TA Instruments
Thermal Analysis & Rheology

MEASUREMENT OF THE PHYSICAL PROPERTIES OF ENGINEERING THERMOPLASTICS USING THERMAL ANALYSIS

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INTRODUCTION

Thermal Analysis is the generic name for a series of measurement techniques traditionally used to determine changes in material properties with temperature. Common thermal analysis techniques include:

- Differential Scanning Calorimetry (DSC) - is the most widely used thermal analysis technique. DSC measures the heat flow in materials and provides information about phase changes (amorphous and crystalline transitions) as well as chemical changes (degradation and reactions).

- Thermogravimetric Analysis (TGA) - measures weight changes associated with thermal events. While TGA is most commonly used to determine compositional analysis, it is also valuable for determining thermal stability. Furthermore, by analyzing multiple TGA curves obtained under different heating rates, it is possible to predict long-term as well as short-term thermal stability.

- Dynamic Mechanical Analysis (DMA) - measures the storage or elastic modulus and the loss or viscous modulus of materials subjected to sinusoidal or static stresses.

- Dielectric Analysis (DEA) - is the electrical analog of DMA in which the current (phase and magnitude) resulting from a sinusoidally imposed voltage are measured. Because mechanical and electrical properties are highly sensitive to small changes in material internal structures, DMA and DEA are more sensitive to low energy transitions, such as the glass transitions of filled epoxy systems, than are other thermal analysis methods. The static stress modes of the DMA further allow long term strength forecasts to be made using the creep or stress relaxation methods at elevated temperatures.

In this paper, the short-term and long-term physical properties of two engineering thermoplastics are explored. The results illustrate the value of thermal analysis for characterizing thermoplastic materials.

THEORY

Short term properties are those instantaneous material values measured over short durations of time. Since polymer properties can change with time, the measurement of properties at one point in time does not ensure that the material will behave similarly at a future time. Fortunately, however, predictions of future behavior can often be made by performing several short term experiments and then analyzing the data using kinetic treatments. This type of predictive testing is most common for thermal degradation and mechanical strength.

Thermal degradation often follows the Arrhenius kinetics model:

$$d\alpha/dt = f(\alpha)\ [Z\exp(-Ea/RT)] \qquad (1)$$

Where α is the fraction of weight lost, $f(\alpha)$ is a function of α not dependent on temperature, Z is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant, t is time and T is Temperature.

At a constant heating rate, $d\alpha/dt = d\alpha/dT*\beta$, where β is the heating rate, Flynn and Wall [1] derived that the activation energy has a small deviation from standard Arrhenius kinetics such that:

$$Ea = -(R/b)\ d(1n\beta)\ /d(1/T) \qquad (2)$$

Where b is an empirically calculated factor (0.457). By plotting the log heating rate against the inverse temperature of a particular weight loss (typically 5%) for several heating rates, the activation energy can be found from the slope of the best fit line. (See Figures 1 and 2)

An alternative method developed by Toops [2] for determining the estimated lifetime from activation energy measurements yields thermal degradation quantities such as 60 minute half-life and time-temperature degradation levels under isothermal conditions. This method is discussed in detail elsewhere [3]. The results of this method have compared well to traditional oven aging tests [4].

Prediction of mechanical properties uses the principle of time-temperature superpositioning, which states that the viscoelastic properties of polymers are interdependent on both time and temperature [5] and that there is an equivalency between the effects of time and temperature [6]. Thus, data collected at one temperature can be superimposed on data at a different temperature by shifting one of the curves along the time axis. In this study the viscoelastic function measured is flexural creep, in which bending displacement of a sample under constant load is measured over time. The measurement temperature is held constant for each experiment and the creep modulus is measured at several temperatures.

The degree of time shifting of the creep curves with respect to a reference can be described by several models. Two such models are the Williams-Landel-Ferry (WLF) equation [7] and the Arrhenius activation model. In this study, the Arrhenius model is used, as it is generally accepted that changes in materials below the glass transition temperature follow simple activation kinetics. The Arrhenius relationship is:

$$\ln(a) = \frac{-Ea}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \qquad (3)$$

Where a is the shift factor of each curve, T is the temperature of the shifted curve, and To is the reference temperature. Using this relationship, the creep compliance or modulus can be predicted over several years from data at elevated temperatures with results comparable to traditional testing [8].

EXPERIMENTAL

The samples for this study were two engineering thermoplastic materials, polyphenylene sulfide (PPS) and polyetherimide (PEI), molded for ASTM tensile tests ("dogbones" per ASTM D638) or flexure tests (ASTM D790). Samples were cut from these molded bars to sizes appropriate for the particular test as noted.

For DSC, 10 mg pieces were crimped into standard aluminum DSC pans. The TA Instruments DSC 2910 with cooling head assembly and Liquid Nitrogen Cooling Accessory (LNCA) was used to perform DSC heating and cooling experiments. Nitrogen purged the DSC cell area at 50 ml/minute. The samples were heated from 0°C to 400°C at 20° C/minute, cooled to 0°C at 10°C/minute and reheated at 20°C/minute to 400°C.

TGA samples, typically 10 mg pieces were loaded onto pre-tared platinum pans on the Hi-Res™ TGA 2950 Autosampler. These samples were heated at rates of 1°C/minute, 5°C/minute and 10°C/minute. The "Abort Next Segment" method segment was used to stop each experiment at 25% weight loss to limit the total time of experimentation.

For the DEA experiments, the thermoplastic materials were pulverized to fine powders in a freezer mill, and then pressed into the ceramic single surface sensor of the DEA 2970 by applying 350 to 500 N of force while heating to 350°C. The dielectric properties were measured during a second heating to 350°C at 3°C/min. Frequencies of 1 Hz to 100 kHz were employed.

