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Dynamic Mechanical Properties of Supported Polymers. I. Application of the Torsional Braid Technique to the Study of Glass Transition Temperatures

ARMAND F. LEWIS and JOHN K. GILLHAM, *Central Research Division, Plastics & Resins Research Unit, American Cyanamid Company, Stamford, Connecticut*

INTRODUCTION

Certain limitations exist with current dynamic mechanical methods in the study of the properties of polymers. In general, dynamic studies on liquids, soft (rubbery) solids, and hard polymers must be carried out on individually designed instruments.[1,2] Equipment for the dynamic measurement of mechanical moduli by free vibrational methods (torsional and flexural pendulums) has been described previously.[3] The applicability of this equipment was limited to hard polymers and to temperature ranges below the region where incipient flow of the polymer occurred. This was in consequence of the weight of the inertia disc. In fact with many other such instruments (forced vibrations,[4] steady-state,[5] etc.) an upper limit in temperature is attained where lack of dimensional stability of the test specimen itself prevents further measurement. Other factors which may be considered as difficulties with dynamic mechanical measurements also exist. For example, specimen fabrication is usually tedious. Therefore the available methods may discourage the employment of these techniques in broad and rapid experimental testing.

In this work, a modification of current techniques was devised in an attempt to circumvent some of the difficulties. The approach involves the simple concept of supporting the polymer on a "mechanically inert" substrate and determining the dynamic mechanical properties of the composite. For example, when a polymer is coated onto a cotton thread or glass fiber braid, by a solution, hot melt, or thermosetting process, then this braid-filled polymer can be used as a supporting member for a torsional or flexural pendulum. Since the supporting material is chosen to be mechanically independent of temperature, the temperature transition behavior of the composite rod should reflect the behavior of the polymer which inhabits the interstices of the braid. Additionally, dynamic mechanical behavior of the polymers could be studied at much higher temperatures. In the rubbery

region, the inertia disc would be supported by the braid, and so these measurements could be extended to investigations on more rubbery and possibly fluid polymers. Thus the scope of applicability of current instruments could be increased.

Studies of dynamic mechanical properties of polymers coated onto metal strips[6–8] and quartz filaments[9] have been reported. Furthermore, the use of fabric braid as a polymer support has been demonstrated in the investigation of cure and glass transition behavior in previous publications.[10,11] These latter communications were, for the most part, introductory and illustrative of specific uses for the method. This present paper describes some of the more detailed work which was performed in an attempt to refine those measurements and to understand the controlling factors in them. In this regard, the parameters considered important in the interpretation of torsional braid measurements are discussed.

EXPERIMENTAL METHODS

Apparatus

A torsional braid apparatus has been designed for the study of the dynamic torsional modulus of supported polymers at low frequencies.[10] A schematic diagram of this device is given in Figure 1. The equipment is

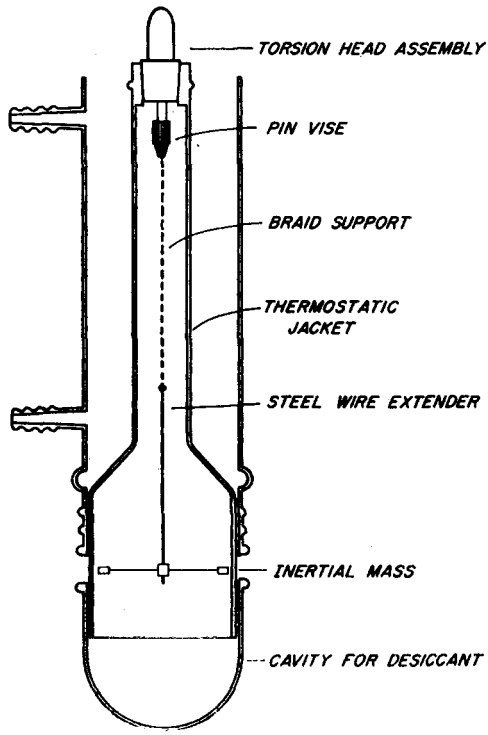

Fig. 1. Schematic diagram of torsional braid apparatus.

manually operated. Attempts to instrument this device for the automatic recording of time-amplitude decay curves were not successful by using available methods.[8] The stress level of the measurements using the fabric braid-supported polymers was too low for facile detection. Therefore, only the modulus of the supported polymer was determined from the observed resonance frequency.

