

Dynamic Mechanical Analysis of High Temperature Polymers

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1. Abstract

This paper investigates the material properties of several high temperature polymers (PBI, PI, PEEK, PAI, PEI and their blends) over a broad temperature range using Dynamic Mechanical Analysis (DMA). The materials are compared through their storage modulus and glass transition temperatures. These comparisons are useful for material selection under different application temperatures, especially high temperature.

2. Purpose

The purpose of this paper is to characterize and compare thermal mechanical behavior of a select group of high-performance polymers using Dynamic Mechanical Analysis (DMA) to provide a comparison of elevated temperature performance expectations.

3. Introduction

Engineering plastics are frequently used for advantages in performance, weight, cost and processability. In each application, environmental factors must be considered when making a material selection. When plastics are considered, service temperature requires special consideration because of the dramatic effect temperature has on plastics' mechanical properties. Hence, understanding the effect of temperature on plastics is extremely important. Each plastic responds differently to increasing temperature. Some plastics experience a slow weakening over several hundred degrees of temperature increase. Others may perform stably over a span of several hundred degrees then weaken and fail in stepwise fashion, or suddenly. Some fail at very high temperatures while others fail at very low temperatures. As such, the performance of candidate plastic materials must be well understood in the context of service temperature and is therefore the focus of this study.

Evaluation and comparison of a materials' response to thermal conditions is an engineering challenge because tests do not always replicate the use environment, or they may respond to just one dimension of concern. There are several tools available to characterize thermal response. Thermal Gravimetric Analysis (TGA) tells us about thermal decomposition. Thermal Mechanical Analysis (TMA) measures thermal transition points. Differential Scanning Calorimetry (DSC) tells us about heat uptake or release as temperature is changed or the material moves through transition points. Dynamic Mechanical Analysis (DMA) tells us about thermal transitions and mechanical properties as a function of time and

temperature. Each has its value, but since our study's purpose is to understand a polymer's mechanical suitability over broad temperature ranges and especially their limitations at elevated temperatures, DMA becomes the better choice for comparison and was so selected.

While the objective herein is to provide a comparison of a select group of engineering plastics under the same elevated temperature conditions, it's important to note that these data represent a snapshot of the subject materials from a small sample set and results may vary from other reports. Differences in processing, thermal history, test fixture, deformation mode, frequency of oscillation, heating rate, etc. can all impact the observed modulus and glass transition temperature (T_g) resulting in deviations from literature. Within this study, however, these variables were controlled to minimize the effect of these treatments on results allowing reasonable comparison in this context.

4. Introduction to Dynamic Mechanical Analysis (DMA)

In characterizing polymers, we must first understand that they can behave as both liquids and solids, and so require special analytical tools. By exhibiting behavior between that of an (ideal) viscous fluid and an (ideal) elastic solid, they are called viscoelastic [1]. Understanding their flow response to temperature is very important to material scientists and engineers; hence, the need to measure it. Dynamic Mechanical Analysis (DMA) is one, perhaps the best, technique to observe and measure this response in polymers. In this project, DMA was used as a tool to characterize the properties of polymers under a broad span of elevated temperatures. For orientation purposes, a brief summary follows on DMA theory drawn from Richard P. Chartoff et al. [1] and TA Instruments' literature [2,3], which are good resources on this topic.

An objective of DMA measurement is to understand mechanical and flow properties as a function of time and temperature. DMA can be used to measure the viscoelastic properties using either transient (e.g. creep and stress relaxation) or dynamic oscillatory tests; all of which are related [1]. The most common test is the dynamic oscillatory test, where a sinusoidal stress (or strain as Equation 4.1) is applied to the material and a resultant sinusoidal strain (or stress as Equation 4.2) and the phase difference, δ , between the stress and strain sine waves are measured. Purely viscous materials exhibit a 90° phase lag. Purely elastic materials exhibit a 0° phase lag. Viscoelastic materials (e.g. polymers) will exhibit an intermediate phase difference as shown in Figure 4.1 [2]. The stress and strain relationships as a function of time are described by Equations 4.1 and 4.2, where σ is the stress, ϵ is the strain, ω is the frequency of strain oscillation, t is the time, and δ is the phase lag between stress and strain.

$$\varepsilon(t) = \varepsilon_0 \sin(t\omega) \quad \text{Equation 4.1}$$

$$\sigma(t) = \sigma_0 \sin(t\omega + \delta) \quad \text{Equation 4.2}$$

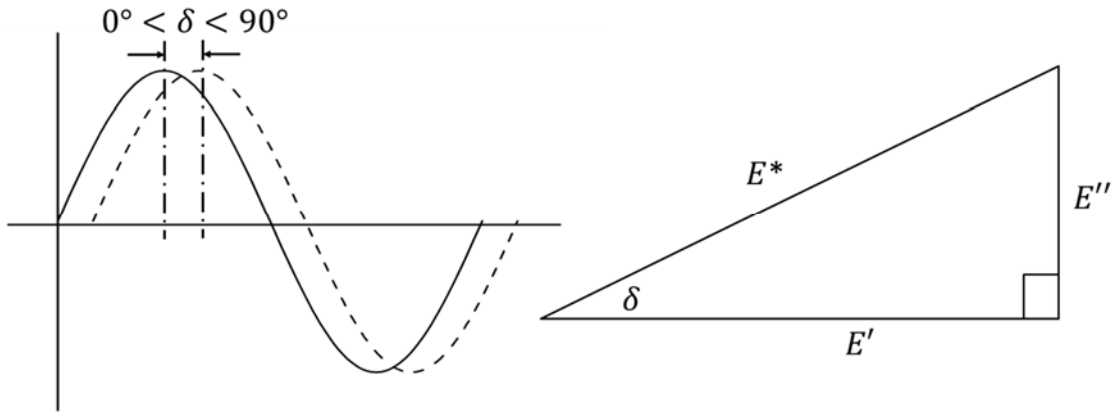


Figure 4.1: Illustration of modulus calculation for a viscoelastic material [2]