DMA samples, typically 40 mm long by 12.5 mm wide by 3.1 mm thick, were cut from the ASTM samples and sanded on the faces to remove the mold shrinkage region and to homogenize the thickness dimension. Samples were mounted in the standard vertical clamps (serrated faces) of the DMA 983 and clamping calibrations were performed according to the method of Reed and Dean [9]. Two series of experiments were performed: fixed frequency temperature scans and elevated temperature creep experiments. In the former, samples were oscillated at 1 Hz with a oscillation amplitude of 0.3 mm corresponding to an approximate 0.1% flexural strain. The DMA 983 oscillates with a constant strain amplitude. The temperature was ramped at 3°C/minute to 275°C. Creep experiments were performed at stress levels of approximately 3 MPa. Experiments were performed at 2.5°C intervals, starting at 20°C and ending at 110°C (PPS) or 170°C (PEI). At each temperature step, the samples were first held for 20 minutes to ensure thermal and mechanical equilibration, then stress was applied for 20 minutes and finally creep recovery was followed for 20 minutes.

RESULTS AND DISCUSSION

SHORT TERM PROPERTIES

The results of the DSC, DMA fixed frequency, and DEA experiments can be seen in Figures 3 to 7. In thermoplastics, the characteristics most important to processing and end-use are the temperature and enthalpy associated with the crystalline melt and/or the glass transition temperature. As can be seen in these thermal curves, the DSC is more sensitive to melting and crystallization, while DEA and DMA are more sensitive to the glass transition. Key quantitative results from the curves are summarized in Table 1.

In addition to the transitions listed in Table 1, a noticeable β transition occurs in the PEI material in the vicinity of 95 to 125°C as can be seen in the DMA and DEA loss curves (Figures 3 to 6).

Table 1 - Material Properties

	PPS	PEI
Tm - DSC melt peak	280.2°C	323.6°C
Melt endotherm heat flow	17.5 J/g	3.17 J/g
Tc - crystallization onset	208.6°C	271.6°C
Heat of crystallization	14.7 J/g	2.76 J/g
Tg - DSC inflection	125.6°C	218.9°C
DMA E' onset	97.3°C	213.3°C
DMA E" peak	124.9°C	223.3°C
DMA Tan δ peak	135.0°C	236.6°C
DEA e" peak (1 kHz)	110°C	237.5°C
Storage modulus at 25°C	16.8 GPa	3.86 GPa
Manufacturers' values		
DTUL (ASTM D648)	>260°C	200°C
Temperature index (UL 746B)	200°C	77°C
Flexural modulus (ASTM D790)	15.8 GPa	2.9 GPa

LONG-TERM THERMAL STABILITY

The TGA thermal degradation curve (early stages of decomposition) for PPS is shown in Figure 8. Using the Flynn and Wall evaluation, the service life curve (Figure 9) can be obtained, as well as the decomposition activation energy (Ea) and the 60 minute half life. The activation energy is used as an indicator of relative material stability (a higher Ea indicates a more stable material). The 60 minute half life is the temperature at which half the material degrades within 60 minutes. The service life curve depends on the condition chosen, but in this case it is the time required for 5% of the material to degrade at a specific temperature. Table 2 compares these parameters for PPS and PEI.

Table 2 - TGA Service Life

	PPS	PEI
60 minute half-life temp.	430°C	477°C
TGA service temp. (1 year)	230°C	318°C
TGA service temp. (10 year)	205°C	292°C
Activation energy	170 kJ/mol	273 kJ/mol

LONG TERM MECHANICAL PROPERTIES

Figures 10 and 11 show the flexural creep curves for PPS and PEI respectively resulting from Time-Temperature superposition evaluation of the raw DMA data. These curves are plotted as log creep modules (1/s) versus log time. 25°C and 50°C are the end-use temperatures chosen for comparison. Figure 12 shows the shift factor curves which help explain the kinetics of the creep behavior observed. Key values are highlighted in Table 3.

Table 3 - Creep Modulus Values

		PPS	PEI
Modulus, 25°C,	1 hour	15.7 GPa	3.08 GPa
	1 year	15.4 GPa	2.88 GPa
	30 years*	15.4 GPa	2.30 GPa
Modulus, 50°C,	1 hour	15.4 GPa	2.94 GPa
	1 year*	14.4 GPa	2.3 GPa
	30 years	13.2 GPa	
Activation energy		442 kJ/mol	92 kJ/mol

* - to maximum time predictable with experimental conditions.

CONCLUSIONS

The most important differences between PPS and PEI are the composition and relative crystallinity, which control the physical and chemical properties of the polymers. These significant differences can be exploited in end-use applications.

PPS has a relatively low glass transition temperature . However a significant portion of this compound is crystalline, as can be seen by the relative sizes of the glass transition and melting peak in DSC. This accounts for its high modulus and low creep. The processing temperature is in the 300°C range, slightly above the crystalline melting at 280°C.

The PEI has a much higher fraction of amorphous phase as reflected in a low heat of fusion and strong glass transition. However, the Tg is quite high, which indicates a high stability material. This material could be processed either around 250-275°C or above 350°C, depending on the viscosities of the material in these ranges. The DEA ionic conductivity of PEI (not shown) is approximately 1000 times greater at 350°C than at 250°C. Since viscosity is inversely proportional to conductivity, the material should flow much more readily at 350°C, though the absolute viscosity at lower temperatures may still be suitable for certain processing situations.