Methods

In previous work,[10] it was pointed out that in a strict sense, the classical equations should not be applied to supported polymers. Therefore, a parameter was introduced, called the relative rigidity, which tended to normalize the data and render it independent of sample dimensions. However, for the present work, attempts have been made to analyze the torsional braid data from a more fundamental (quantitative) viewpoint. Such factors as the applicability of the classical equations and the effect of amount of polymer on the support and the braid length have been investigated.

In applying the classical equation to the modulus calculation of the braid-supported polymer the method of averaging the radius of the composite rod is very important. In the rigidity modulus equation $G = 8\pi lIf^2/r^4$, the radius of the rod, r, enters in as $(1/r^4)$, which makes r an extremely critical parameter. Since in most cases, the maintenance of a uniform radius of a braid-supported polymer is impossible, the employment of a proper averaging procedure for the radius must be resorted to. In this work, radii were measured along the rod at about 1 cm. intervals and averaged as $1/r^4$ along the 20 cm. sample length; l. This gave reproducible measurements of the modulus. It is felt that further refinements are possible by using a shape factor[15] in the equation. However, this was not attempted at this time.

The void fraction in the impregnated braid was determined from the difference in the volume as calculated from the actual physical dimensions $V_{act.}$ (averaging a series of r^2 values, where r is measured with a micrometer and using $V_{act.} = \pi(r^2)l$), and the volume of solids present. The volume of solids was determined by summing the volume of support material and polymer in the composite. The actual measured weight and known density of the individual components were used for this latter determination.

Materials

The polymers were applied by successively dipping the braid support into 10 or 20% by weight purified polymer in reagent grade benzene. The polystyrene was obtained as an unmodified thermally catalyzed polymer.[12] The poly(methyl methacrylate)(PMMA), and poly(*n*-butyl methacrylate) (PBMA), were prepared in this Laboratory using a suitable peroxide catalyst. The poly(ethyl methacrylate)(PEMA), was obtained from the Borden Monomer-Polymer Laboratories. All polymers were purified by dissolving and precipitating at least two times and then were dried in a

vacuum oven at 40 to 80°C. The intrinsic viscosities of these polymers were checked and were found to be in a high enough range to reflect the behavior above the critical entanglement molecular weight.

The cotton thread was Coats and Clark's O.N.T., extra strong, button and carpet thread. Before use, it was boiled for an hour in aqueous sodium carbonate (2%) and soap solution to remove sizing. The approximate dimensions of the torsional thread specimen used were 20 cm. length and 0.035 cm. radius. The mechanical properties of the uncoated cotton thread were found to be virtually independent of temperature up to about 260°C. The apparent torsional modulus of the thread was measured as 3×10^7 dynes/cm.^{2}.

TORSIONAL BRAID STUDIES

Experimental results of the temperature transition behavior of three poly(alkyl methacrylates), as measured on the torsional braid apparatus,

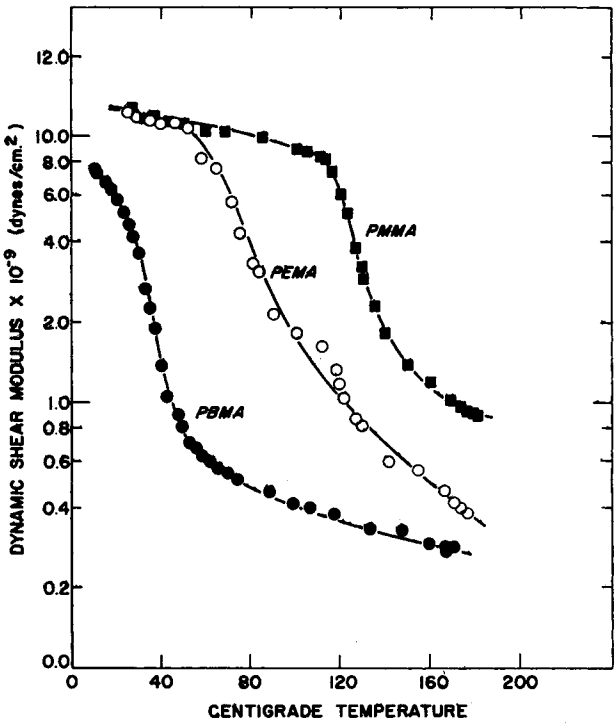

Fig. 2. Dynamic shear moduli of cotton thread filled poly(alkyl methacrylates).

