Dynamic Analysis of Flat-Spring Supported Polymers

JIANFU DING, GI XUE,* and RONGSHI CHENG

Department of Chemistry, Nanjing University, Nanjing, 210008, The People's Republic of China

SYNOPSIS

A flat-spring supported sample technique has been developed for studying the dynamic mechanical properties of a polymer in all its mechanical states, especially for materials with insufficient tensile strength for tensile mode test. The results obtained by this new technique show good agreement with the data from tensile mode tests for poly(ethylene terephthalate) and polystyrene. A high crystallization rate in temperature region 110–160°C for a quenched poly(ethylene terephthalate) and a secondary relaxation at the temperature of 100°C above T_g for a monodispersed polystyrene with a molecular weight of 3×10^5 could be measured quantitatively by the flat-spring supported polymer technique. This is an important improvement over the existing supported sample techniques.

INTRODUCTION

Several sample supporting techniques have been reported both in studies of the viscoelastic properties of polymeric samples with insufficient strength, such as elastomeric materials and low molecular weight polymers, and in the studies of the reactions or other processes occurring in polymer melt, such as crosslinking reactions. A method which has been extensively used is "torsional braid analysis" (TBA) developed by Gillham et al.[1,2] It has been applied to measure the viscoelastic properties of polymers in the high temperature range, the effects of additives and the aging processes on polymers, the curing reaction of thermosetting resins, and the liquid–liquid relaxation of polymer melt.[3,4] However, this method suffers from a few disadvantages,[5] such as a lack of quantitative information about the complex modulus and its loss and storage components, difficulty in changing the test frequency for different tests, and variation of the test frequency during a single test.

As the dynamic viscoelastometer, Rheovibron, become more frequently used in investigating the viscoelastic behavior of polymers, more attention has been paid to developing new methods of supporting samples with low strength for the Rheovibron study. An interesting technique termed "dynamic spring analysis" (DSA), was described by Naganuma.[6,7] The investigated materials were supported by a spiral spring. This technique was employed in studying dynamic mechanical properties of amorphous polymers and the curing reactions of thermosetting resins. Later, the DSA technique was developed by Senich et al.[5,8] to obtain quantitative values of the storage and loss moduli of polymers. However, several disadvantages exist in this method. First, the agreement between the storage and loss moduli measured with DSA and those measured with a tensile mode test by Rheovibron was rather poor at the temperature below T_g. For example, the storage modulus of polystyrene film analyzed with the tensile mode by Rheovibron at 25°C is 10^{10} dynes/cm^2, whereas it was 3×10^7 dynes/cm^2 when measured with DSA. So, the reliability of the method for quantitatively analyzing DSA data in this technique could not be detected by the experimental results. Secondly, the spiral spring–polymer composites were prepared by applying polymer solutions on the spring skeleton. It is difficult to form a uniform sample with the helically coiled spring, and inhomogeneous samples might introduce errors and make for poor reproducibility in the measurements. Furthermore, since the composite samples must be made from polymer solutions, this technique is not suitable for crystal samples and nondissolvable polymers.

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 45, 987–991 (1992)
 CCC 0021-8995/92/060987-05$04.00

We improved the DSA technique by using a flat-spring instead of the helical one used by Naganuma.[6,7] The flat-spring polymer composite can be prepared by many conventional processing techniques such as moulding, casting, dipping from polymer solution or melt, and so on. The unique feature of this improvement is that the formed composite sheet could be made quite uniform by applying a thermal press. We called this improved technique "dynamic flat-spring analysis" (DFSA). DFSA made it possible to measure various kinds of polymers. Good agreement of the storage and loss moduli as measured by DFSA and a tensile mode test on a Rheovibron could be reached for polystyrene (PS) and for poly(ethylene terephthalate) (PET) over a wide temperature range. We expect that the DFSA technique can be applied to the quantitative study of the viscoelastic properties of various kinds of polymers, and of curing reactions, crystal processes, and polymer melt relaxation, and so on.