Service temperature and material lifetime are functions of composition and crystallinity. A material's maximum service temperature is described by three functions: the modulus of the material, the temperature and rate of thermal degradation, and the long term creep properties. PPS has high strength up to 225°C. The modulus decreases over that temperature range from 16 GPa to 6 GPa, which is still quite strong. Furthermore, the decay of creep modulus at 50°C over 30 years is less than 15%, which also indicates good retention of strength. Further creep or stress relaxation studies at higher temperatures are warranted. The maximum service temperature based on a 5% material loss over 30 years is also in the 200°C range. Thus, the thermal stability of the PPS is quite good, and a high service temperature can be expected, assuming high chemical resistance.

The temperature range of PEI may be somewhat more limited. Although the glass transition is higher, the material strength drops to a small fraction of its room temperature value at the glass transition. Thus, although PEI has much better resistance to thermal degradation than does the PPS, the maximum temperature may be limited to well below 200°C.

The creep behavior of PEI at low temperatures is dominated by the β transition at ca. 100°C rather than the glass transition. The low activation energy of this transition results in high stability at lower temperatures, such that PEI has low creep motion with almost no change in behavior (creep % and strength) until well above 100°C. Closer to the glass transition, however, the behavior does begin to change and the material begins to creep significantly. Hence, as expected, Figure 11 shows modest changes in creep behavior at the temperature used in this study.

REFERENCES

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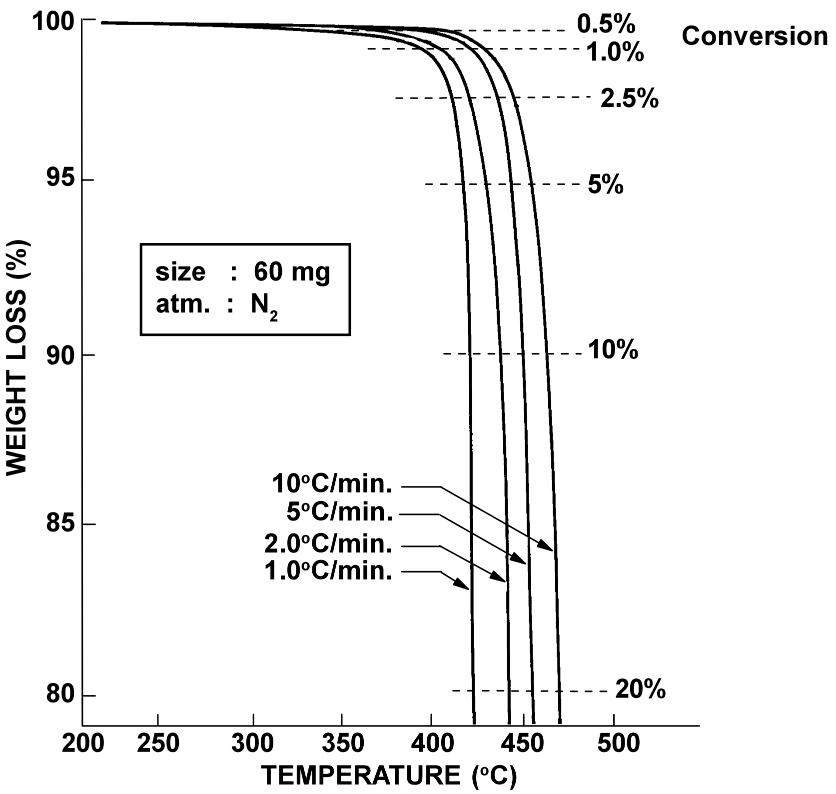

Figure 1. **WIRE INSULATION THERMAL STABILITY**

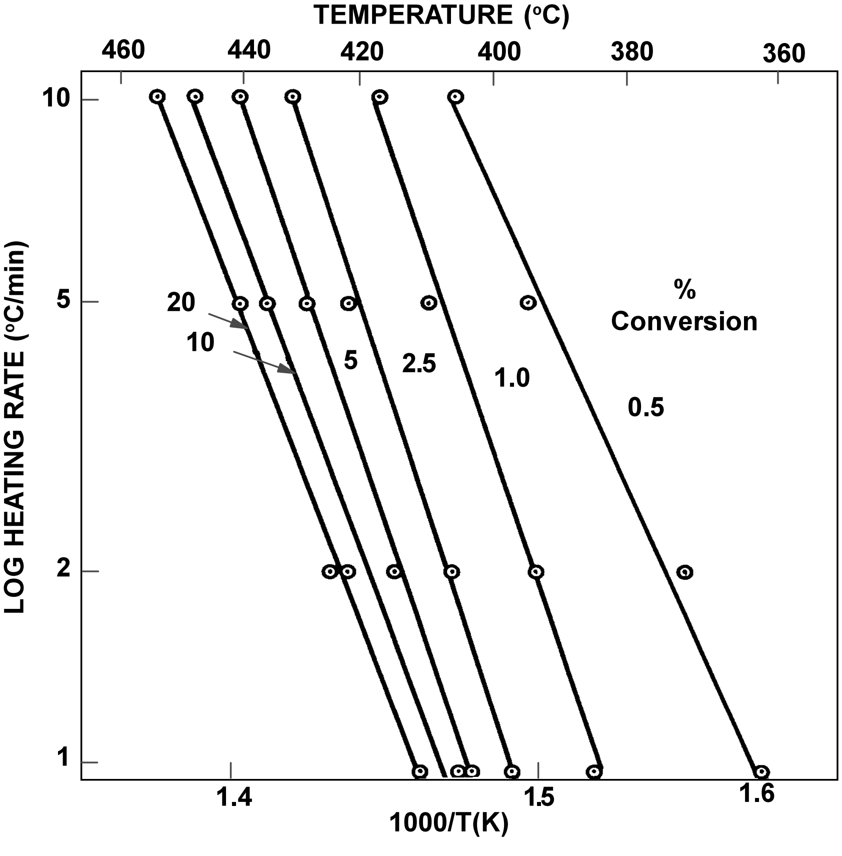

Figure 2. **LOG HEATING RATE VS. TEMPERATURE OF CONSTANT CONVERSION**
(WIRE INSULATION)