are given in Figure 2. It is obvious that the modulus-temperature behavior of these supported polymers is similar to that of the unsupported polymers. However, the temperature run was carried out well into the rubbery region; to a much higher temperature than would be possible if the polymers were

TABLE I
Glass Transition Temperatures as Measured by Torsional Braid Method

Polymer	$T_{g(lit.)}$[b], °C.	$T_{g(obs.)}$, °C.	Average difference, °C.
PMMA	110	120–140	20
PEMA	62	70–90	18
PBMA	27	30–50	13
Polystyrene[a]	100	105–125	15
			Total average = 16°C.

[a] See Figure 3.
[b] Dilatometric values.

not supported. At present, the glass transition temperature can be estimated by the inflection in the modulus curve although this is not well defined. Table I gives a list of transition temperatures estimated in this way. The values are higher than literature (dilatometric) values by about 15°. A 10° rise in transition temperature can be attributed to the fact that a dynamic method is used (1 cycle/sec.). In addition, fillers are known to raise the transition temperature when measured using dynamical tests by another 5° or so.[18]

Of further interest in Figure 2 is the relative degree of stiffness of the polymers shown by the level of modulus obtained. Selecting the condition

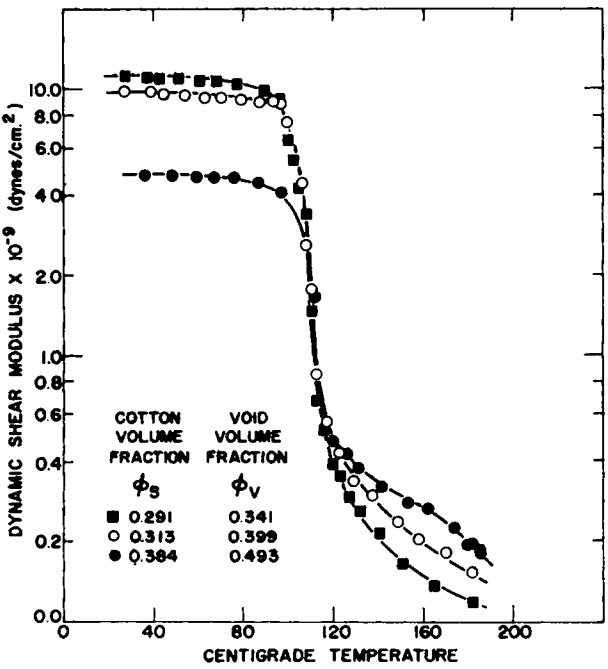

Fig. 3. Dynamic shear modulus of cotton thread filled polystyrene.

TABLE II
Effect of Volume Fraction of Voids and Cotton on the Measured Torsional Braid Modulus of Polystyrene

Glassy region			Rubbery region		
Sample designation	ϕ_v	$G \times 10^{-9}$ (dynes/cm.^{2}) at 30°C.	Sample designation	ϕ_s	$G \times 10^{-9}$ (dynes/cm.^{2}) at 170°C.[b]
1	0.540	3.8	10	0.180	0.060
2	0.517	4.1	6	0.203	0.090
3	0.493	4.8	4	0.284	0.152
4	0.407	9.0	8	0.219	0.130
5	0.399	9.8	5	0.313	0.189
6	0.383	8.8[a]	1	0.320	0.163
7	0.367	10.9	9	0.336	0.190
8	0.341	11.2	2	0.360	0.205
9	0.324	11.7	7	0.361	0.300
10	0.299	10.0[a]	3	0.384	0.240

[a] Spurious results excluded in the mathematical analysis of the data.
[b] All data used in mathematical analysis.

of room temperature, the rigidity of the series should be PMMA > PEMA >PBMA. This behavior is not followed by the data presented. Reasons for this were found to be attributed to the fact that the level of rigidity observed depends on the amount of polymer impregnated in the braid. Therefore, a study was conducted in order to establish more clearly what effect the amount of polymer on the braid has on the measured transition temperature and modulus. Some typical results are shown in Figure 3 for polystyrene. It appears that the transition temperature (as measured by the inflection) is independent of the amount of polymer on the braid. Of striking interest is the cross-over of the rigidity level as the polymer changes from the glassy to the rubbery state. Such a condition may well serve to confine the glass transition temperature estimation to a narrower range (see Table II).