The material's overall resistance to deformation is described by its complex modulus, E^* , calculated by dividing the stress by strain (Equation 4.3) [2].

$$E^* = \sigma / \varepsilon \quad \text{Equation 4.3}$$

The complex modulus has an elastic (or storage) component, E' , which measures a material's stored energy, and a viscous (or loss) component, E'' , which measures energy dissipated as heat [1]. From E^* and the measurement of δ , the storage modulus E' can be obtained by Equation 4.4 [2] – as illustrated in Figure 4.1. It is the elastic component that is related to the sample's stiffness.

$$E' = E^* \cos(\delta) \quad \text{Equation 4.4}$$

The loss modulus, E'' , is the viscous component as obtained by Equation 4.5 [2]. It is related to the sample's ability to dissipate mechanical energy through molecular motion.

$$E'' = E^* \sin(\delta) \quad \text{Equation 4.5}$$

The tangent of phase lag, or $\tan(\delta)$, is another common parameter that provides information on the relationship between the elastic and inelastic components (Equation 4.6) [2]. It is a measure of dampening.

$$\tan (\delta) = \frac{E''}{E'} \quad \text{Equation 4.6}$$

In addition to characterizations of modulus, DMA can provide measures of thermal transitions like the glass transition temperature, T_g . This will be discussed in Section 6.1.

5. DMA Experimental Setup

5.1 Equipment

TA Instruments Dynamic Mechanical Analyzer Model Q800 was used to conduct the tests. There are several DMA fixtures available for use, e.g., three-point bending, single cantilever and tensile. The three-point bending fixture was chosen as the testing fixture for this study. The dynamic strain oscillatory test method was used in the three point tests with the frequency ω set to 1 Hz (as in Equation 4.1), and its oscillation amplitude set to 15 μm . The tests were conducted in a nitrogen environment over the range from the ambient temperature to the temperature at which the materials lost their resistance. The heating rate was 10°C/minute.

The storage modulus, loss modulus and $\tan \delta$ were recorded during the tests. The storage modulus was used as the major property for characterization and comparison.

5.2 Materials

Of interest is the class of high temperature engineering polymers, including the imidized polymers and polyaryletherketones for their common selection in high performance applications. These are the top tier materials on the following polymer performance pyramid (Figure 5.1) which were tested in this study: PBI, PI, PEEK, PAI, PEI and their blends.

