 187, f = 13.9$.

ascribe the higher T_g 's to a frequency effect since the DMA system frequency is around 15 Hz at T_g .

Stadnicki et al.²¹ reported T_g 's for both of these anionic PS standards at 0.63 Hz; they observed T_g at 109 $^{\circ}\text{C}$ and 111 $^{\circ}\text{C}$ for PS-37,000 and PS-110,000, respectively. Blanchard et al.³⁹ showed by DSC that T_g increases from a value of 100.1 $^{\circ}\text{C}$ at an extrapolated heating rate of 1 K/min to 111 $^{\circ}\text{C}$ at 80 K/min for a polystyrene of MW 50,000. Whether there is a residual effect of the substrate in raising T_g is not clear yet. Extensive molecular weight series studies via binary blends are in progress to address this question.

Some preliminary work was carried out using PS homopolymers on various length shims. The net result was that, as the length of the shim increased (holding width and thickness dimensions constant), the resonant frequency of the composite sample decreased, and thus the DMA sensitivity to damping processes correspondingly was reduced. When longer (1 in. and 1 $\frac{1}{4}$ in.) shims were used, both the T_g and T_{II} damping peaks were markedly reduced in magnitude and clarity.

As alluded to earlier, we also have begun investigations into $T > T_g$ transition phenomena in two series of styrene random copolymers. Figure 5 presents heating traces only of one representative member each of the styrene-ethyl acrylate (58 wt % styrene) and the styrene-acrylonitrile (70 wt % styrene) copolymer series. Once again, both copolymers show strong T_g loss peaks with a substantial high temperature process we believe corresponds to T_{II} .

The perforated shim technique and sandpaper-etched surfaces are essential parameters in increasing the adherence of glassy polymers to shim supports. Initial attempts to coat smooth brass shim stock with styrene polymers consistently failed due to poor polymer-metal adhesion.

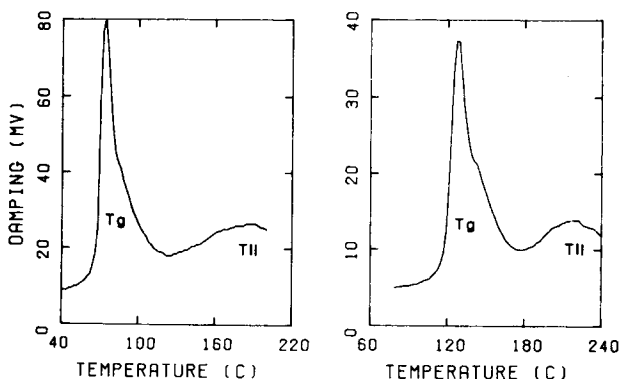


Fig. 5. Evidence for the T_{II} transition in two series of random copolymers having styrene as a comonomer is shown by styrene-ethyl acrylate, 58 wt % styrene (left) and styrene-acrylonitrile, 70 wt % styrene (right). Relative damping peak temperatures ($^{\circ}\text{C}$) and corresponding resonant frequency values (Hz) are given. S/EA-58/42: $T_g = 73, f = 15.6; T_{II} = 190, f = 13.0$. SAN-70/30: $T_g = 128, f = 13.0; T_{II} = 220, f = 12.1$.

For the three PIB's and gutta percha, there was virtually no sample flow noted upon heating some 150 degrees above their respective T_g or T_m transitions. Much of the PS work has been plagued with flow problems, however. A principal inhibitor of flow appears to be high MW, high meaning something over several hundred thousand and into the 10^6 range.

To test this assumption, a blend of two parts (by weight) PS-37,000 with one part PS-2,000,000 was prepared. Figure 6 shows a heating trace for this blend. The T_g value has increased somewhat over that of the PS-37,000 sample shown in Figure 4 while the T_{II} transition is virtually unchanged. Furthermore, following heating up to 250°C , the blend sample showed markedly reduced flow effects. This observation convinces us that the T_{II} peaks we define are indeed inherent polymer transitions and do not arise from a physical flow or viscosity effect.

