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CHARACTERIZATION OF A POLYIMIDE SILOXANE BY THERMAL ANALYSIS *

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ABSTRACT

Films of a polyimide siloxane copolymer in a thickness of 20×10^{-3} in have been characterized using thermal analysis. The thermal stability and the kinetics of decomposition have been investigated by thermogravimetry. The activation energy of decomposition was calculated to be about 1.7 eV. The approximate lifetime of the copolymer at different elevated temperatures was also estimated. The glass transition has been mutually examined by differential scanning calorimetry, thermomechanical analysis, and dynamic mechanical analysis. It was found that the glass transition temperature depends not only on heating rates but also on loading conditions. It can be derived that the mechanism of the glass transition in this copolymer involves two interconnected steps, namely, volume change and phase ordering.

INTRODUCTION

Because of several advantages [1–4], such as low dielectric constant, superior adhesion, low moisture absorption, and ease of processing polyimide siloxanes have been recommended [1] for microelectronic applications such as protective overcoating and use as dielectric interlayers. Since polyimide siloxanes are thermoplastic segmented copolymers containing a siloxane segment along the backbone chain of the polyimide, it is expected that these copolymers maintain some of the excellent properties of polyimide, for example high temperature stability and mechanical strength, and some of the desirable properties of siloxane, such as ductility, adhesion, and low moisture permeability, as well as low water solubility. In addition, polyimide siloxanes are usually fully imidized [3] and can be dissolved in solvents having a lower boiling point, such as diglyme (b.p. 162°C). This can simplify the application process by replacing a prolonged polymer curing step at a high temperature with a baking procedure at a lower one. However, it requires sufficient understanding of this rather new material for appropriate applications. It is the intention of this paper to disclose some

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properties of this copolymer using thermal analysis, including thermogravimetry (TG), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA).

EXPERIMENTAL

The polyimide siloxane used in this study was purchased from Hüls. The material came in the form of solid rectangular sheets with approximate dimensions of 4 in ×5 in ×0.02 in and was prepared from the commercial product -SPI129 at 150 °C by drying out solvent (diglyme plus xylene) overnight. The testing samples were either punched (for TG, DSC, and TMA tests) or cut (for the DMA test) from the sheets. According to the data sheet of the material, this copolymer contains about 11% silicon. Its chemical structure should be similar to that given in ref. 1.

The thermal stability and the decomposition of the copolymer were measured using a Du Pont 951 thermogravimetric analyzer (TGA) under nitrogen environment at five different heating rates. The kinetics of the decomposition were analyzed using a Du Pont TGA decomposition kinetics program based on a rate equation of the following form

$$\frac{\mathrm{d}C}{\mathrm{d}t} = f(C)[Z\exp(-E/kT)] \qquad (1)$$

where C is the fraction reacted, $f(C)$ is a function of C and is assumed to be $1 - C$ for a first order reaction, Z is the pre-exponential factor, and E is the activation energy.

The glass transition temperature was cross-investigated using a Du Pont 910 differential scanning calorimeter (DSC), a 943 thermomechanical analyser (TMA) and a 983 dynamic mechanical analyzer (DMA). The tests of each module were also conducted at a series of different heating rates. Since these instruments (especially the TMA and DMA) show better sensitivity when the sample thickness is larger than 10×10^{-3} in, samples of approximately 20×10^{-3} in in thickness were used throughout the study.

RESULTS AND DISCUSSION

Figure 1 shows the decomposition curves measured by TG at five different heating rates. The activation energies at five different decomposition fractions (i.e. 5, 10, 15, 25, and 35% as indicated in Fig. 1) were calculated from the slope of the straight lines used to fit the relationship between the logarithm of heating rates and $1000/T$ as shown in Fig. 2. It was observed that above a decomposition fraction of 10% the activation energy of the decomposition reaches a constant value, namely about 1.74 ± 0.02 eV. Based