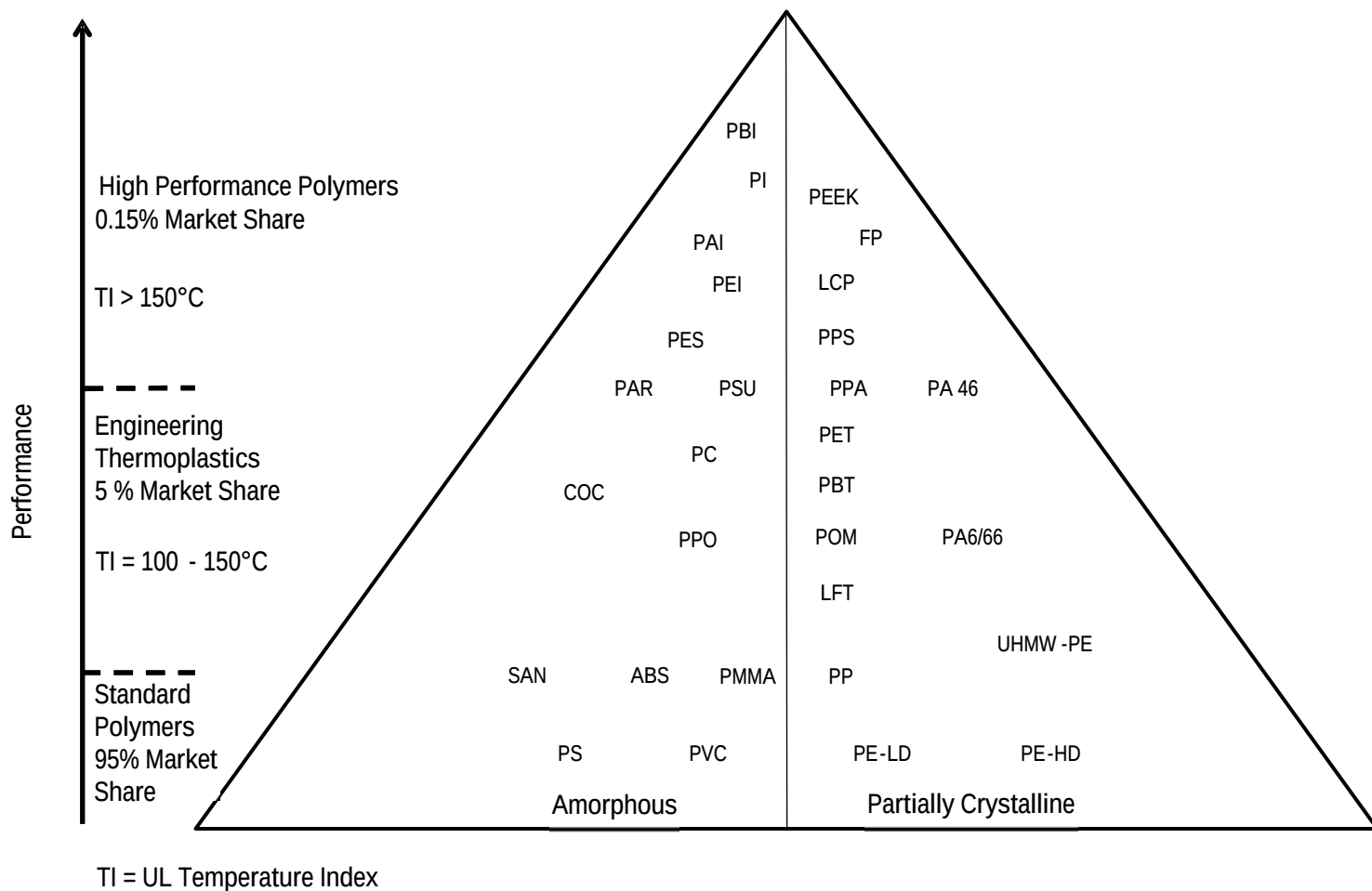


Figure 5.1 Polymer Performance Pyramid

The test group includes neat resins, carbon filled, glass filled and lube grade variants; specifically:

- Polyetherimide (PEI):
Ultem® 1000: unfilled PEI
Ultem® 2300: glass fiber filled PEI
- Polyetheretherketone (PEEK):
Vitrex® PEEK 150G: unfilled PEEK
Vitrex® PEEK 150GL30: glass fiber filled PEEK

- Polybenzimidazole (PBI):
Celazole® U-60: unfilled PBI
- Blends of Polybenzimidazole/Polyetheretherketone (PBI-PEEK):
Celazole® TU-60: unfilled PBI-PEEK
Celazole® TF-60C: carbon fiber filled PBI-PEEK
Celazole® TF-60V: glass fiber filled PBI-PEEK
Celazole® TL-60: lube grade PBI-PEEK
- Blends of Polybenzimidazole/Polyetherketoneketone (PBI-PEKK):
Celazole® TK-60: unfilled PBI-PEKK
- Polyamideimide (PAI):
Torlon® 4203: unfilled PAI
Torlon® 4301: lube grade PAI
- Polyimide (PI):
Vespel® SP1: unfilled PI
Vespel® SP21: lube grade PI

Each sample was in molded form; rectangular, with length about 55.0 mm; width about 12.5 mm; and thickness about 3.1 mm. All the samples were dried before testing. One sample was used per test.

6. Results and Discussions

6.1 Glass Transition Temperature

The glass transition temperature (T_g) is the temperature beyond which the long-range translational motion of the polymer chain segments is active [4]. At this temperature, on heating, the glassy state changes into the leathery state [5]. Below T_g , the translational motion of the segments is frozen and only the vibrational motion is active [6]. At the T_g , amorphous thermoplastics show a rapid decline of strength and modulus. In contrast, crystallinity substantially preserves these mechanical properties [4]. In DMA testing, the T_g can be determined by: (1) the onset of the E' drop; (2) the peak of the $\tan(\delta)$; or, (3) the peak of the E'' curve [1]. In this paper, the T_g was determined as the onset of the E' drop for its direct relationship to mechanical properties of interest for the materials tested and clarity of detection. The T_g 's, as determined by the tests, are summarized in Table 6.1.

In Table 6.1 we can see that the PBI resin has the highest T_g , 411°C, and that the T_g of PAI is also quite high at 288°C. For PI (Vespel® SP1 and Vespel® SP21), the T_g is not evident as modulus decays almost linearly with temperature.

Table 6.1: Test material details and their T_g 's

Material Name	Resin	Filler	T_g °C
Celazole® U-60	Polybenzimidazole (PBI)		411
Vespel® SP1	Polyimide (PI)		Note 1
Torlon® 4203	Polyamide-imide (PAI)		288
Ultem® 1000	Polyetherimide (PEI)		217
Victrex® PEEK 150G	Polyetheretherketone (PEEK)		151
Celazole® TU-60	PBI-PEEK compound (PBI-PEEK)		154
Celazole® TK-60	PBI-PEKK compound (PBI-PEKK)		169
Victrex® PEEK 150GL30	Polyetheretherketone (PEEK)	Glass filled	153
Celazole® TF-60V	PBI-PEEK compound (PBI-PEEK)	Glass filled	165
Ultem® 2300	Polyetherimide (PEI)	Glass filled	221
Celazole® TF-60C	PBI-PEEK compound (PBI-PEEK)	Carbon filled	155
Vespel® SP21	Polyimide (PI)	Lubricated	Note 1
Torlon® 4301	Polyamide-imide (PAI)	Lubricated	279
Celazole® TL-60	PBI-PEEK compound (PBI-PEEK)	Lubricated	154

Note 1: No T_g was detectable for Vespel SP1 or SP21 in these tests; however, other Polyimides do show a T_g which may be found in the literature.

6.2 Storage Modulus

Storage modulus (E') is a measure of the elastic component of the stored deformation energy and provides a useful measure of a material's mechanical properties [1]. Figure 6.1 shows how the storage modulus of pure polymers in bulk form change with increasing temperature. At a given load and oscillation, storage modulus is a function of material chemistry, molecular weight, crystallinity, degree of crosslinking, and filler type/content. As such, we will break down the discussion of these aspects at a high level. For brevity, in the absence of further specification, comments about modulus hereafter refer to storage modulus.