EXPERIMENTAL

Materials

PET film was used as purchased from Nanjing Chemical Com. PS was synthesized by an anionic polymerization, to give a product whose molecular weight (M_n) is 3.0×10^5 and having a molecular weight distribution (M_w/M_n) of 1.10.

Preparation of a Flat-Spring

The flat-spring was wound from a constantan wire with a diameter 0.2 mm. Its width was 2.0 mm and the pitch was 0.25 mm. as shown in Figure 1. The prepared spring was etched in a dilute HCl solution to remove surface oxides, rinsed with distilled water, and dried in nitrogen prior to use.

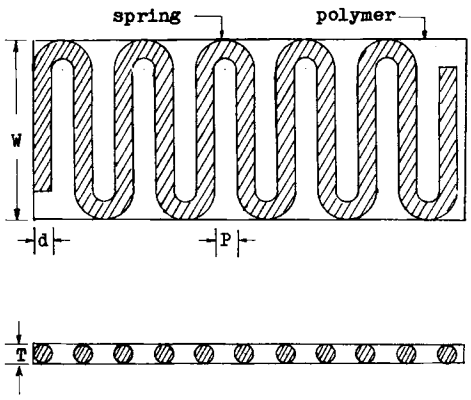

Figure 1 Schematic representation of a DFSA composite sample.

Preparation of Flat-Spring Polymer Composites

A cleaned flat-spring was sandwiched between two pieces of PET film each with 0.1 mm thickness. The sandwiched material was pressed between a pair of mold plates and gradually heated to the melting point of PET under vacuum; it was held at this point for 0.5 h. For an annealed sample, the heated material was cooled slowly to room temperature at a rate of 1°C/min, while for the quenched sample, the hot material was cooled quickly by immersing into an ice–water mixture.

PS was dissolved in chloroform. The solution was casted onto a flat-spring on a glass plate. After the solvent had evaporated, the sample was heated at 150°C for 3 h and then pressed in a mold at 150°C for 0.5 h. The composite then was cooled to room temperature at a rate of 1°C/min.

Each composite sample was cut to a width of 2.0 mm. The length is greater than 15 mm and the thickness equals the diameter of the spring wire.

Dynamic Mechanical Measurement

A Rheovibron DDV-II-EA dynamic viscoelastometer with common clamps was used to measure the mechanical properties for the flat–spring supported polymer and to do the tensile mode test for thin films. The measurement was performed in a nitrogen atmosphere from −150 to 250°C, with a heating rate of 2.0 or 1.0°C/min. The test frequencies were 3.5, 11, 35, and 110 Hz. The correction for instrument compliance was performed by Rheovibron automatically.[9]

RESULTS AND DISCUSSION

A Quantitative Analysis for DFSA with a Parallel Model

For the two-component system of the spring and the polymer, the dynamic mechanical behavior can be described with a parallel model.[5,6] If the length of the composite sample was L, and the strain of the sample was $\mathcal{E}$ during the mechanical measurement. The average length of polymer in the composite sample equals $(1 - \phi_s)L$ (ϕ_s is the volume fraction of the spring). The strain of polymer equals

$\mathcal{E}/(1-\phi_s)$, so the complex modulus of the spring-polymer composite can be expressed as:

$$E_c^* = \frac{1}{1-\phi_s} E_p^* + E_s^* \quad (1)$$

where E_c, E_p, and E_s represent the complex modulus of composite, polymer, and the spring, respectively.[10] The complex modulus can be separated into real and imaginary parts. Then the storage modulus of the polymer in the composite can be obtained from the following expression:

$$E'_p = (1-\phi_s)(E'_c - E'_s) \quad (2)$$

Since the response to stress of the spring can be seen to be totally elastic, its contribution to the composite loss behavior is small. The storage modulus and loss tangent of the spring were measured simultaneously at the frequencies 3.5, 11, 35, and 110 Hz, and the results are shown in Figure 2. It can be seen that the value of the storage modulus is 1.2×10^8 dynes/cm^2 and that in the range from ambient to 250°C, the loss modulus is 100 times less than the real part. So in the study of spring–polymer composites, we can neglect the contribution of the spring to the loss modulus. The loss modulus of the polymer can be expressed as,