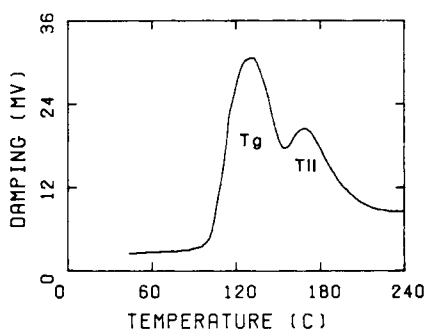


Fig. 6. Binary blend of two parts PS-37,000 with one part PS-2,000,000 showing T_g and T_{II} . The high MW component serves to inhibit sample flow. Comparison with the result on PS-37,000 homopolymer (upper left trace of Fig. 4) shows a somewhat broadened T_g and an essentially unchanged T_{II} . PS-2,000,000 would show a very slight T_{II} due to the MW effect on T_{II} ; thus the T_{II} peak observed in the blend is due wholly to the lower MW component. Identical T_{II} values (170°C) for the homopolymer and blend of PS-37,000 indicate the nonshear nature of the perforated shim stock technique. Relative damping peak temperatures ($^{\circ}\text{C}$) and corresponding resonant frequency values (Hz) are $T_g = 131, f = 12.7$ and $T_{II} = 169, f = 12.9$.

One very attractive feature of the perforated shim stock technique is that minimal amounts of sample are required. Typical two-side coatings in the central perforated region may range from a few mg up to about 100 mg at most. Very definitive damping profiles of traditionally strong transitions (T_g and T_m) and controversial weak secondary relaxations (T_{ll} and T_u) have been satisfactorily obtained in the range of 20–40 mg.

Another attractive feature of the technique is its application to polymer systems which are mechanically weak and brittle below T_g . Although the emphasis in this communication is on the temperature range above T_g or T_m , we do note that we have had marked success in studying low-MW PS samples (below their T_g 's) when coated onto perforated shims, but could not fabricate coherent specimens suitable for DMA without a support.

Many methacrylate polymers are also quite brittle. In particular, we have looked at poly(cyclohexyl methacrylate) (PCHMA) coated onto a perforated shim support. We were able to examine this specimen from -120°C to 200°C without difficulty, observing strong T_g and T_{ll} damping peaks (above room temperature) and a substantial low temperature loss process caused by the molecular motion of the cyclohexyl ring at -65°C and 15 Hz.

DISCUSSION

As already alluded to, a T_{ll} process in PIB has been observed by Gillham et al. using TBA.^{35,40} Gillham et al. also have reported extensively on T_{ll} phenomena in polystyrene homopolymers and blends using both TBA and DSC techniques.^{21–23,27} The liquid–liquid transition has been labeled as an experimental artifact arising from flow effects at a given temperature (or viscosity range) above T_g .^{28,29}

In the present study, the shim stock is deformed in flexure, as emphasized by Starkweather and Giri.³¹ The polymer coating is likewise deformed in flexure except possibly at the interface between polymer and substrate. Hence the criticism voiced against TBA^{28–30} should not apply to the shim stock technique.

This view is confirmed by the experiment with the blend of low and high molecular weight PS shown in Figure 6. T_{ll} occurs at 170°C on heating in the blend, and at 170°C for the case of homopolymer PS-37,000 shown in Figure 4. Yet the calculated value of \bar{M}_w for the blend is 705,000. The higher value of Newtonian viscosity for the blend would shift T_{ll} up in temperature if a Nielsen-type artifact were operating, just as the apparent T_{ll} observed in TBA shifts to higher temperatures as molecular weight increases. This point will be checked in much greater detail by experiments currently in progress.