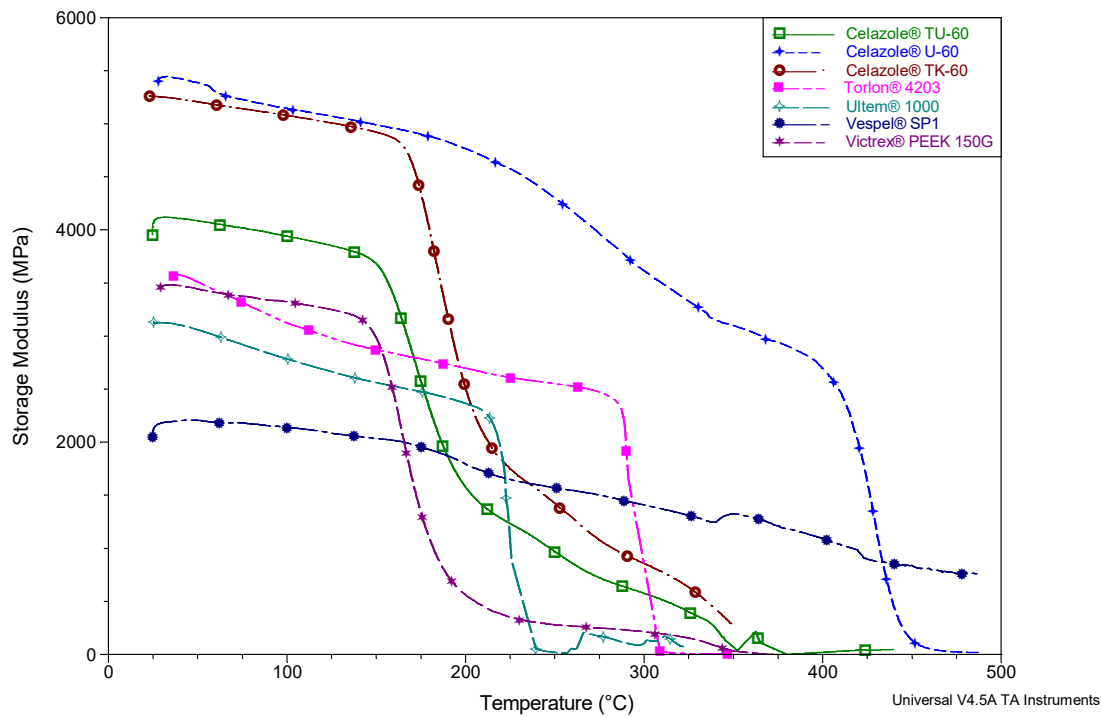


Figure 6.1: The storage modulus (E') of neat resins

Imidized Polymers

For this study, we selected four imidized polymers. The three primarily amorphous imidized polymers – PBI, PAI and PEI show similar trends with temperature even though the moduli differ in absolute value and the point of rapid decay occurs at three distinct temperatures. The respective points of rapid decay occur at their T_g , indicating three

different maximum thresholds for use. For Vespel PI, a more crystalline imidized polymer, the decay in modulus is essentially linear with temperature with no apparent T_g ; an observation also reported on by Kemmish [4].

Celazole PBI U-60 has the highest modulus of the group. It's ~250% of Vespel SP1 PI from ambient to 300C; ~190% of Ultem 1000 PEI from ambient to PEI's T_g of 217C; and ~170% of Torlon PAI from ambient up to PAI's T_g of 288C. Beyond their respective T_g 's the modulus of the amorphous thermoplastics drops sharply. As a generalization, the modulus of these imidized polymers is quite similar when they reach their respective T_g 's; i.e. for PBI at T_g 411C the modulus is 2600 MPa; for PAI at T_g 288C the modulus is 2300 MPa; for PEI at T_g 217C the modulus is 2200 MPa; and for PI, not at the T_g which isn't clearly seen, but at 25C the modulus is 2200 MPa. This gives a useful ranking of the imidized polymers for thermomechanical purposes.

Polyaryletherketones and their Compounds

Next, we shall look at the semicrystalline polyaryletherketone thermoplastics and their compounds with PBI – also Figure 6.1. Semicrystallines differ from amorphous thermoplastics in that they retain some working modulus beyond their T_g due to the crystallinity inhibiting chain mobility. Starting with pure PEEK, note the relatively rapid decrease in modulus when the material crosses its glass transition temperature (T_g 151C) indicating mobility in the amorphous phase. Then note how it holds stably at about 500-250 MPa from its T_g +50C out to the melting temperature 343C (T_m) as the modulus is supported by the crystalline portion of the polymer before ultimately giving way.

With the introduction of PEEK-PBI polymer compounds, we see an increase in modulus. For example, comparing TU-60 (PBI-PEEK compound) with straight PEEK, we observe ~700MPa average increase in modulus at any given temperature. PBI pulls up the modulus of PEEK well after crossing PEEK's T_g . This suggests that by compounding PBI with a polyaryletherketone we immobilize the amorphous zones, creating a matrix with enhanced properties relative to the PAEK component [7].

Filled Systems

We are also interested to see how glass and carbon fibers, and lubricant additives affect the storage modulus of different resins. A comparison of the polymers with and without fillers shows a significant effect.