$$E''_p = (1-\phi_s)E''_c \quad (3)$$

and the loss tangent of the polymer in the composite can be calculated from following expression:

$$\tan \delta_p = \frac{E''_c}{E'_c - E'_s} \quad (4)$$

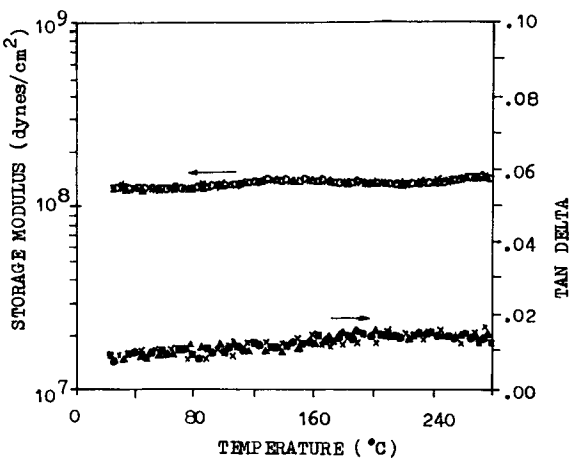

Figure 2 Storage modulus and loss tangent of the flat-spring as function of temperature: (□), (■) 3.5 Hz; (○), (●) 11 Hz; (*), (×) 35 Hz; (△), (▲) 110 Hz.

The loss tangent of the polymer and that of the composite have the following relationship:

$$\tan \delta_p = (1 - E'_s/E'_c)^{-1} \tan \delta_c \quad (5)$$

Comparison of DFSA and Tensile Mode Test of PET Sample

In order to verify the reliability of the DFSA technique, we measured the storage modulus and loss tangent of an unoriented PET sample. The results from both DFSA and the tensile mode test are shown in Figure 3. The two samples were subjected to the same heating history. They were heated at 280°C for 0.5 h and then slowly cooled to room temperature at a rate of 1°C/min. From Figure 3, we find that the storage modulus of PET calculated from DFSA data with Equation (2) coincides completely with the data obtained from the tensile mode test; the loss tangent and the positions of α- and β-relaxation show good agreement for both tests.

Besides showing excellent coincidence with the normal tensile mode test for storage modulus and loss tangent, DFSA exhibits its superiority in studying the dynamic mechanical properties of a quenched sample of semicrystal polymer. Since the crystallinity of a quenched sample is very low, this kind of polymer shows remarkable creep and elongation under tensile mode testing, and this measurement cannot be carried out at temperatures near T_g. DFSA can overcome this difficulty. Figure 4 compares the results from DFSA and a tensile mode test for a quenched PET. It is clear that the test by tensile mode can be sustained only to 95°C, while the DFSA can be performed to 250°C. The plot of loss tangent versus temperature shows two relaxation peaks in the temperature range from ambient to 250°C. They occur at 95°C and 135°C. The peak at 95°C corresponds to the glass transition of amorphous PET. According to the time–temperature superposition principle, the transition temperature of 95°C measured with a frequency of 110 Hz agrees with the value of 82°C by Thompson and Woods with 1.2 Hz.[11] The shoulder peak at 135°C is due to the segmental motion of the amorphous chains in the crystal domain which was formed during heating process. It is interesting to observe the curve of storage modulus versus temperature, where one can find that the value of the storage modulus increases with temperature from 110°C to 160°C. This indicates that PET shows a high crystallization rate in this temperature region. The measurement clearly displays the variation in modulus of the polymer sample with increasing crystallinity. This DFSA technique