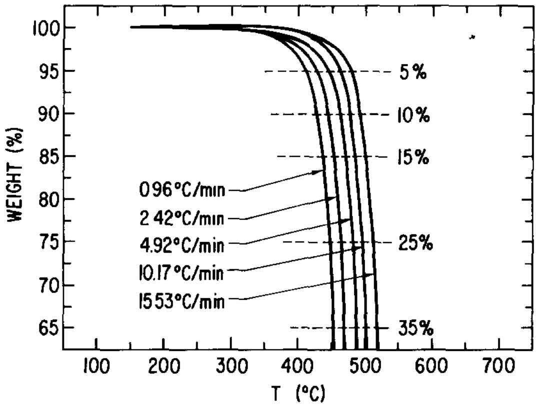

Fig. 1. TG measurements of decomposition of the as-received polyimide siloxane at five different heating rates.

on the activation energy at a decomposition fraction of 15%, the pre-exponential factor (Z) can be obtained and thus the lifetime of the copolymer at different elevated temperatures can be estimated, as shown in Fig. 3. For example, under a nitrogen environment this polyimide siloxane copolymer can last about 100 years at about 195 °C; in contrast it lasts only a couple of hours at about 400 °C. From a plot of lifetime versus temperature (Fig. 3), the thermal stability of the copolymer can be easily defined and the suitability of using this material in a particular application at elevated temperatures can be easily determined.

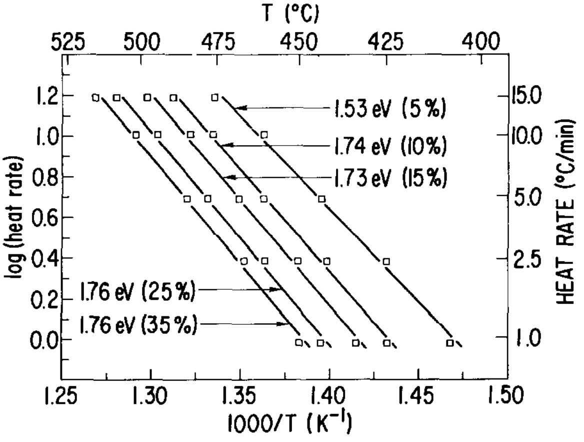

Fig. 2. Plots of log(heating rate) vs. 1000/T at the five different decomposition fractions indicated in Fig. 1, where T is the temperature. The activation energy associated with each decomposition fraction was calculated from the slope of the corresponding straight line fitted by linear regression analysis.

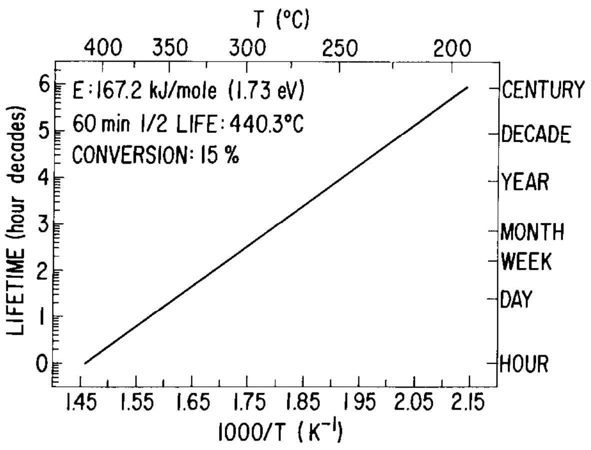

Fig. 3. Lifetime of the polyimide siloxane at elevated temperatures in a nitrogen environment.

Figure 4 shows the DSC thermograms at five different heating rates. It is readily apparant that the glass transition temperature of the copolymer is a function of heating rates and covers a range from 125 °C to 250 °C. However, it was found that the reproducibility of the DSC measurements was poor. For example, a couple of tests conducted at 10 °C min^{-1} showed a glass transition temperature at 143 °C instead of the 210 °C shown in Fig. 4. Although it is confusing, the structural non-uniformity and the influence of residual stress may be able to account for this discrepancy, especially when it is known that the samples used for the DSC tests were punched out from the sheet in the form of a circular disc having a diameter of about 3/16 in.