Below the T_g the modulus of glass filled PEI Ultem 2300 is about 200% that of straight PEI Ultem 1000; the glass fiber adding ~2600 MPa to the modulus. Ref. Figure 6.2.

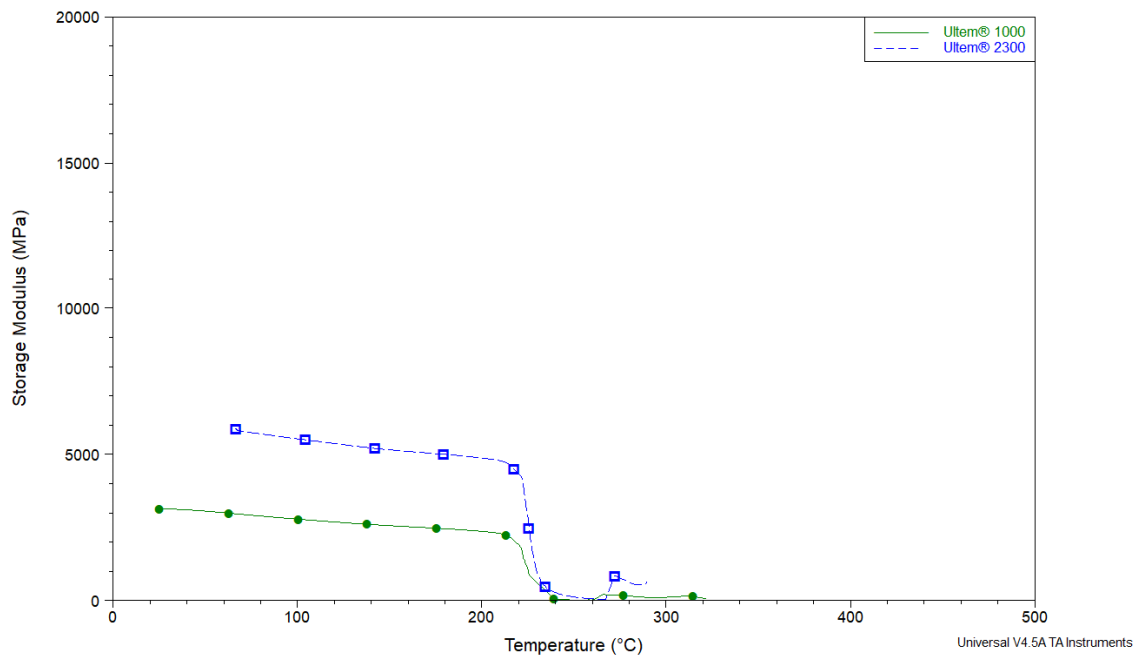


Figure 6.2: Storage modulus (E') of unfilled and glass filled PEI

Below the T_g the modulus of glass filled PEEK Victrex 150GL30 is about 290% that of straight PEEK 150G, adding ~6400 MPa. Above the T_g there is a diminishing effect of ~5900 – 2600 MPa. Ref. Fig 6.3.

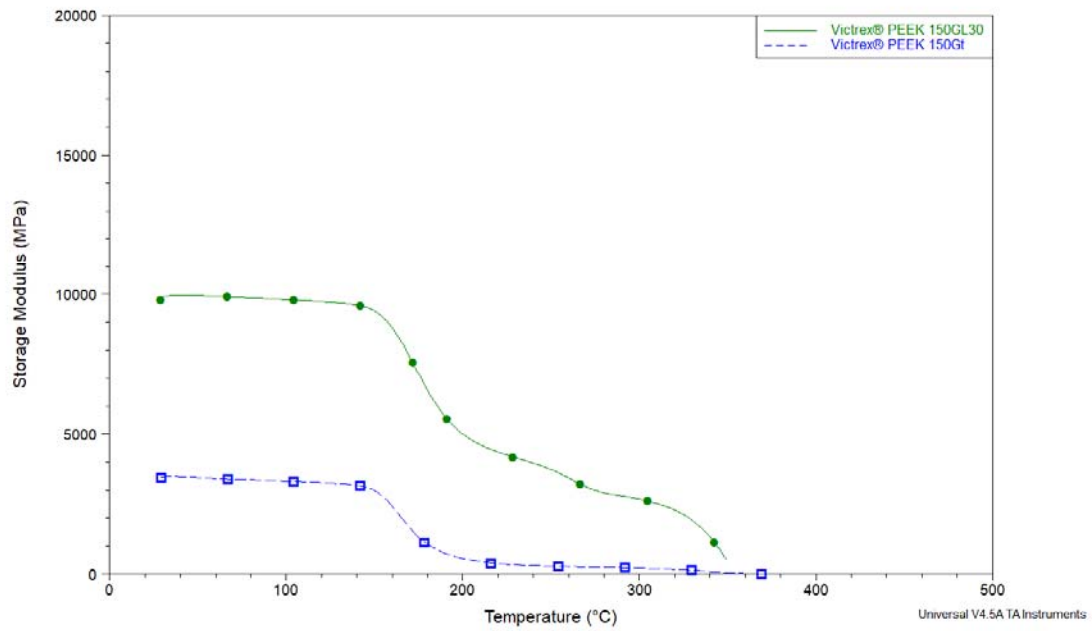


Figure 6.3: Storage modulus (E') of unfilled and glass filled PEEK

Now looking at the modulus of PBI-PEEK blends, with and without additives: Below the T_g of PEEK the modulus of glass filled PBI-PEEK compound TF-60V is about 290% that of PBI-PEEK TU-60, adding ~7300 MPa. Above the T_g there is a diminishing effect of ~7400 – 3200 MPa. Ref. Figure 6.4.