Further investigation of the phenomenon has lead to an important concept for treating such data. This involves the approach which considers the supported polymer as a "filled" system. Analysis of the system from this viewpoint results in the conclusion that it is composed of three phases; a volume fraction of polymer ϕ_p, a volume fraction of support (braid, etc.) ϕ_s, and a volume fraction of voids ϕ_v. This analysis has been considered with respect to explaining Figure 3. It is proposed that in the glassy state, the pure (unfilled) glassy polymer would be more rigid than the braid-filled polymer. The reason for this is that voids are present in the latter system and lower the rigidity. On the other hand in the rubbery state, the braid is acting as a true support. Thus, the braid-filled rubbery polymer is stiffer than the pure (unfilled) rubbery polymer. Evidence to support this conclusion is found by the roughly linear correlation between (*a*) the measured modulus in the glassy region and the volume fraction of

voids and (*b*) the measured modulus in the rubbery region and the volume fraction of support. Such trends are shown in Table II for the polystyrene–cotton system. Note that the overall trends in the data reflect the fact that the volume fraction of voids, ϕ_v, controls the measured modulus in the glassy region and the volume fraction of cotton, ϕ_s, controls the modulus in the rubbery region. Additionally, ϕ_v and ϕ_s are *independent* quantities, meaning that the ϕ_v, setting the value of modulus in the glassy region, does not necessarily influence the level of modulus the sample will attain in the rubbery state. Although in Figure 3 the ϕ_v and ϕ_s show reciprocal trends with the rigidity data, this is fortuitous.

Of basic importance is the fact that the torsional braid rigidity modulus can be treated as polymer with the braid as a filler. Equations are known which describe the influence of fillers (as discrete particles) on the modulus of a composite filled polymer. In this present work an equation, which is a modification of the Eilers[14] type was found to fit the braid data reasonably well. This proposed expression is:

$$G/G_0 = 1 + \frac{k_s\phi_s + k_v\phi_v}{(1 - [S_s'\phi_s + S_v'\phi_v])^2} \tag{1}$$

where G is the measured modulus, ϕ_s and ϕ_v are the volume fraction of support and void, respectively, G_0 the shear modulus of the pure (unfilled) polymer, and k_s, k_v, S_s', and S_v' are constants. The constants in eq. (1) were determined from a mathematical analysis of the data in Table II by the least squares method. The results of this mathematical analysis are given in Table III. These parameters apply to the polystyrene–cotton thread system.

TABLE III
Least Squares Estimation of Parameters in Equation (1)
(Data from Table II) for Polystyrene–Cotton Thread System)

Condition	k_s	k_v	S_s'	S_v'	$G_0 \times 10^{-9}$ (dynes/cm.^{2})	$(\text{RMS}^a)^{1/2} \times 10^{-9}$
Glass, 30°C.	0.33	−0.43	1.15	0.40	13.4	0.3
Rubber,[b] 170°C.	−3.85	+10.38	2.92	−1.33	0.020	0.02

[a] Goodness of fit index; residual mean square.

[b] In the rubbery region, the parameters were not well determined. That is, many different compensating sets of values for the parameters can be found which will give equally good fits of the data.

During the mathematical treatment of the glassy data, two points in the data were found to be spurious and are so designated in Table II. These points were further investigated and it was discovered that they were

results of repeat experiments. Both were the results of attempts to put a large volume fraction of polymer into the braid. Upon closer examination, it was shown that these braids had the majority of the polymer coated on the outer periphery of the thread; furthermore, the cross section of the coated braid was irregular (shrinkage effects). This was an observation from which an important conclusion was drawn, i.e., in order to analyze supported polymer data according to the filler analogy, the amount of polymer in the composite must be controlled. The polymer must be impregnated into the braid, not coated onto it. In addition, the cross section of the composite must be maintained as circular as possible.

