Thermochimica Acta, 212 (1992) 189–195
Elsevier Science Publishers B.V., Amsterdam

Thermomechanical analysis of a segmented rigid-rod polyimide film [1]

Fred E. Arnold, Jr., Stephen Z.D. Cheng and Frank W. Harris

Institute and Department of Polymer Science, College of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH 44325-3909 (USA)

(Received 22 October 1991; accepted 26 May 1992)

Abstract

Thermomechanical analysis making use of an extension probe has been applied to characterize a series of organo-soluble segmented rigid-rod polyimide thin films. The polyimide discussed in this paper was synthesized from 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB). The polymerization was performed in refluxing *m*-cresol via a one-step process in which the poly(amic acids) were not isolated. The glass transition temperature (T_g) and the linear coefficient of thermal expansion (CTE) of 6FDA–PFMB along the film surface direction are studied at different applied tensile stresses. By extrapolation to zero stress, a T_g of 322°C and a CTE of 4.94×10^{-5} °C^{-1} are obtained.

INTRODUCTION

Thermomechanical analysis (TMA) can be used to determine the glass transition temperature (T_g) and the linear coefficient of thermal expansion (CTE) of amorphous and semicrystalline materials. The glass transition of bulk materials is usually measured by a penetration mode in which the sample is mounted under a pointed probe positioned perpendicular to the surface of the sample. The sample is then heated at a specified heating rate, and the temperature at which the probe penetrates the sample is defined as the glass transition temperature. After the glass transition temperature the probe reaches a constant rate of penetration.

Correspondence to: S.Z.D. Cheng, Institute and Department of Polymer Science, College of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH 44325-3909, USA.

[1] Presented at the 20th Annual NATAS Conference, Minneapolis, MN, 20–26 September 1991.

Although the glass transition temperature of a bulk material can be obtained via a penetration mode, if a material is brittle, as in the case of some high temperature thermosets or ceramics the degree of penetration of the probe does not produce an adequate signal. A compression mode can be utilized in which a flat probe is placed on top of the sample at a specified constant force and the material is then heated. As the material is heated an expansion will be observed. The compression mode will measure the bulk expansion perpendicular to the surface of the sample. However, it is extremely difficult to measure thermal expansion behavior perpendicular to the film surface because of the film thickness. In order to study the T_g and CTE in thin films with a typical thickness of 10–30 μm or single filaments with a typical diameter of 10–40 μm, an extension mode of TMA must be employed.

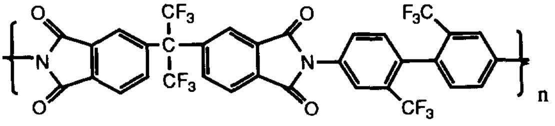
Thermomechanical analysis of unoriented thin films via an extension mode involves mounting the sample between two vertical clamps and applying a known tensile stress to the sample. The percentage elongation as a function of temperature is recorded. Upon heating, the material begins to expand in the direction of the applied stress. The CTE in the solid state is taken as the slope of the percent elongation versus temperature plot in the linear portion of the solidus line. Upon further heating, the relationship between the percentage of elongation and the temperature becomes transient and nonlinear before the liquidus line is reached. The onset temperature at which a dramatic increase in this nonlinearity occurs is the T_g. Both these two material parameters are dependent on the applied stress along the direction of the film surface.

It is essential with consideration of possible microelectronic applications to determine precisely the glass transition temperature as well as the linear coefficient of thermal expansion in polymeric thin films. Polyimide films are potential candidates for use in very large scale integrated circuits, which require a high glass transition temperature and a low coefficient of thermal expansion. In this paper we introduce our experimental procedure using the extension mode of a thermomechanical analyzer to obtain precise and reproducible values of T_g and CTE.

EXPERIMENTAL

Materials and sample preparation

Recently, a series of organo-soluble segmented rigid-rod polyimides have been synthesized in our laboratory [1]. The polyimide discussed in this paper was synthesized from 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB). The polymerization was conducted in refluxing *m*-cresol in a one-step process. The intermediate poly(amic acids) were thus not isolated. The chemical structure of 6FDA-PFMB is shown in Formula 1, and has a molecular weight of the repeating unit of 728.5 g mol^{-1}.



Formula 1.

6FDA–PFMB films were solution cast from a 2% (w/w) solution on a glass plate. The films were dried at 150°C for 5 h under reduced pressure in a vacuum oven and then heated for 3 h at 250°C. The thickness of the films ranges from 10 to 20 μm. Precise control of the concentration is necessary in order to control the final thickness of the films.