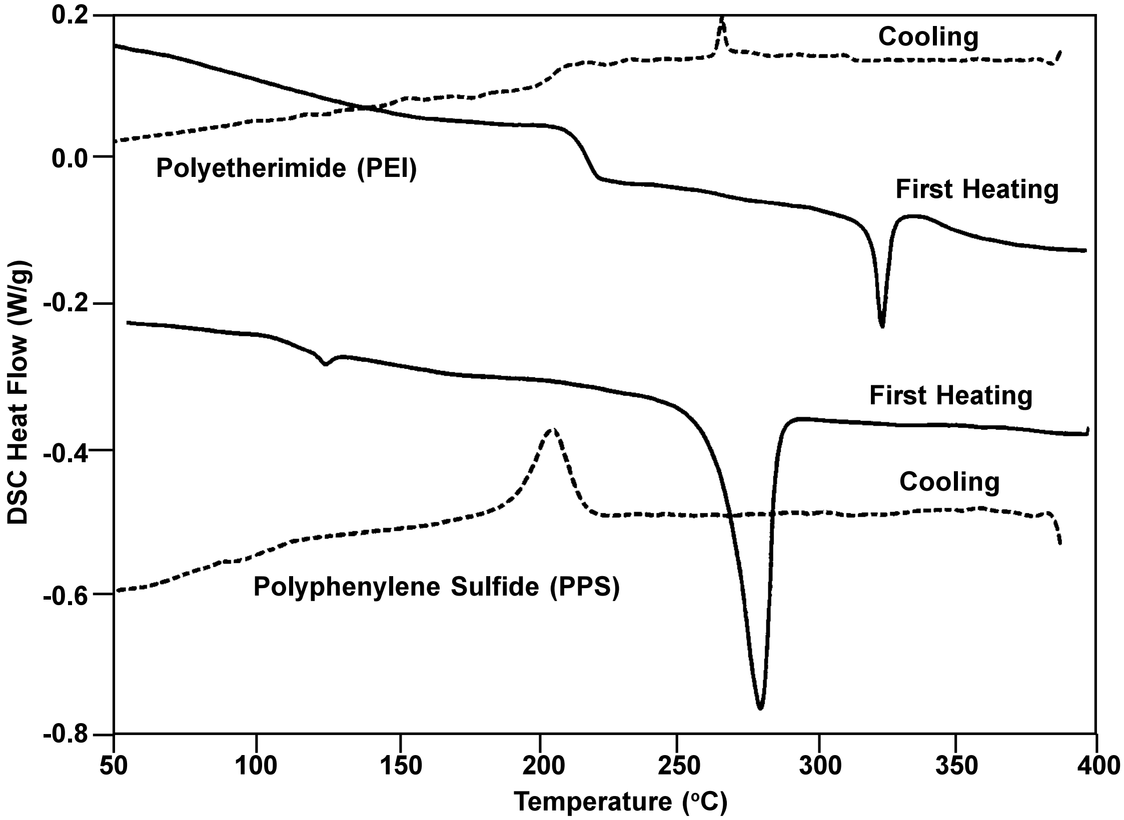

Figure 3. **DSC THERMAL CURVES OF THERMOPLASTICS**

Solid Line is first heating, dotted line is cooling.