The data in the rubbery region were found to be more scattered than the glassy data. A possible reason for this scatter is that these numbers were compiled assuming temperature independence of the volume fraction values ϕ_s, ϕ_v, and ϕ_p. One would not expect this to be true, especially for the volume fraction of voids parameter. Therefore, the volume fraction values experimentally observed with the glassy composite, 30°C., may not be identical to those existing in the rubbery composite, 170°C. Nevertheless, both sets of data, glassy and rubbery, conformed reasonably well to eq. (1). In the glassy region, 30°C., $G_0 = 13.4 \times 10^9$ dynes/cm.^{2} which compares well with the literature value of 11×10^9 dynes/cm.^{2}.[13] The G_0 value in the rubbery region, 170°C., 0.020×10^9 dynes/cm.^{2}, could not be compared directly because no data of this kind are available in the literature. However, the value seems reasonable.

The effect of specimen length was also found to be important in torsional braid studies. With data obtained on cotton braid samples of different length, it was observed that a sharp decrease in modulus occurs below a specimen length of about 10 cm. This behavior is what would be expected when the sample is excessively strained. Here fatigue and mechanical failure in the composite structure would occur. It is therefore recommended that sample lengths be kept above about 15 cm. in cotton thread supported polymer studies. The greater the length, the less is the strain to which the sample is subjected. It is suggested that at the greater lengths the system approaches an idealized system.

CONCLUDING REMARKS

The content of this paper describes new approaches to the study of polymer properties. Here the use of the torsional braid device has been demonstrated for studying glass transition temperatures and to a less definitive extent the mechanical modulus of polymers. Of basic merit is the fact that only a small amount of sample (less than 0.1 g.) is required to make these measurements and that the apparatus is simple and easy to operate. However, limitations due to the qualitative nature of this method may always exist. Nevertheless, it is felt that useful information can be derived from such studies, but the exact interpretation of such measurements must await further understanding of the controlling parameters.

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Synopsis

An analysis of the parameters involved in torsional braid measurements is given. It is found that the amount of polymer on the braid controls the level of rigidity modulus attained by the composite specimen, but does not affect the measured glass transiton temperature of the polymer. Treating the torsional braid system as a fabric braid filled polymer system, an empirical relation is given relating the measured modulus, G, to the modulus of the unfilled polymer, G_0, and the volume fractions of voids, ϕ_v and support ϕ_s. This equation takes the form,

$$G/G_0 = [1 + (k_s\phi_s + k_v\phi_v)]/[1 - (S_s'\phi_s + S_v'\phi_v)]^2$$

where k_s, k_v, S_s', and S_v' are constants. This equation is evaluated for the polystyrene–cotton thread system. The effect of braid length on the measured modulus is discussed.

Résumé

On donne une analyse des paramètres contenus dans des mesures de torsion de tresses. On trouve que la quantité de polymère controle le niveau du module de rigidité atteint par les différents échantillons mais qu'elle n'influence pas la température de transition du polymère. Considérant le système de torsion comme un système de torsion formé d'un polymère et d'une charge, on donne une relation empirique qui relie le module mesuré (G) au module du polymère dépourvu de charge (G_0) et les fractions de volume des trous ϕ_v et du support ϕ_s. Cette équation prend la forme

$$G/G_0 = [(1 + (k_s\phi_s + k_v\phi_v)]/[1 - (S_s'\phi_s + S_v'\phi_v)]^2$$

où k_s, k_v, S_v', et S_s' sont des constantes. Cette équation est évaluée pour le système de fils de polystyrène–coton. On discute l'effet de la longueur de la tresse sur le module mesuré.

Zusammenfassung

Eine Analyse der bei Schnurtorsionsmessungen auftretenden Parameter wird gegeben. Die Menge des Polymeren in der Schnur bestimmt die Höhe des Steifigkeitsmoduls der zusammengesetzten Probe, hat aber auf die gemessene Glasumwandlungstemperatur des Polymeren keinen Einfluss. Zur Behandlung des Schnurtorsionsystems als eines mit Textilschnur gefüllten Polymersystems, wird eine empirische Beziehung zwischen dem gemessenen Modul, G, dem Modul des ungefüllten Polymeren, G_0, und dem Volumbruch an Leerstellen, ϕ_v, und Träger, ϕ_s, angegeben. Diese Gleichung lautet

$$G/G_0 = [1 + (k_s\phi_s + k_v\phi_v)]/[1 - (S_s'\phi_s + S_v'\phi_v)]^2$$

wo k_s, k_v, S_s' und S_v' Konstante sind. Diese Gleichung wird am System Polystyrol-Baumwollfaden ausgewertet. Der Einfluss der Schnurlänge auf den gemessenen Modul wird diskutiert.

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