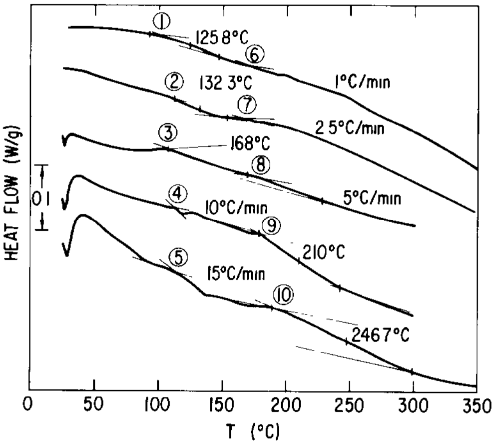

Fig. 4. DSC thermographs of as-received polyimide siloxane films tested at five different heating rates. Points ①-⑤ and ⑥-⑩ are lower and upper onset transition points respectively.

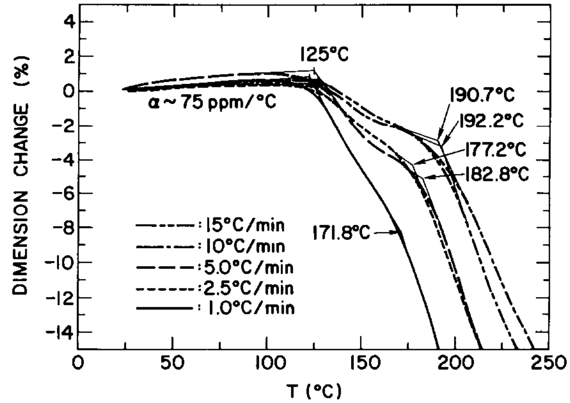

Fig. 5. Results of TMA tests at different heating rates.

Nevertheless, two sets of onset transition points can be roughly identified in Fig. 4, as indicated by points ①-⑤ and ⑥-⑩ respectively. And they do not depend on the heating rate, just as usually expected. If averages are taken, the lower onset point for the glass transition is about 109 ° C and the upper one is about 177 ° C. This indicates that there are either two phases or two different transformation steps involved in the glass transition.

TMA measurements were also made on samples in the shape of a circular disc (diameter 1/8 in) but under a load of about 11.5 g. This load was found to be necessary to guarantee the reproducibility of the results. Figure 5 shows that the material obviously has two transition points. One is at about 125 ° C, where the sign of the slope of the thermal expansion curve changes. Prior to this temperature, the thermal coefficient of expansion can be estimated to be $75 \pm 5 \times 10^{-6}\ {}^{\circ}C^{-1}$. The other is apparently a function of heating rates and is within the range 172–192° C, where an obvious shoulder is formed. The average is about 183° C, which is in agreement with the average upper onset point obtained in DSC measurements, (177 ° C). Since the results are reproducible, these two transition points are not artificial. The first transition at 125 ° C is apparently independent of the heating rate, and is presumably not a thermally activated process (contrary to the second transition).

Although a DMA frequency multiplexing test (covering a range of 0.075–7.5 Hz) showed that the internal friction (tan δ) spectra change with frequency as shown in Fig. 6, no well-defined relationship can be drawn from Fig. 6 since in most cases there is either no well-defined transition peak or the peak corresponds to an unreasonably high tan δ value. The reason for this is probably that the samples used in the present study are not sufficiently thick for conducting appropriate frequency multiplexing tests using the Du Pont DMA. Nevertheless, measurement at 2.5 Hz produced a smooth transition (Fig. 7) at a temperature comparable to those recorded in

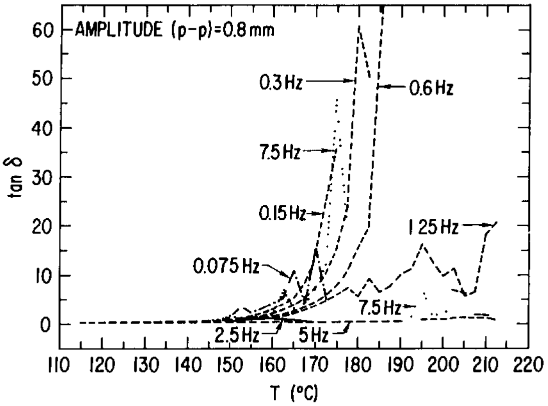

Fig. 6. Results of DMA frequency multiplexing (0.075–7.5 Hz) tests.