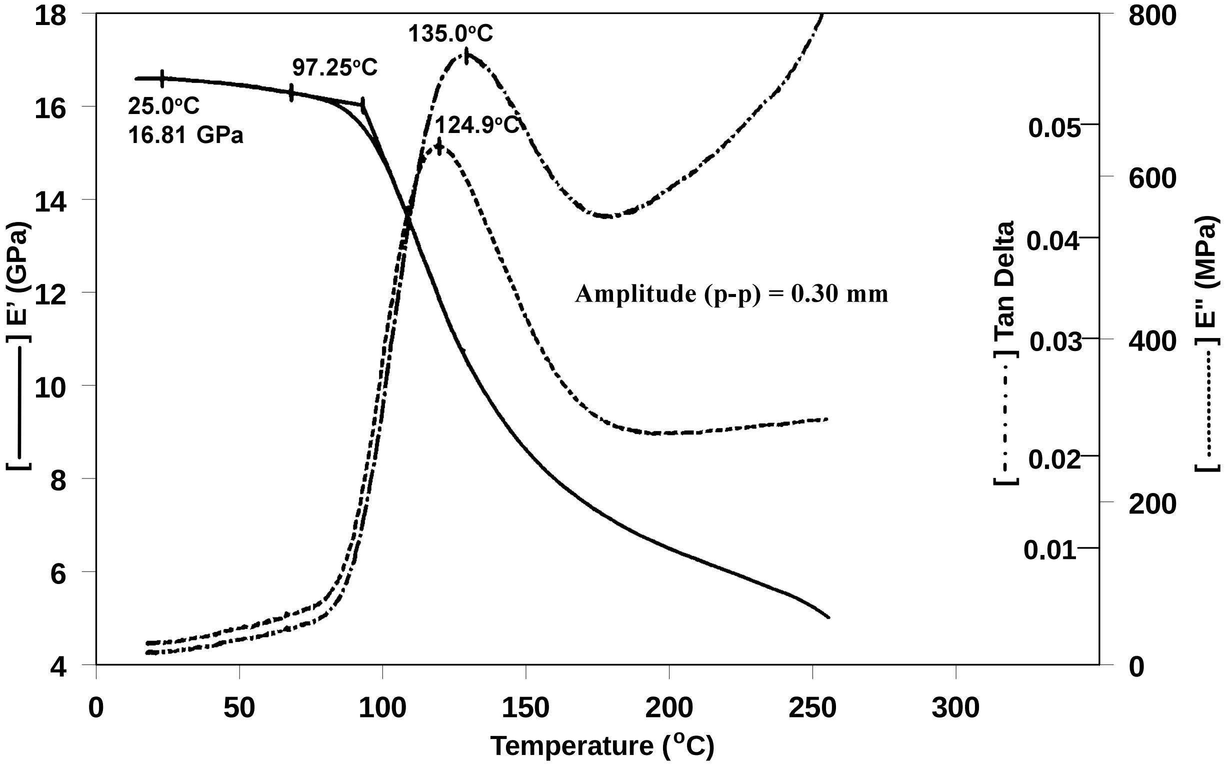

Figure 4. **DMA THERMAL CURVES OF POLYPHENYLENE SULFIDE**

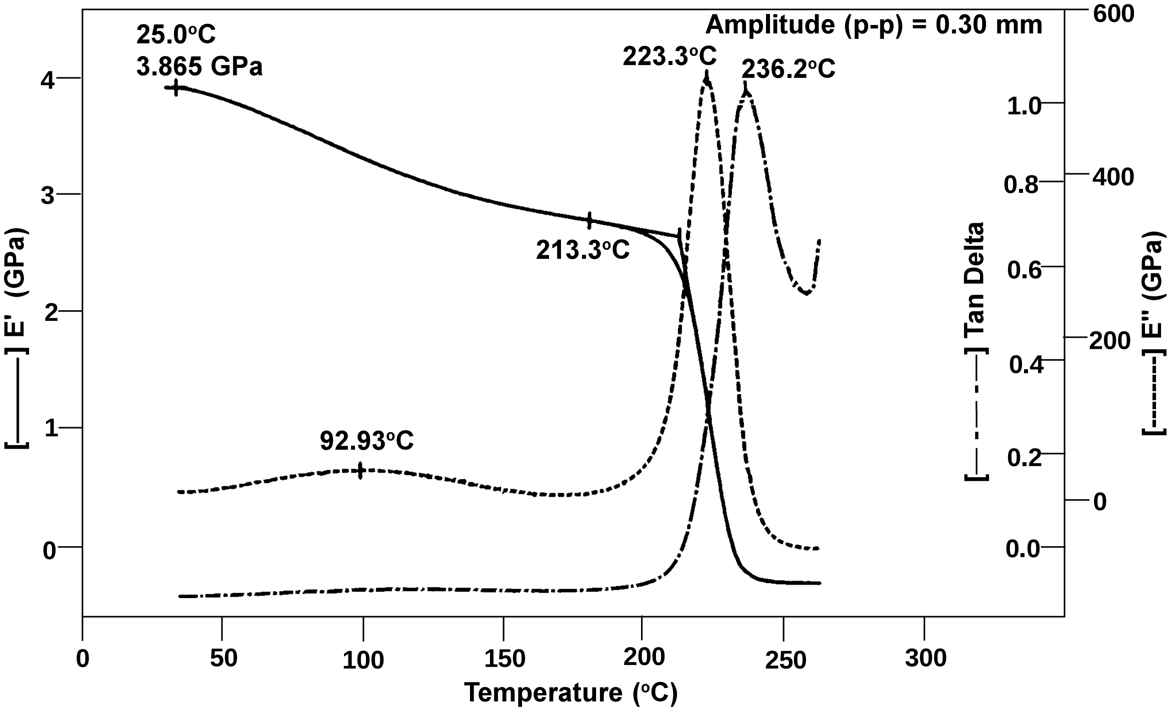

Figure 5. DMA THERMAL CURVES OF POLYETHERIMIDE

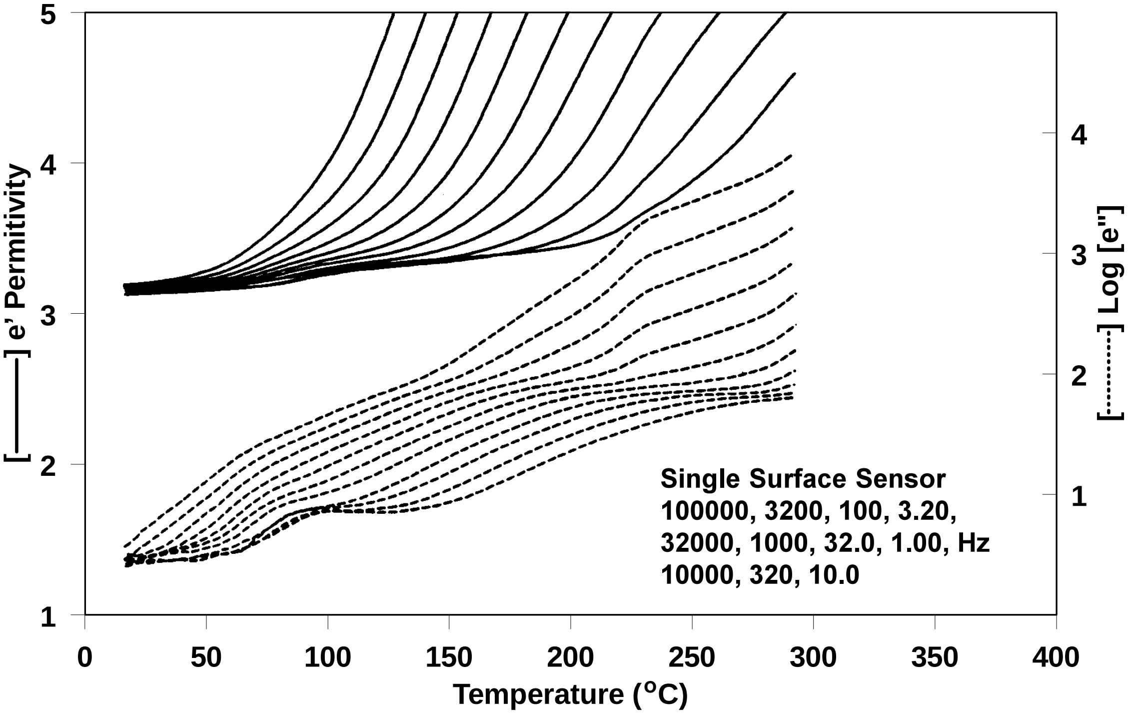