Below the T_g of PEEK the modulus of carbon filled PBI-PEEK compound TF-60C is about 470% that of PBI-PEEK TU-60, adding ~14,800 MPa. Above the T_g there is a diminishing effect of ~11,200 – 4000 MPa. Ref. Figure 6.4

Below the T_g of PEEK the modulus of lube-grade PBI-PEEK TL-60 is about 370% of PBI-PEEK TU-60, adding ~10,800 MPa. Above the T_g there is a diminishing effect of ~8100 – 3200 MPa. Ref. Figure 6.4.

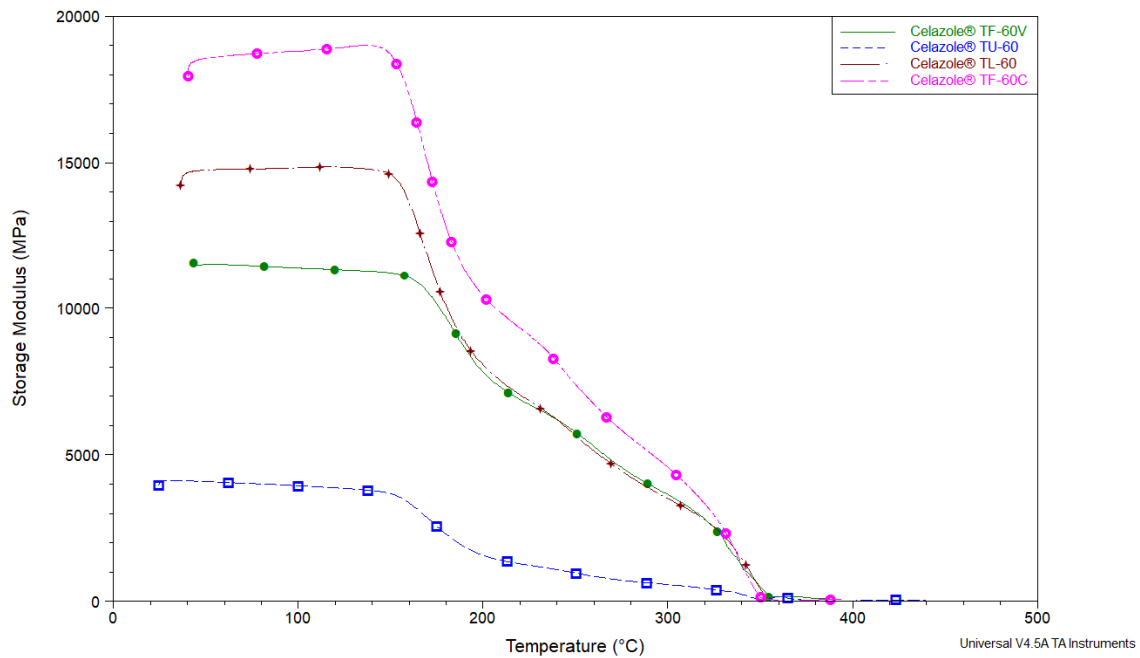


Figure 6.4: Storage modulus (E') of unfilled and filled PBI-PEEK blends.

Now looking at the modulus of neat and lube grade PAI: Below the T_g the modulus of lube grade PAI Torlon 4301 is 170% that of straight PAI Torlon 4203; the lube package adding ~2400 – 1700 MPa to the modulus. Ref. Figure 6.5.

