University of Massachusetts Amherst

From the Selected Works of William MacKnight

1978

A Critical Analysis of the Use of Sample-Supportive Techniques in the Measurement of Dynamic Mechanical Relaxation Processes

William MacKnight, *University of Massachusetts Amherst*

R. M. Neumann

G. A. Senich

Available at: https://works.bepress.com/william_macknight/65/

A Critical Analysis of the Use of Sample-Supportive Techniques in the Measurement of Dynamic Mechanical Relaxation Processes

R. M. NEUMANN, G. A. SENICH and W. J. MACKNIGHT

*Polymer Science and Engineering Department
and Materials Research Laboratory
University of Massachusetts
Amherst, Massachusetts 01003*

It is shown that the technique of dynamic spring analysis (DSA) gives rise to a dynamic mechanical loss dispersion well above the glass transition temperature, T_g , analogous to the T_u process observed in torsional braid analysis. A mechanical model is proposed which explains why any composite sample consisting of an elastic support coupled to a viscous liquid must necessarily produce such a relaxation regardless of whether the liquid is monomeric or polymeric in nature. Loss tangent measurements performed on a series of polystyrenes of varying molecular weight and on glycerol using both DSA and a Rheometrics mechanical spectrometer show that the relaxation observed in DSA is not of molecular origin.

INTRODUCTION

Recent years have witnessed an increased interest in the use of sample supported techniques to study polymers having very low elastic moduli (1-3). When amorphous polymers are studied by these methods, a relative maximum in the loss tangent is often observed in addition to the peak associated with the glass transition process. Gillham *et al.* (1) observe such a process by means of the torsional braid analysis (TBA) technique and refer to it as a liquid-liquid transition, whose characteristic temperature is T_u . The origin of this T_u transition has evoked some controversy concerning whether it reflects a molecular process or whether it is an artifact of the TBA technique. Recently, Nielsen has suggested that T_u as observed in polymer melts is not of molecular origin (4).

We believe that Nielsen's hypothesis is correct although the argument he presents is insufficiently quantitative to settle the controversy. In this paper, we propose a spring-dashpot model representative of the actual polymer-support composite which predicts a relative maximum in $\tan \delta$, whose temperature location at constant frequency is solely a function of the Newtonian viscosity of the supported material. We observed the T_u transition for a series of polystyrenes as well as glycerol at four different frequencies using the dynamic spring analysis (DSA) technique (2).

When the same temperature and frequency region was examined by a Rheometrics mechanical spectrometer (RMS) for one of the samples, no dispersion was observed. Indeed, the relation between G'' , the shear loss modulus, and angular frequency, ω , was found to be $G'' = \omega \eta$ at fixed temperature.

EXPERIMENTAL

Four monodisperse polystyrene samples of $\bar{M}_w/\bar{M}_n < 1.1$ were employed in this study. Polystyrenes of $\bar{M}_n$ equal to 4000, 19,800, and 37,000 were obtained from the Pressure Chemical Company, Pittsburgh, Pennsylvania. The $\bar{M}_n = 2000$ sample was furnished by Arrow Laboratories, Joliet, Illinois. A sample of HH101 polystyrene resin obtained from the Monsanto Company having the following characteristics was also studied: $\bar{M}_n = 9.0-9.5 \times 10^4$, $\bar{M}_w = 2.6-2.8 \times 10^5$. The glycerol was Eastman technical grade.

Twenty-turn steel springs made from 0.3 mm diameter wire, and having an outer diameter of 3.3 mm were used to support the materials in the DSA study; see Fig. 2. Details of the composite geometry and sample preparation process are available (2). All the polystyrene samples were dried under vacuum after solution coating from toluene had been completed. The monodisperse polymers were kept at 30°C above their respective T_g 's for at least 72 h while the HH101 resin was dried at 160°C for 17 h. A glycerol sample was prepared by depositing the liquid with a hypodermic syringe onto a spring which was held stretched in the clamps of the Rheovibron. All samples were analyzed at several frequencies in a dry nitrogen atmosphere at a nominal heating rate of 1.5°C/min on a Rheovibron DDV-IIB dynamic viscoelastometer.

The Rheometrics mechanical spectrometer was employed in the dynamic cone and plate mode to obtain the loss and storage shear moduli of 4000 $\bar{M}_n$ polystyrene as a function of frequency at four different temperatures. A 25 mm diameter plate and a 0.1 rad cone were used throughout. The powdered polymer sample was intro-

Fig. 5. Schematic illustrations showing changes in velocity profile and reduction of interfacial shear stress by: 1) increasing skin layer thickness, 2) decreasing skin layer viscosity, 3) decreasing total rate, and 4) increasing die gap.