either DSC or TMA tests. It may be observed in Fig. 7 that after the transition temperature, the storage modulus as a function of temperature reversed its monotonous decreasing trend, reached a peak, and then returned to a descending trend at an apparently different rate from the one prior to the transition temperature. Based on a rough estimation, i.e. the modulus of the polymer in a glassy state is of the order of 1.0 GPa and that in a rubbery state is about one order of magnitude lower, i.e. 0.1 GPa, the transition shown in Fig. 7 is a strong indication of glass transition from a glassy to a rubbery state.

Furthermore, it was found that this transition temperature changes with the heating rate (Fig. 8). It is interesting to note that this heating rate dependence is more significant for heating rates greater than 2.0 °C min^{-1}. The activation energy of glass transition can be measured by plotting

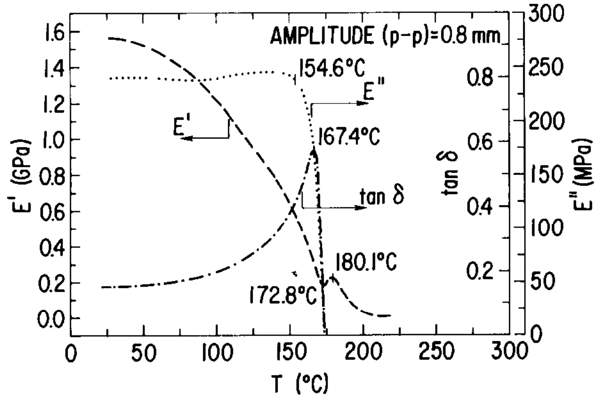

Fig. 7. A typical DMA result tested at 2.5 Hz. Here E' is the storage modulus, E'' the loss modulus, and tan δ the internal friction. The heating rate in this case is 5 °C min^{-1}.

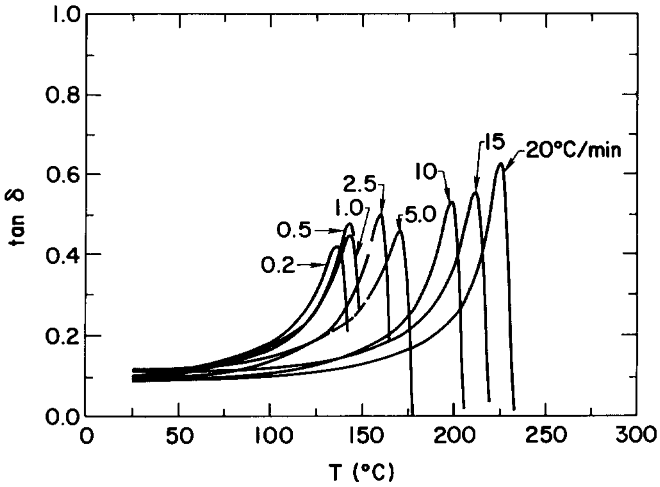

Fig. 8. Plots of tan δ vs. temperature as a function of heating rates for as-received samples.

$\ln[(\mathrm{d}T/\mathrm{d}t)/T^2]$ against $1/kT$, based on an analysis by Kissinger [5]

$$\mathrm{d}\left(\ln \frac{1}{T_\mathrm{m}^2}\frac{\mathrm{d}T}{\mathrm{d}t}\right)\Big/\mathrm{d}\left(\frac{1}{kT_\mathrm{m}}\right) = -E \qquad (2)$$

where T_m is the peak transition temperature, $\mathrm{d}T/\mathrm{d}t$ is the heating rate, E is the activation energy, and k is the Boltzmann constant. Figure 9 shows clearly that there are two mechanisms with two different activation energies associated with the glass transition. Also, the activation energies of these two mechanisms appear to be unaffected by thermal annealing at temperatures at or above T_g. Nevertheless, it is worth noting that the peak values of tan δ measured from the annealed samples (shown in Fig. 10) are significantly