Figure 6. DEA THERMAL CURVES OF POLYPHENYLENE SULFIDE

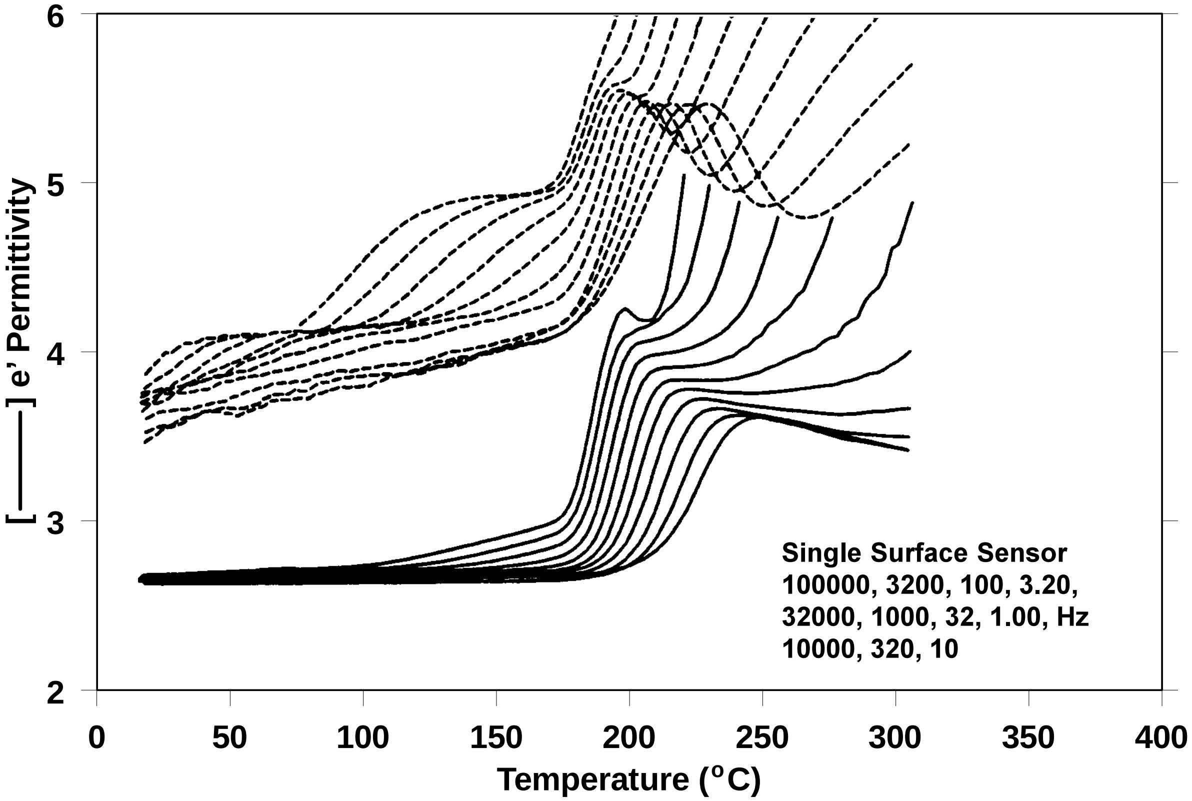

Figure 7. DEA THERMAL CURVES OF POLYETHERIMIDE

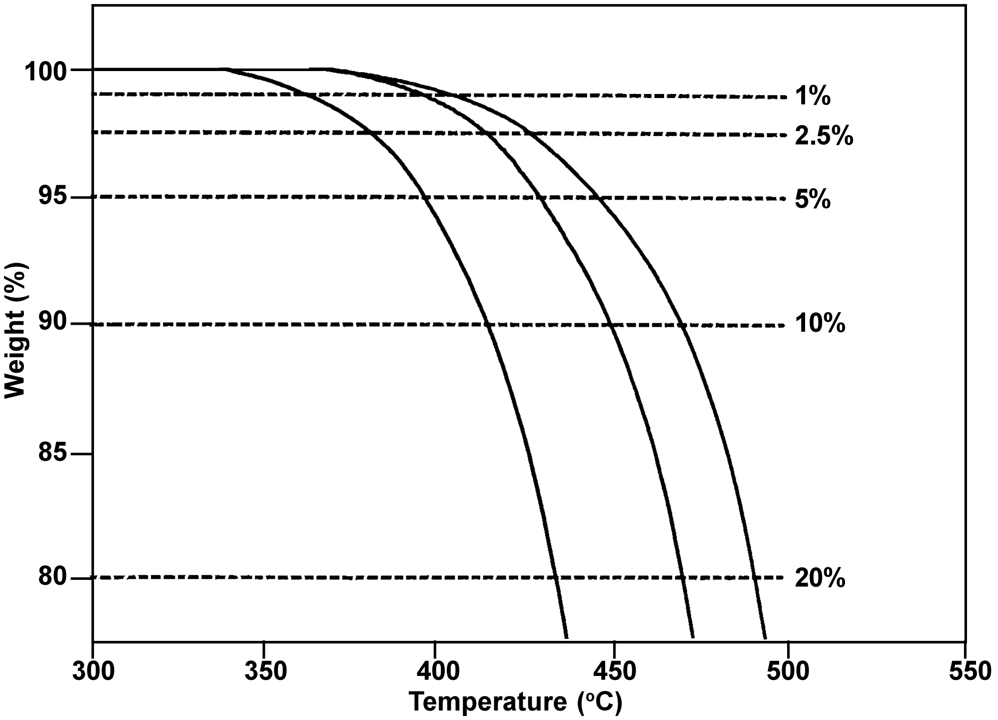