DETERMINATION OF "CRITICAL INTERFACIAL SHEAR STRESS"

The four most important variables (skin layer viscosity, layer thickness ratio, total rate, and die gap) were varied *independently* over a range of shear stress which gave stable to unstable flow in the three-layer ABS 213/STYRON 470/ABS 213 structure.

The point of incipient instability must be determined by a rather arbitrary visual judgment. Six persons evaluated all the samples, where each variable spanned the range from stable to unstable flow while maintaining other conditions constant. The consensus of the judges on the occurrence of incipient instability was good.

The interfacial shear stress was calculated from the known coextrusion conditions at incipient instability for each variable and the two material constants, K and n , for each polymer as determined by Instron rheometer data. It was determined that interlayer melt fracture developed at an interfacial shear stress of approximately 5×10^5 dynes/cm², regardless of which independent variable was varied.

These results support our hypothesis that interfacial flow instability is related to a "critical interfacial shear stress."

CONCLUSIONS

- In the three-layer system, ABS 213/STYRON 470/ABS 213, transition from stable flow to interfacial flow instability can be caused by changes in any one of the following variables: skin layer viscosity, layer thickness ratio, total extrusion rate, and die gap opening.
- In all cases, incipient interfacial flow instability occurred at an interfacial shearing stress of about 5×10^5 dynes/cm². The value of 5×10^5 dynes/cm² for the "critical interfacial shear stress" refers to the specific system studied (ABS 213/STYRON 470/ABS 213). The transition to unstable flow may occur at a different stress level in other systems.
- A sheet produced at the point of incipient instability would probably still be commercially acceptable, since very critical visual judgment was employed. Severe instability occurred at higher shear stresses. (The steady-state analysis used in this work of course cannot provide a meaningful value for shearing stress in the regime of severe instability.)
- Interfacial flow instability can be reduced or eliminated by: increasing the skin layer thickness, increasing the die gap, reducing the total extrusion rate, or decreasing the viscosity of the skin layer polymer. (This last remedy for the interfacial instability problem may in some cases introduce a systematic nonuniform layer distribution because of viscosity mismatch, as described in the Introduction.)
- The non-Newtonian model of multilayer flow, together with the value of "critical interfacial shear stress," can be used in scale-up calculations based on laboratory rheological data.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of R. A. Tigner for writing the computer program.

REFERENCES

1. J. H. Southern and R. L. Ballman, in "U.S. Japan Seminar on Polymer Processing and Rheology," D. C. Bogue, M. Yamamoto, and J. L. White, Eds., Appl. Polym. Symp., No. 20 (1973).
2. J. L. White, R. C. Ufford, K. R. Dharod, and R. L. Price, *J. Appl. Polym. Sci.*, **16**, 1313 (1972).
3. C. D. Han, *J. Appl. Polym. Sci.*, **17**, 1289 (1973).
4. A. E. Everage, Jr., *Trans. Soc. Rheol.*, **17**, 629 (1973).
5. W. J. Schrenk, *Plastics Eng.*, **30**, No. 3, 65 (1974).
6. D. S. Chisholm and W. J. Schrenk, U. S. Patent 3, 557,265.

duced onto the preheated platens and allowed to liquify before the proper cone gap was fixed. A strain of 2 percent was used in all the determinations. At frequencies greater than 1 Hz, a ten cycle average was used for each modulus determination; at all frequencies the moduli were obtained from an average of at least ten measurements.

THEORY

Figure 1 displays the mechanical model used to characterize the composite sample used in the DSA technique. The model can be generalized to other sample-supportive methods by replacing the Hooke's Law moduli E_i (spring constants) with the appropriate moduli. Spring #1 is in series with a Voigt element, designated 2, consisting of spring #2 in parallel with a dashpot of viscosity η . Figure 2 indicates that a real composite will have a portion of the end loop uncoated; the uncoated part corresponds to E_1 in the model. If the polymer is sufficiently rigid, its dynamic tensile modulus simply can be added to E_2 since it is in parallel with E_2 . However, if the sample behaves as a simple viscous liquid, the spring loops surrounded by liquid are driven through the liquid in the manner of a dashpot.

The complex tensile compliance, D_2^* , for a Voigt element is (5):

$$D_2^* = D_2' - iD_2'' \quad (1)$$

where

$$\tan \delta = \frac{\omega \eta}{1 + E_2/E_1(1 + \omega^2 \tau^2)}$$

Fig. 1. This spring-dashpot model is proposed to account for the T_H relaxation.