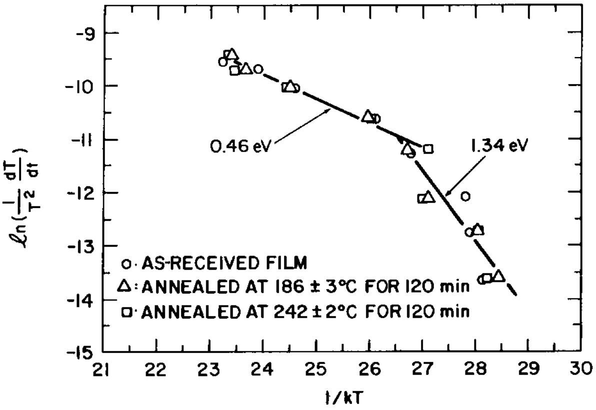

Fig. 9. Plot of $\ln[(\mathrm{d}T/\mathrm{d}t)/T_\mathrm{max}^2]$ vs. $1/kT_\mathrm{max}$, where T_max is the peak transition temperature. The activation energies obtained from the slope of the lines are indicated.

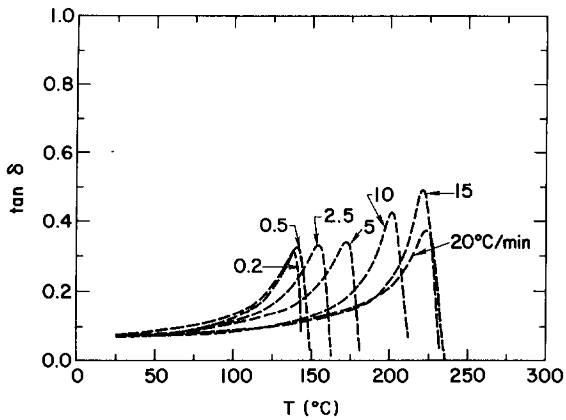

Fig. 10. Plots of tan δ vs. temperature as a function of heating rates for annealed samples, which were annealed at 242 ± 2° C for 120 min.

smaller than those obtained from the as-received samples. This indicates that in annealed samples the number of transformation events is dramatically reduced.

It is well known that as well as deformation, free volume plays an important role in glass transitions in polymeric materials. Furthermore, the dimension yield can result from a non-thermally activated process. For example, the material can be plastically drawn at room temperature once the load goes beyond the yield stress level. Apparently, the transition with a change in dimension from expansion to contraction at 125° C shown in Fig. 5 is a result of yielding, where the applied load (11.5 g) reached a yield stress level (similar to a compressive test conducted at an elevated temperature). Since the transition at this point is not thermally activated, no phase transition is expected, but only ensemble-free volume squeezing-out (or out-diffusion). The second transition in the range 170–200° C measured by TMA is apparently a phase transition having an activation energy (of about 2.13 eV) and the required dilation [6,7] (corresponding to the shoulder formation) for transformations (or ordering) to occur.

In DMA measurements, the sample is subjected to an alternating tensile and compressive dynamic force as a result of the sample being tested in an oscillating flexure mode. Based on the above analysis of TMA results, under conditions of no static tensile or compressive load the glass transition can be assumed to occur with both free-volume out-diffusion and ordering (or phase transition) simultaneously. This can be verified by the DMA measurements. For both as-received (Fig. 8) and annealed samples (Fig. 10), there is a tendency that at a higher heating rate the transition occurs at a higher temperature with a higher tan δ value. It may also be noted that the transition at higher heating rates (with an activation energy of 0.46 eV) occurs much more readily than the one at lower heating rates (with an activation energy of 1.34 eV). This can be explained as follows. At higher heating rates, besides the effect of temperature lag, the structure of the material may not be able to respond in time by diffusing enough free volume out and conducting sufficient ordering simultaneously. When the temperature reaches a critical point all remaining transformations (including the delayed ones) will occur spontaneously. Since at a higher heating rate there will be more delayed transformation events, at the critical temperature the transformation signal (tan δ) will be higher. In addition, based on an understanding obtained from a glassy bubble raft [6], a transition having a lower activation energy can correspond to a transformation site having a larger free volume. This is exactly the case for the transition at higher heating rates. Since a larger amount of free volume remains in the material owing to delayed material response, the main transition can occur much more easily, with a lower activation energy. In contrast, for lower heating rates (less than 2 °C min^{-1}) the material responds in step with the temperature rises by diffusing out comparably large amounts of free volume and proceeding with gradual ordering at lower elevated temperatures. The spontaneous transition thus occurs at a lower temperature with a higher activation energy and with a lower transformation signal (since there are fewer delayed transformation events).