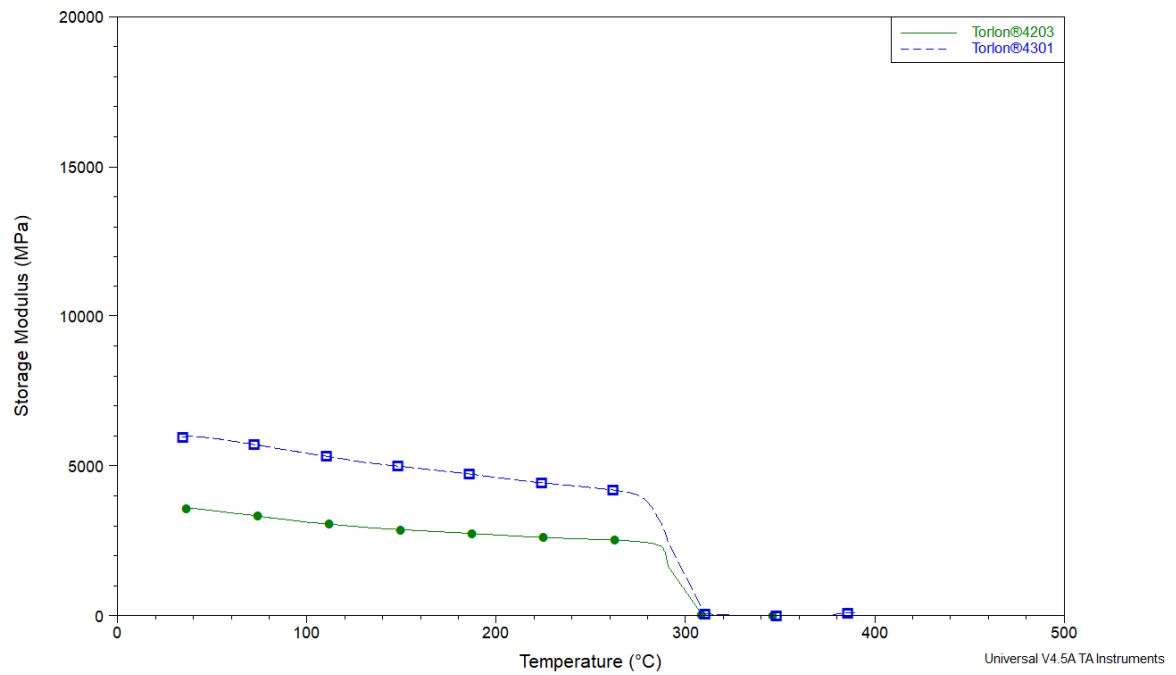


Figure 6.5: Storage modulus (E') of unfilled and lube grade PAI

Now looking at the modulus of neat and lube grade PI. From 100 to 300C, the modulus of lube grade Vespel SP21 is about 180% that of the base grade PI Vespel SP1, adding ~2000 – 1100 MPa over the range. Ref. Figure 6.6.

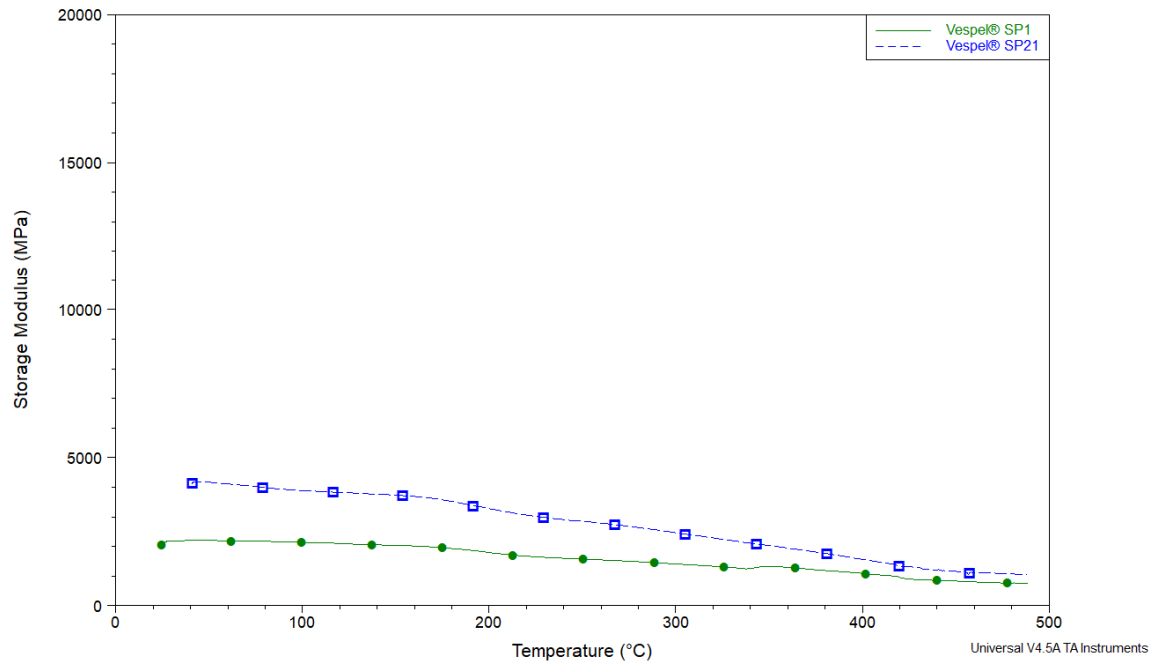


Figure 6.6: Storage modulus (E') of neat and lube grade PI

In every case as we look at Figures 6.2 – 6.6 we see a polymer's basic signature modulus/temperature profile to carry through to the filled product, but with a substantial increase in modulus with the addition of filler.

On comparing the modulus of glass filled polymers amongst one another we have the view as presented by Figure 6.7.