Fig. 2. The DSA-composite is shown schematically.

$$D_2' = [E_2(1 + X^2)]^{-1}, D_2'' = X D_2', \text{ and } X = \frac{\omega \eta}{E_2}.$$

Similarly, for spring #1,

$$D_1^* = D_1' - iD_1'' \quad (2)$$

where $D_1' = \frac{1}{E_1}$ and $D_1'' = 0$.

The complex compliance for the composite is D^* , where $D^* = D_1^* + D_2^*$ because of the series arrangement. The loss tangent for the composite, $\tan \delta_c$, is given by

$$\tan \delta_c = \frac{D''}{D'} \quad (3)$$

where $D^* = D' - iD''$, $D' = D_1' + D_2'$, and $D'' = D_1'' + D_2''$.

$$\tan \delta_c = \frac{X}{1 + \frac{E_2}{E_1}(1 + X^2)} \quad (4)$$

It is readily demonstrated that $\tan \delta_c$ attains a relative maximum when the following value of the viscosity is attained.

$$\eta_{max} = \frac{E_2}{2\pi\nu} (1 + E_1/E_2)^{1/2} \quad (5)$$

where ν = frequency in Hertz.

The model predicts that T_H corresponds to an isoviscous state; that is, for a given frequency a relative maximum will be observed in the composite loss tangent at η_{max} . η_{max} is solely a function of the two different spring constants characteristic of the given composite sample.

RESULTS

Figure 3 depicts the DSA composite loss tangent, $\tan \delta_c$, plotted vs temperature at four different frequencies for monodisperse polystyrene, $\bar{M}_n = 4000$. No transition is observed at temperatures in the vicinity of the DSC-observed T_g (77°C); this will be discussed subsequently. Figure 4 presents plots of $\log(G'')$ vs $\log(\text{frequency})$ at four different temperatures obtained from a RMS. $\tan \delta$ is not shown because G' could not be accurately determined by this method. The RMS data constitute a search of the same temperature-frequency region in which

Fig. 3. The DSA-composite loss tangent for polystyrene-4000 is shown as a function of temperature at four different frequencies.

Fig. 4. $\log G'$ vs $\log \nu$ is shown for polystyrene-4000 at four different temperatures.

transitions are observed by DSA. Not only are the DSA-observed transitions absent, but the slopes are constant and approximately equal to unity. Table 1 shows the slopes and viscosities calculated from a least-squares-fit of the data displayed in Fig. 4. For a simple liquid possessing Newtonian viscosity, the following relationship is valid (6):

$$G'' = \omega \eta \quad (6)$$

Table 1. Slopes and Viscosities for $\bar{M}_n = 4000$ Polystyrene Obtained from a Rheometrics Mechanical Spectrometer

Temperature (°C)	Slope	$\eta \times 10^{-4}, \eta = \frac{G''}{\omega}$ (poise)
126	0.995	1.8
118	0.993	8.5
109	0.969	48.
101	0.913	2.7×10^2

or

$$\log G'' = \log \nu + \log 2\pi\eta$$

The values of the slope and viscosity indicate that in this temperature-frequency region, the sample behaves as a Newtonian liquid, and, therefore, that the DSA loss process (T_{II}) is not of molecular origin.

Figure 5 displays $\tan \delta_c$ (DSA) plotted vs temperature at four different frequencies for glycerol. Again a series of well-defined relative maxima is evident at temperatures well above the estimated T_g of -90°C (7). Crystallization in the region above T_g can be ruled out because no abrupt change in the storage modulus of the composite was observed. Equation 5 predicts that for a given composite sample the product of the viscosity, η_{max} , and the frequency should be a constant. Table 2 indicates that this prediction is confirmed for both the polystyrene and glycerol composites. It must be noted that the T_{max} precision is $\pm 1^\circ\text{C}$ which can result in considerable error in the selection of the appropriate literature viscosity. The fluctuation in $\eta\nu$ for a given composite at the four different frequencies is well within this projected error in the estimated viscosity.

Figure 6 displays $\tan \delta_c$ vs temperature behavior, measured at 11 Hz by DSA, for five polystyrene samples differing in molecular weight. They are all monodisperse with the exception of the $\bar{M}_n = 92,500$ sample for which $\bar{M}_w/\bar{M}_n = 2.9$. The two highest molecular weight specimens display shoulders in addition to the primary maximum, which suggests the occurrence of a second loss process. We suggest that the lower temperature-dispersion corresponds to a true molecular process, the one usually associated with T_g , whereas the higher temperature dispersion is the T_{II}

Fig. 5. The DSA-composite loss tangent for glycerol is shown as a function of temperature at four different frequencies.