Equipment and experiments

A TA TMA 2940 thermomechanical analyzer was used to determine the glass transition temperature (T_g) and the coefficient of thermal expansion (CTE) of 6FDA–PFMB thin films. The films possess an in-plane anisotropic order in which the chain molecules are packed parallel to the film's surface, as observed through both transmission and reflection modes of wide angle X-ray diffraction experiments [2]. Thin ribbon-shaped samples with thicknesses ranging between 10 and 20 μm and a typical cross-sectional area of 0.033 mm^2 were mounted between two vertical clamps and a small initial stress was applied in order to keep the sample flat. The virgin film was then heated from 30 to 300°C at a heating rate of 25°C min^{-1} and held isothermally at 300°C for 5 min under a dry nitrogen atmosphere. After the heat treatment the sample was gently cooled back to room temperature in order to avoid thermal hysteresis [3]. In order to study the effect of the initial applied stress during the heat treatment, three different tensile stresses (0.5, 1.0 and 2.0 MPa) were applied to the 6FDA–PFMB films. After heat treatment the films were heated from 30 to 400°C at a heating rate of 15°C min^{-1}. Both the T_g and the CTE were measured as a function of the applied tensile stress in the region 30–400°C.

RESULTS AND DISCUSSION

Figure 1 shows a plot of T_g of 6FDA–PFMB versus the magnitude of the applied tensile stress in a stress region between 1 and 10 MPa (the samples have been heat treated with an initial applied stress of 1.0 MPa). As the applied stress is increased the glass transition temperature linearly shifts to lower values. The linear extrapolation yields a glass transition temperature at zero applied stress ($\sigma = 0$) of 322°C with a slope of 9.04°C MPa^{-1}. This slope illustrates how sensitive the glass transition temperature

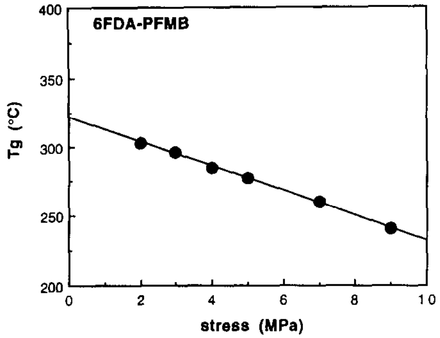


Fig. 1. Relationship between the glass transition temperature (T_g) and the applied stress for 6FDA-PFMB film.

is with respect to an applied stress. We speculate that this stress dependency of T_g should be associated with chain packing, chain rigidity and chain linearity. The microscopic explanation of the decrease in T_g with an increase in the applied stress was earlier suggested to be caused by an increase in free volume associated with an applied stress [4]. Quantitative treatment was proposed several years ago by Chow [5,6]. He predicted that, as σ (applied stress) becomes small and approaches zero, the glass transition temperature exhibits a linear dependence on the applied stress when the strain rate can be considered negligible. On the other hand, with increasing applied stress, the T_g decreases faster than this linear relationship and a nonlinear relationship evolves. Our results indicate that the stress range used in our experiments is still within the linear relationship between T_g and the applied stress. The extrapolated glass transition temperature agrees well with the T_g from the data obtained with differential scanning calorimetry [7].

Figure 2 shows the CTE (50–200°C range) as a function of the applied stress, with an initial applied stress of 1 MPa during the prior heat

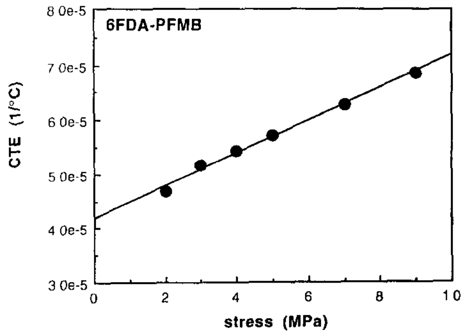


Fig. 2. Relationship between the linear coefficient of thermal expansion (CTE) and the applied stress for 6FDA-PFMB film.

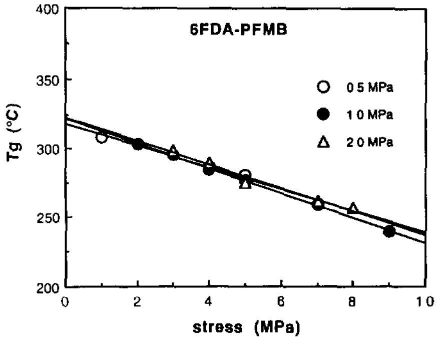


Fig. 3. Same relationship as in Fig. 1, but at three different initial stresses (0.5, 1.0 and 2.0 MPa) during the heat treatment.

treatment. As the magnitude of the applied stress is increased, the CTE in the solid state increases linearly in the stress region 1–10 MPa. In order to eliminate the stress dependence on the CTE it is necessary to extrapolate to zero stress. The extrapolated value obtained from Fig. 2 is a CTE of 4.18×10^{-5} °C^{-1}.