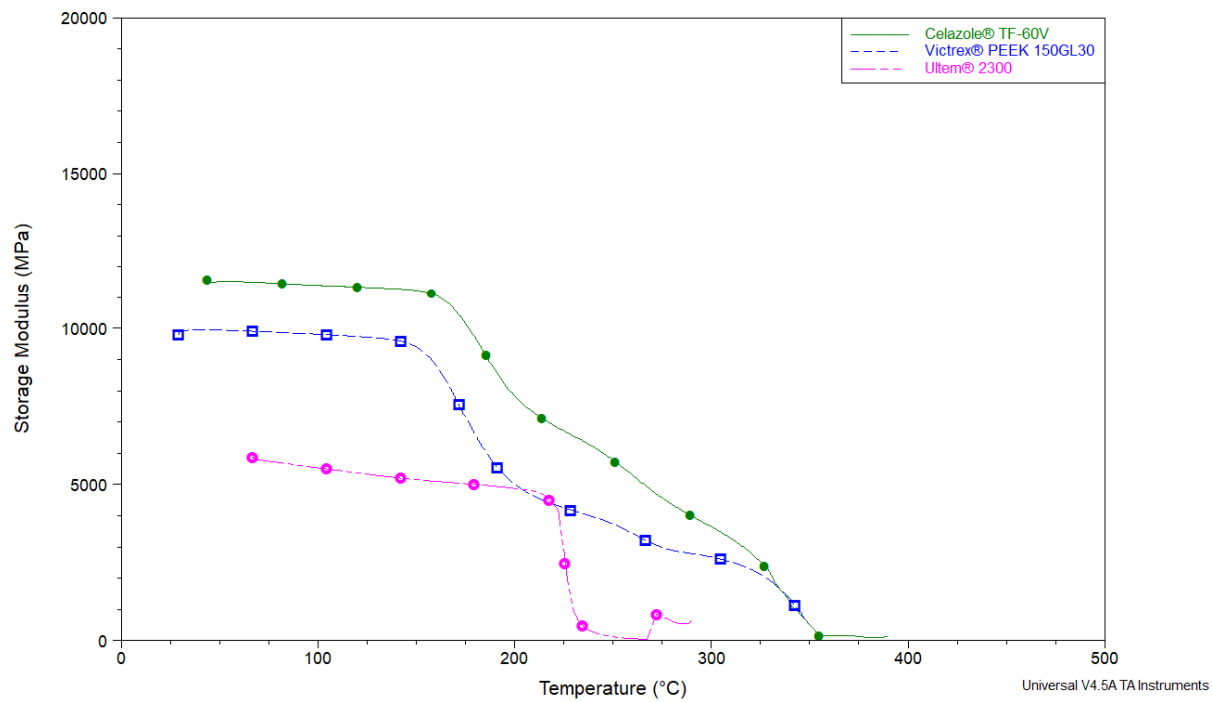


Figure 6.7: Storage modulus (E') of PBI-PEEK, PEI, and PEEK – all with glass filler

On comparing the modulus of lube grade polymers amongst one another we have the view as presented by Figure 6.8.

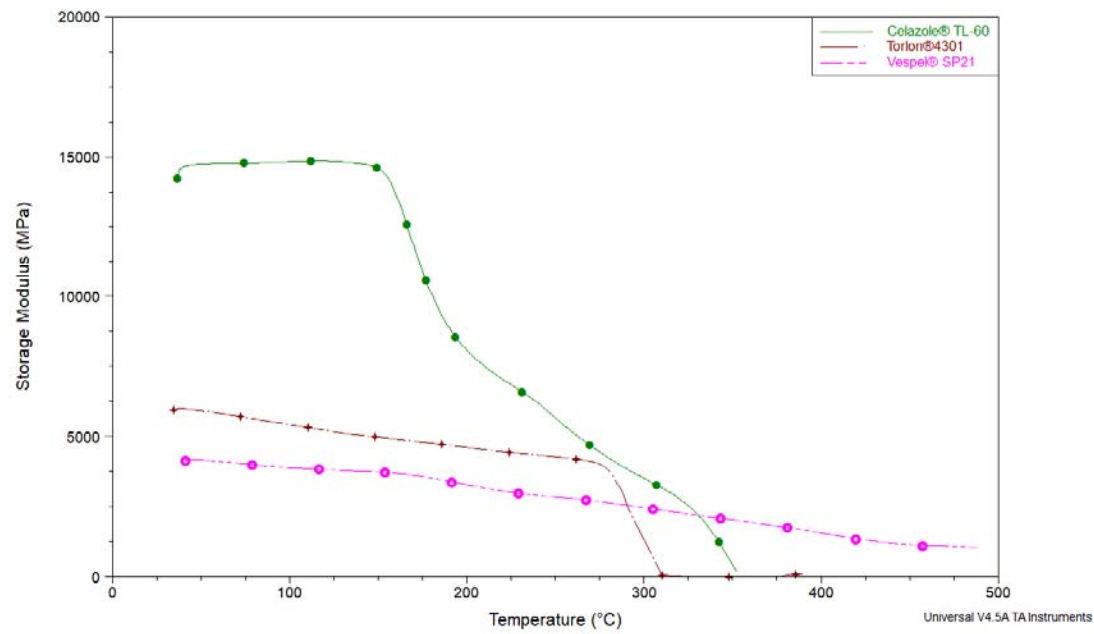


Figure 6.8: Storage modulus (E') of PBI-PEEK, PAI, and PI – with various lube-grade fillers

7. Conclusions

From the above discussions based on the Dynamic Mechanical Analysis (DMA) three-point bending tests on the subject polymers, the following conclusions can be drawn:

DMA is a very useful tool to evaluate thermal mechanical behavior of polymers over an extended thermal range and assists in the determination of a polymer's suitability for use at high temperature.

Using DMA, we have shown the effect of several hundred degrees of temperature increase on the subject polymers' mechanical and flow properties and quantified important thermal transitions.

For unfilled amorphous thermoplastics, the T_g represents a meaningful thermal limit for materials used under load.

As crystallinity increases, as demonstrated by semicrystalline Victrex 150G PEEK, there is still useful storage modulus beyond the T_g .

We have measured and shown the elastic component of stored deformation energy for a group of un-filled and filled high-performance polymers, enabling a useful comparison of their mechanical properties at temperature.

For the bulk form of the neat resins tested (PEI, PAI, PI, PBI-PEEK and PBI-PEKK), Celazole® U-60 (PBI) has the best resistance to temperature to 411°C as measured by T_g and elastic storage modulus.

The compounding of PBI with PEEK enhances the storage modulus by ~700MPa up to 250C.

Amongst the materials studied, additives can significantly affect a bulk materials modulus. Carbon fiber filler had the largest effect in enhancing storage modulus – up to 470%. Glass fiber fillers enhanced storage modulus 200 – 290%. Lubricant packages enhanced storage modulus 180 – 370%.

8. References

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