The sample of gutta percha (*trans*-polyisoprene) was chosen as the initial candidate for T_u testing because it had a relatively high MW and showed strong T_u evidence on DSC.³⁷ Gutta percha also would seem to be an ideal polymer structurewise for potential residual structures in the melt because of its more extended chain character. DSC observations on *Hevea* rubber (*cis*-polyisoprene) did not show evidence for a T_u transition.³⁷ DMA results on gutta percha corroborate and amplify the preliminary DSC observations in this laboratory. T_u is presumed to be the temperature at which any quasiordered structures finally break up above T_m in semicrystalline polymer systems.^{7,36}

The perforated shim geometry serves well to inhibit sample flow. A key ad-

ditional element in near total flow abatement is high sample molecular weight. The marked success on PIB and gutta percha vs. the various PS's is ascribed mainly to total sample immobility due to their relatively high molecular weights and comparatively low entanglement molecular weights of around 15,000. Also, for the same molecular weight, PS is far less entangled than is PIB. In contrast to PIB, PS has an entanglement molecular weight of 35,000.

One problem we are addressing is the effect of flow on T_{ll} , particularly in PS homopolymers, copolymers, and binary blends. Preliminary studies with blends of low MW PS-37,000 and high MW PS-2,000,000 lead us to believe that one can sufficiently immobilize low MW species by loadings with very high viscosity, high MW components. T_{ll} remains intact, even though flow effects become minimized. This would seem to indicate that T_{ll} is not an artifact due to sample flow at some point above T_g .

Kramer et al.¹² mixed PIB's of molecular weights 55,000 and 2.3×10^6 into butyl rubber at levels of 25 and 50 wt %, the butyl rubber being subsequently vulcanized. They showed that the soluble PIB responded in a dynamic mechanical experiment independent of the host polymer network. We believe that the low-MW PS component blended with PS-2,000,000 can and does behave independent of its host, thereby further extending the useful range of the shim stock support method to observe low molecular weight samples in their liquid state.

Most of the flow problems we try to avoid in the perforated shim stock technique are vertical in nature, arising from gravitational effects on the liquid sample. An equally important concern is to avoid horizontal sample flow to the DMA clamps. It is critical to apply the polymer coating only in the central perforated region of the shim support. If any portion of a sample comes in contact with a clamp, substantial pooling of polymer onto the clamp will occur upon heating the sample above its softening point. For this reason, we stress the importance of allowing for a small gap of blank shim area between the clamp regions and the polymer coated region. (See the inset of Fig. 1 for clarification.)

The effect of polymer-metal shear at the interface arising from large differences in the thermal expansion coefficients of the metal support and the polymer coating is another concern. We are considering the use of several different support substrates (other metals, coatings, and high T_g polymers) to better match the thermal expansivities and thereby avoid shear at the microlevel at the support-polymer interface.

Perhaps the strongest argument to be made for the reality of $T > T_g$ and $T > T_m$ transitions is that they are present in both heating and cooling scans. If T_{ll} and T_u are *bona fide* molecular processes which serve to add an extra increment of fluidity to a polymer liquid, then one should clearly expect to see vertical sample flow upon heating due to gravity's effect on the more relaxed specimen (for low to medium MW materials). If, upon cooling, a transition process should again be evident, in this case it must arise from mechanical energy damping by an intrinsic molecular process of the polymer.

We find the use of perforations in the shim stock support to be essential in studying polymers having low intrinsic adhesion to metals, such as the styrene polymer systems we have investigated to date. The holes allow the two-sided polymer coating to effectively hold itself together and to the metal support.

There is, however, a wide variety of polymer and copolymer systems with high

intrinsic metal adhesiveness character. Such systems can be readily studied on smooth shim supports. We have looked at a few different systems in a preliminary manner.

One system studied³⁷ is a commercial product of the Dow Chemical Co. known as Zetabon®.⁴¹ This product is comprised of aluminum and/or steel sheet stock coated on one or both sides with an inherently adhesive ethylene copolymer containing carboxylic acid groups. The material is used for protective coverings in communications and power cables.