In addition, from the dramatically reduced signal given by the annealed samples in DMA (Figs. 8 and 10) tests, we may conclude that thermal annealing at an elevated temperature can significantly reduce the number of transformation events. Nevertheless, structural investigation is required in order to determine whether the decrease in the number of transformation events merely results from annealed-out free volume together with ordering, or additionally is caused by further polymerization or cross-linking.

By plotting $\ln[(\mathrm{d}T/\mathrm{d}t)/T_g^2]$ versus $1/kT_g$ (where T_g is the glass transition temperature), we may obtain from eqn. (2) an activation energy of 2.13 eV for TMA measurements (Fig. 5) and 0.21 eV for DSC measurements (with heating rates greater than 2.5 °C min^{-1}) (Fig. 4). These are different from that obtained from DMA tests. The discrepancy probably results from the different loading conditions for different types of measurement. For instance, the samples in the TMA tests were under a compressive force, the DSC samples were in open pans and thus were not subjected to a force, and the samples in the DMA tests were under an oscillating force. Since a compressive force tends to hinder the transformations associated with the glass transition by reducing the amount of free volume, it is a reasonable conclusion that under a compressive force the glass transition requires a much higher activation energy than that under no load.

Furthermore, it can be discerned easily from all three thermal analytical techniques that higher heating rates are more suitable for detecting the upper transition temperature and, in contrast, the lower transition temperature is more easily identified with lower heating rates. It was found that

$T_g(U)/T_g(L) \approx 1.18$ for DSC, 1.15 for TMA, and 1.21 for DMA (where $T_g(U)$ is the upper glass transition temperature and $T_g(L)$ is the lower one). Since this fits a general rule for semicrystalline polymers [8], i.e. $T_g(U)/T_g(L) \approx 1.1$–$1.3$, it may be concluded that this segmented copolymer behaves more or less as a semicrystalline (homo)polymer.

CONCLUSIONS

The thermal stability and decomposition kinetics of a polyimide siloxane were analyzed using TG. The activation energy of decomposition was found to be about 1.7 eV, and the lifetime at different elevated temperatures was estimated. The glass transition of the copolymer was determined by DSC, TMA, and DMA techniques and was found to be a function of heating rates and load conditions. By cross-analyzing the results obtained from these methods, a mechanism of glass transition involving free-volume out-diffusion and phase ordering can be derived.

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REFERENCES

1 G.C. Davis, B.A. Heath and G. Gildenblat, G.E. Technical Information Series, No. 82CRD331, 1982.
2 Altisil SPI-100 Series, Polyimide Siloxane Preliminary Data Sheet and User Guidelines, G.E. Microelectronic Materials.
3 C.J. Lee, J. Electron. Mater., 18 (1989) 313.
4 C.A. Arnold, J.D. Summers, Y.P. Chen, R.H. Bott, D. Chen and J.E. McGrath, Polymer, 30 (1989) 986.
5 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
6 A.S. Argon, in D.R. Uhlmann and N.J. Kreidl (Eds.), Glass: Science and Technology, Vol. 5, Academic Press, New York, 1980, p. 79.
7 A.S. Argon and L.T. Shi, Phil. Mag. A, 46 (1982) 275.
8 D.W. van Krevelen and P.J. Hoftyzer, Properties of Polymers, Elsevier, Amsterdam, 1976, p. 126.