Figure 8. TGA DECOMPOSITION OF PPS AT 1, 5 AND 10°C/MIN

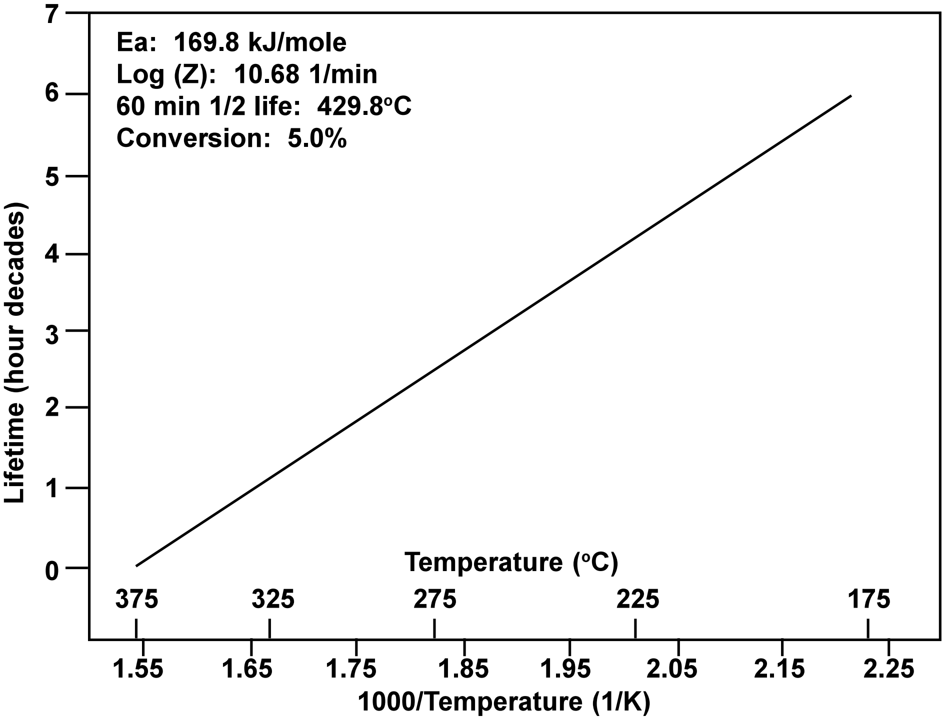

Figure 9. SERVICE LIFETIME OF PPS

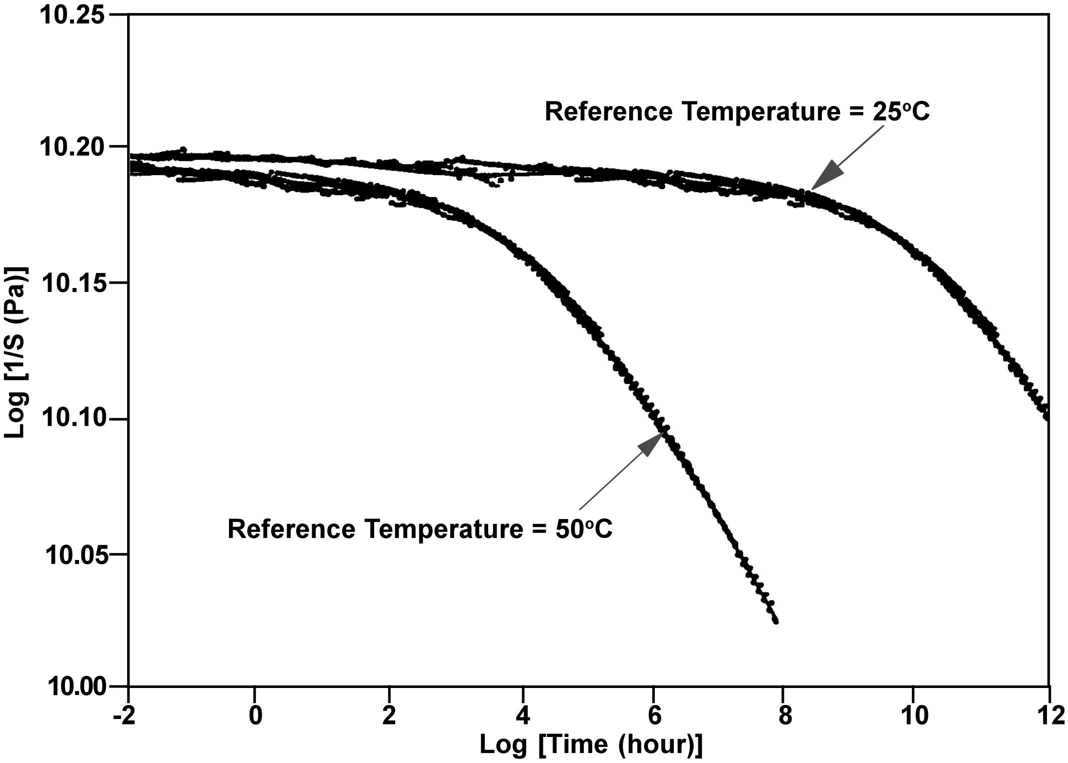

Figure 10. CREEP MODULUS LIFETIME CURVES AT 25°C AND 50°C FOR PPS