Table 2. The Products of Frequency and Viscosity for Polystyrene-4000 and Glycerol at the Temperatures Where $\tan \delta_c$ is a Maximum as Determined by DSA

Material	$T_{max}, ^\circ\text{C}$	ν, Hz	$\eta \times 10^{-4}, \text{poise}$ Lit. value*	$\eta\nu \times 10^{-4}$
Polystyrene 4000	142	100	0.20 ref.(10)	22
	134	35	0.58	20
	125	11	2.2	24
	119	3.5	6.2	22
Glycerol	-41	3.5	5.9 ref.(11)	21
	-35	11	1.5	17
	-30	35	0.60	21
	-23	110	0.20	22

* The polystyrene-4000 literature values were obtained by means of an empirical equation relating viscosity, temperature and molecular weight found in ref. (10).

analogous to the single dispersion seen for the $\bar{M}_n = 2000, 4000$, and $19,800$ composite samples. The fact that a second relaxation is first evident at $\bar{M}_n = 37,000$ is consistent with the belief that the molecular chains here are just attaining sufficient length to allow entanglement coupling (8). The absence of an appreciable T_g -related relaxation in low molecular weight polystyrenes and glycerol in DSA reflects a lack of sensitivity of the spring arrangement to molecular processes which originate in the glassy regions of these materials. Here, presumably the ends of the spring, E_1 , account for most of the deformation. The DSC-measured T_g 's for the five polystyrene samples in the order of increasing molecular weight are ($^\circ\text{C}$): 60, 77, 101, 105, 106.

CONCLUSIONS

We have presented proof that the T_u transition as observed in the DSA technique is an instrumental artifact produced by the composite nature of the specimen. This conclusion is based on experimental evidence as well as on theoretical analysis. The T_u phenomenon observed here should occur whenever the zero-shear viscosity of the sample reaches the critical value as given by Eq 5, regardless of whether the material is monomeric or polymeric.

Furthermore, we believe that our explanation is also valid for the T_u transition observed in TBA (1,9). Here, the T_u transition was found to correspond to an isoviscous state when a series of polystyrenes of varying molecular weight were examined. Most noteworthy, however, is the fact that T_u was observed for a polystyrene sample of $\bar{M}_n = 585$ by TBA. This sample has a chain length of approximately six monomer units. We doubt that any type of polymeric behavior should occur for a material of such low molecular weight and suggest that TBA experiments be conducted with monomeric substances such as glycerol.

In general, any technique using composite materials can be expected to produce dispersions when the zero-shear viscosity of the sample causes spring-dashpot behavior. While we recognize that high molecular weight amorphous polymer melts can give rise to a second molecular relaxation at temperatures higher than those

Fig. 6. The DSA-composite loss tangent for polystyrene at 11 Hz is shown as a function of temperature for five different molecular weights.

of the T_g -associated relaxation, i.e., entanglement slippage, we believe that the onus rests on the researcher to prove that a given composite relaxation such as T_u is truly of molecular origin.

ACKNOWLEDGMENTS

Use of the facilities of the Materials Research Laboratory at the University of Massachusetts is gratefully acknowledged.

REFERENCES

1. J. K. Gillham, J. A. Benci, and R. F. Boyer, *Polym. Eng. Sci.*, **16**, 357 (1976).
2. G. Senich and W. J. MacKnight, accepted by *J. Appl. Polym. Sci.*
3. S. Naganuma, T. Sakurai, Y. Takahashi, and S. Takahashi, *Kobunshi Kagaku*, **29**, 105 (1972).
4. L. E. Nielsen, *Polym. Eng. Sci.*, **17**, 713 (1977).
5. J. J. Aklonis, W. J. MacKnight, and M. Shen, "Introduction to Polymer Viscoelasticity," p. 152, John Wiley, New York (1972).
6. J. D. Ferry, "Viscoelastic Properties of Polymers," p. 45, John Wiley, New York (1970).
7. Arno K. Schulz, *Z. Naturforsch.*, **9A**, 944 (1954).
8. J. D. Ferry, *Op. Cit.*, p. 409.
9. S. J. Stadnicki and J. K. Gillham, *Am. Chem. Soc. Polym. Prepr.*, **16**, (1), 559 (1975).
10. T. G. Fox and P. J. Flory, *J. Polym. Sci.*, **14**, 315 (1954).
11. "Handbook of Chemistry and Physics," p. F-40, The Chemical Rubber Co., Cleveland (1972-3).