General understanding of the coefficient of thermal expansion relies on the intermolecular cohesive energy, chain rigidity and chain linearity. However, a quantitative relationship between CTE, chemical structure and molecular packing is still awaited. We speculate that the CTE in thin films is also affected by the in-plane anisotropic nature of the chain molecules.

Figures 3 and 4 illustrate the effect of the initial applied stress during the heat treatment on the T_g and the CTE for the 6FDA–PFMB films. It is evident that the different initial applied stresses do not significantly affect the glass transition temperature. Nevertheless, a stress dependence can be observed in the CTE data. For example, an extrapolated value of 4.59 ×

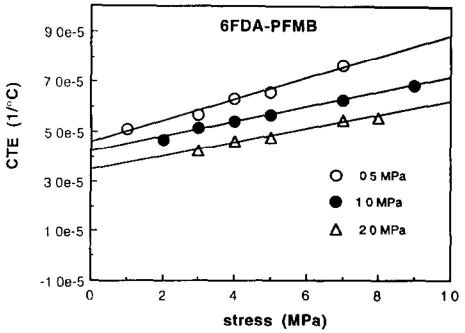


Fig. 4. Same relationship as in Fig. 2, but at three different initial stresses (0.5, 1.0 and 2.0 MPa) during the heat treatment.

10^{-5} °C^{-1} is observed when an initial stress of 0.5 MPa is used during the heat treatment, and a CTE of 3.48×10^{-5} °C^{-1} is observed using an initial stress of 2.0 MPa. Apparently, on increasing the initial stress during the heat treatment a decrease in the CTE can be observed. Extrapolating this initial stress to zero yields a CTE of 4.94×10^{-5} °C^{-1}, which agrees quite well that for with polyimides of similar molecular structure [8,9]. This behavior actually corresponds to that of a thin film with fixed edges during annealing. As a result, by increasing the applied stress during the heat treatment some additional anisotropy may be introduced into the film. This effect may also explain the difference in the slopes of the applied initial stress versus CTE data.

Furthermore, we expect that both the T_g and the CTE will exhibit anisotropic behavior when one measures the film along the directions parallel to and perpendicular to the film surface. Nevertheless, using TMA to measure the T_g and the CTE in the direction perpendicular to the film surface is difficult. We are presently designing a new approach to obtain both material parameters including those in the direction perpendicular to the surface of the film [10].

Finally, in the case of polyimides synthesized via a two-step process where the poly(amic acids) are isolated, it is important to concern ourselves with the effect of the imidization conditions, type of imidization (thermal or chemical), and thermal and mechanical histories previously applied. All these factors will influence the morphology, resulting in changes in the thermomechanical properties of the films.

CONCLUSIONS

Thermomechanical analysis via an extension probe enables us to investigate the linear coefficient of thermal expansion and the glass transition behavior of the 6FDA–PFMB thin film parallel to its surface direction. Both material parameters are dependent on the applied stress, and it is thus necessary to extrapolate to zero stress in order to remove the stress dependence. It is also important to take the thermal and mechanical histories of the film into account. This method can also be applied to CTE and T_g studies of other polyimide films.

ACKNOWLEDGMENTS

This work was partially supported by Hercules Inc. One of the authors (SZDC) gratefully acknowledges the support of his Presidential Young Investigator Award (DMR-91-57738) from the National Science Foundation.

REFERENCES

1 F.W. Harris and S.L.C. Hsu, High Perform. Polym., 1 (1989) 1.
2 S.Z.D. Cheng, F.E. Arnold, Jr., S.L.C. Hsu and F.W. Harris, Macromolecules, 24 (1991) 5856.
3 B. Wunderlich, Thermal Analysis, Academic Press, New York, 1990.
4 I.M. Ward, in Mechanical Properties of Solid Polymers, Wiley, New York, 1971, Chap. 11.
5 T.S. Chow, Polym. Eng. Sci., 24 (1984) 915, 1079.
6 T.S. Chow, J. Polym. Sci. Polym. Phys. Ed., 25 (1987) 137.
7 S.L.C. Hsu, PhD. Dissertation, University of Akron, 1991.
8 S. Numata and T. Miwa, Polymer, 30 (1989) 1170.
9 T. Matsura, Y. Hasuda, S. Nishi and N. Yamada, Macromolecules, (1991) 5001.
10 F.E. Arnold, Jr., S.Z.D. Cheng, J.C. Lee and F.W. Harris, Mater. Chem., submitted for publication.