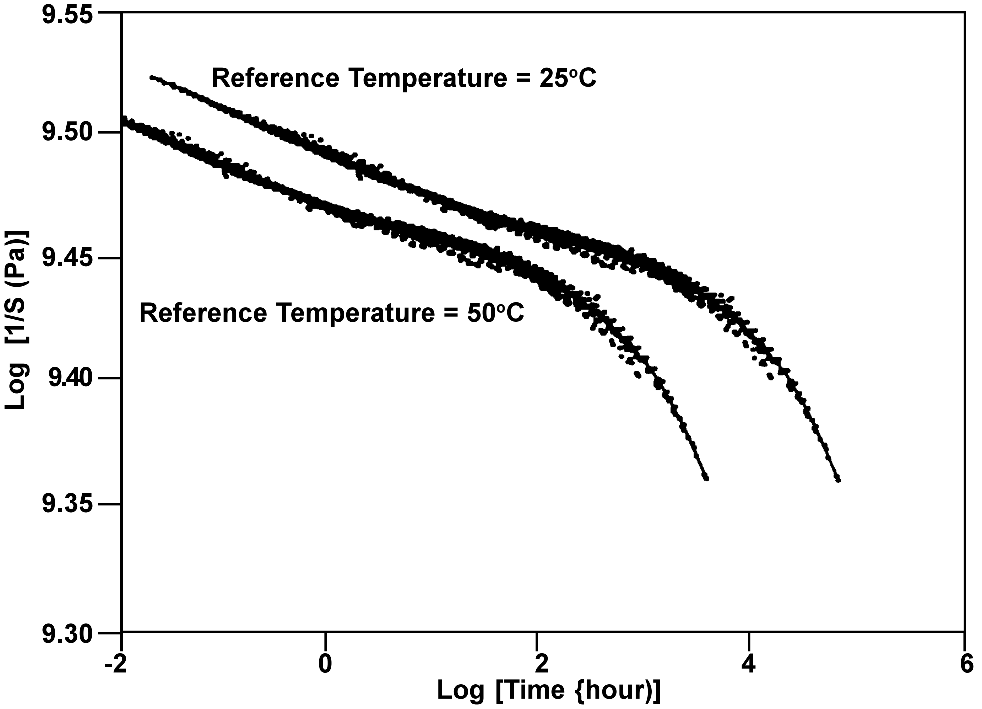

Figure 11. CREEP MODULUS LIFETIME CURVES AT 25°C AND 50°C FOR PET

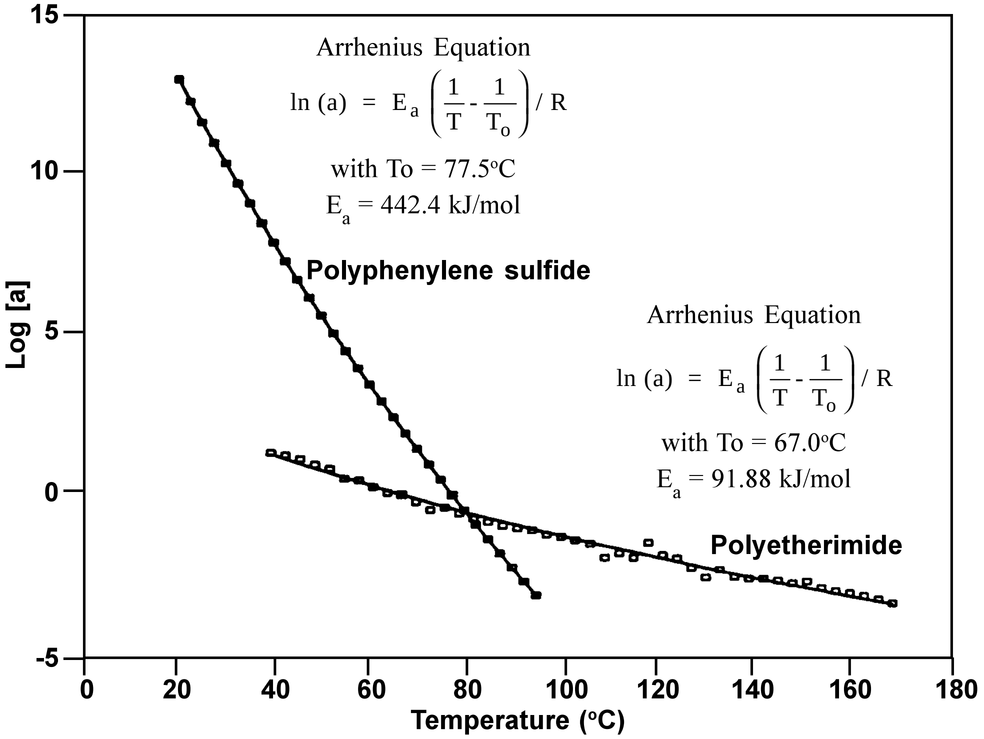

Figure 12. SHIFT FACTOR CURVES FOR PPS AND PEI