The food and beverage industry also is a heavy user of coated metal materials. We have looked at both aluminum beverage can and steel fruit juice can coated metal sheet stock. Although the coatings are extremely thin (<1 mil), substantial damping profiles were observed corresponding to inherent polymer transitions.

The DuPont DMA has also been applied to the study of paint coatings on metals by Grentzer et al.⁴² Since our preliminary work on Zetabon and can coatings parallels the work of Grentzer et al.,⁴² we will not elaborate on it further here.

Although we consider the appearance of T_{ll} and T_u damping peaks on cooling runs to be definitive confirmation of real molecular level relaxations, a reviewer was not as convinced. We further note that replicate runs of two to three coated shim samples give identical transition damping peak profiles, and duplicate runs on any given specimen also give reproducible results. Scan speed effects were studied on the PIB samples reported herein, and even after some 12–15 cycled runs over a month's time, at temperatures up to 100 degrees above T_{ll} , the character and position of both T_g and T_{ll} peaks remain constant. Replicate and duplicate runs on the various polystyrenes also showed consistent T_{ll} behavior.

SUMMARY

A simple device has been employed to extend the useful temperature range of polymer analysis via DMA by over 100°C. The technique involves the use of a perforated shim stock support. At the outset it may be a panacea to study both $T > T_g$ and $T > T_m$ weak secondary polymer transitions. Polymer samples traditionally receive little mechanical testing on a routine basis in the range above their T_g or T_m softening points because of the corresponding loss of structural integrity. The perforated shim stock technique offers a means of mechanical property study well into the liquid range of both amorphous and semicrystalline polymers.

The utility of the technique was shown in its application to the study of T_{ll} in PIB and PS systems and T_u in gutta percha. The small sample size requirement (20–40 mg) is another advantage, especially when very little material may be available of new experimental materials or specially prepared tactic polymers.

The perforations in the shim support are essential for studying polymers of poor metal adhesion character, allowing a specimen to hold itself together to the metal support. Finally, the application to low MW and/or otherwise inherently brittle materials allows observations well below their glass transition temperature range.

Future work will concentrate on alleviating some sample flow problems by loading low MW materials with high MW polymers, and matching polymer-substrate interface expansivities to minimize shear effects.

Dr. Howard Starkweather of the DuPont Experimental Station advised us prior to his publication³¹ about his shim stock work during a visit to Midland in the summer of 1980 after we had described our encapsulation studies⁹ to him. We immediately recognized the potential of this technique for investigating the T_{ll} region of amorphous polymers. An early application to PIB has been reported.⁴³

We are indebted to Dr. K. Varadarajan for initial investigations on the use of the shim stock method for studying the multiple transition behavior of PIB during his postdoctoral appointment at our Institute.

We recognize with appreciation the following individuals who supplied various polymer samples to us: (1) Prof. Edgar Andrews, Queen Mary College, London, England, for the sample of gutta percha, (2) Prof. Philip L. Kumler, State University of New York, Fredonia, N.Y., for a set of styrene-ethyl acrylate copolymers, and (3) Dr. Rudolph H. Stehl, Dow Chemical Co., Midland, Mich., for a series of styrene-acrylonitrile copolymers.

Dr. J. Heijboer, TNO, Delft, Netherlands, sent us reprints of the early articles from *Acustica*.^{16,17}

We are grateful to S. R. Vranish, Dow Chemical Co., Midland, Mich., and P. U. Bakhru, Dow Chemical Co., Granville, Oh., for the Zetabon coated metal specimens.

We finally wish to thank Kathleen M. Panichella (MMI) for the preliminary DMA work on Zetabon and DSC work to characterize the T_u transition in various semicrystalline polymers.

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Received October 18, 1982

Accepted January 21, 1983