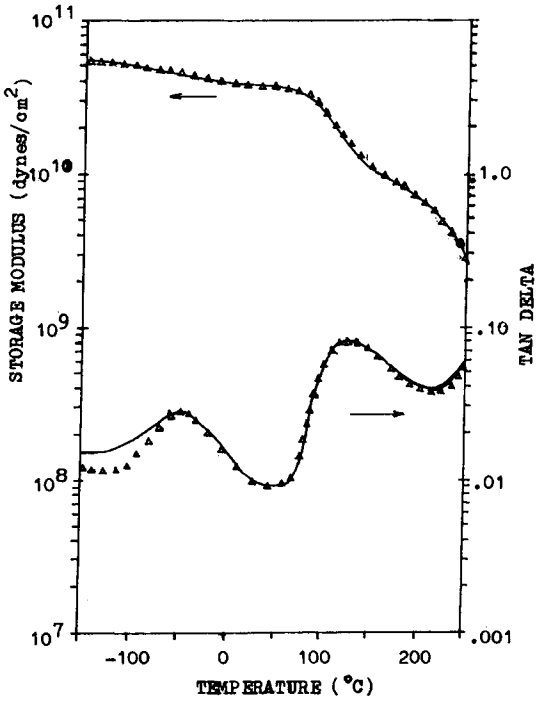

Figure 3 Storage modulus and loss tangent versus temperature of PET measured by (△) tensile mode test, and by (----) DFSA.

possesses a high potential for the study of crystallization processes of polymers.

Dynamic Mechanical Analysis of Polystyrene

For a nonpolar amorphous polymer such as polystyrene, dynamic mechanical analysis by the tensile mode test can be sustained only to a temperature near T_g; the determination of its glass transition temperature usually could not be made exactly. The DFSA technique shows its advantage in analyzing such a polymer. Figure 5 displays the curve of loss tangent and storage modulus versus temperature of a monodispersed PS, studied by DFSA. The measurement was performed with the frequencies of 3.5, 11, 35, and 110 Hz simultaneously. The plots of loss tangent show the glass transition at 117.5, 120.5, 123.5, and 128.0°C for the four different test frequencies.

At higher temperatures, another relaxation peak was found at 229, 236, 241, and 245°C with the test frequencies of 3.5, 11, 35, and 110 Hz respectively. This peak is due to the large scale movement of polymer chains, and corresponds to the transition from the rubbery state to the viscous flow region. It is usually considered that this transition has a strong dependence on molecular weight and its dispersion, with the higher molecular weight system having a higher transition temperature.

It is interesting to observe a third relaxation in the loss tangent curves below T_g. The peaks at 45°C and 80°C correspond to the test frequences of 110 Hz and 35 Hz, respectively. After reheating the same sample, it was revealed that this relaxation could not be reproduced, although the behavior of the loss tangent of glass relaxation did not change as compared to the first heating. We suggest that the relaxation observed below T_g corresponds to the internal stress existing in the interfacial region between the spring metal and the polymer. Thus, in order to get excellent results from DFSA, an annealing treatment for composite samples must be applied before the DFSA measurements are performed.

The plots of storage modulus (E') in Figure 5 show that the value of E' is larger with a higher measuring frequency in temperature region from −110°C to 250°C. This phenomenon parallels the result in the tensile mode test, and agrees with the time–temperature equivalence principle. An elastomeric plateau was also observed in the E' curve from 130°C to 180°C.

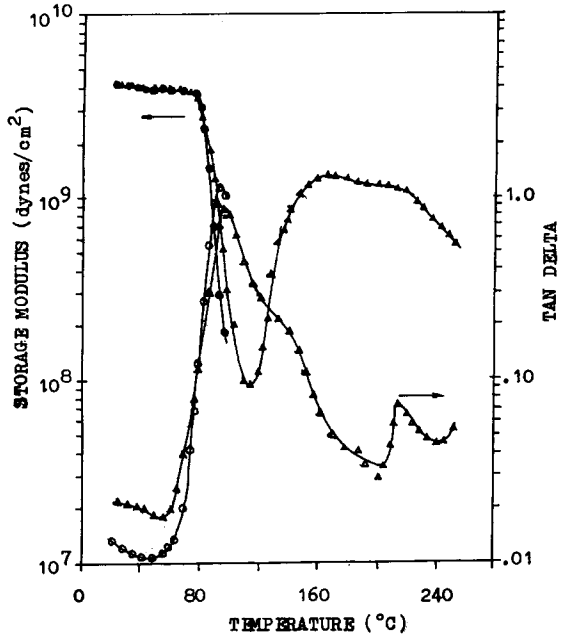

Figure 4 Storage modulus and loss tangent versus temperature of the quenched PET from (●), (○), a tensile mode test and (▲), (△) DFSA.

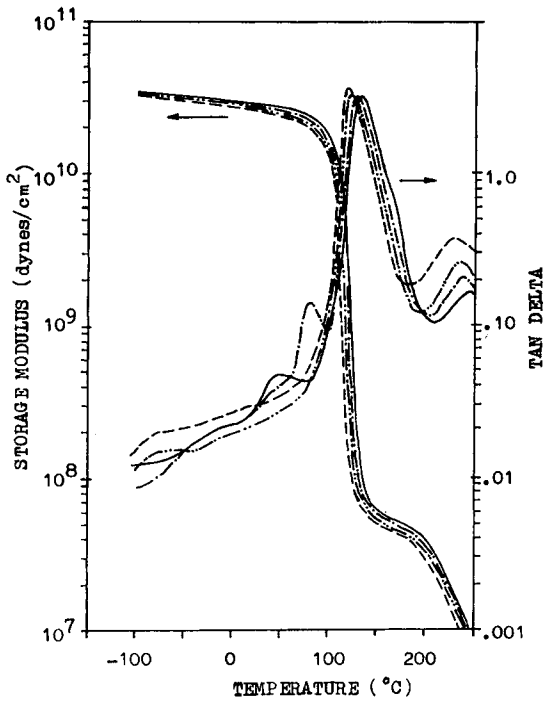

Figure 5 Storage modulus and loss tangent of PS from DFSA as function of temperature: (----) 3.5 Hz; (- · · - · ·) 11 Hz; (- · - ·) 35 Hz; and (——) 110 Hz.

CONCLUSION

We have demonstrated that the dynamic mechanical properties of polymers in all of their mechanical regions could be measured by use of flat–spring supported composites. This dynamic flat–spring analysis (DFSA) for polymers has advantages over torsional braid analysis (TBA)[1,2] and spiral-spring analysis (DSA).[6,7] The results from DFSA and from the tensile mode test on Rheovibron show good agreement. DFSA can be used to study the viscoelastic properties of materials with insufficient strength, such as quenched PET, and PS above T_g, while the tensile mode test is effective only below T_g.

The viscoelastic behavior of the quenched PET sample measured by DFSA displays an apparent crystallization process with a high rate at temperatures from 110°C to 160°C. In this region, the storage modulus increases with the increase in temperature. This technique applied to a monodisperse PS with a molecular weight of 3×10^5 shows a secondary relaxation at a temperature 100°C above T_g. Both results indicate that the DFSA technique has potential for investigating the mechanical properties of polymers above T_g.

REFERENCES

1. A. F. Lewis and J. K. Gillham, *J. Appl. Polym. Sci.*, **6,** 422 (1962).
2. J. K. Gillham, J. A. Benci, and R. F. Boyer, *Polym. Eng. Sci.*, **16,** 357 (1976).
3. R. F. Boyer, *Rubber Chem. Tech.*, **36,** 1303 (1963).
4. S. J. Stadnicki, J. K. Gillham, and R. T. Boyer, *J. Appl. Polym. Sci.*, **20,** 1245 (1976).
5. G. A. Senich and W. J. Macknight, *J. Appl. Polym. Sci.*, **22,** 2633 (1978).
6. S. Naganuma, T. Sakurai, Y. Takahashi, and S. Takahashi, *Kobunshi Kagaku,* **29,** 105 (1972).
7. S. Nagamuna, T. Sakurai, Y. Takahashi, and S. Takahashi, *Kobunshi Kagaku,* **29,** 519 (1972).
8. R. M. Neumann, G. A. Senich, and W. J. MacKnight, *Polym. Eng. Sci.*, **18,** 624 (1978).
9. D. J. Massa, *J. Appl. Phys.*, **44,** 2595 (1973).
10. C. Y. Yap and H. L. Williams, *Polym. Eng. Sci.*, **22,** 254 (1982).
11. A. B. Thompson and D. W. Woods, *Trans Faraday Soc.*, **52,** 1383 (1956).

Received April 1, 1991
Accepted August 30, 1991