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Characterization of the Thermoresponsive Shape-Memory Effect in Poly(ether ether ketone) (PEEK)

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ABSTRACT: We conducted a systematic experimental investigation to characterize the shape-memory effect in a commercial poly(ether ether ketone) (PEEK), which is a very important high-temperature polymers at present. The focus was on the influence of the programming conditions and heating temperature for recovery on the shape-recovery ratio (R_r). We concluded that PEEK is not only an important engineering polymer as it is traditionally known but is also an excellent high-temperature shape-memory polymer. For a residual programming strain of 30%, the maximum R_r was about 90%. It was revealed that it was practically feasible to program PEEK at room temperature and to lower the recovery temperature from its melting temperature range to around its glass-transition temperature. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39844.

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INTRODUCTION

After being severely and quasi-plastically deformed, shape-memory materials (SMMs) are able to recover their original shape when the right stimulus is applied.[1–3] This phenomenon is known as the *shape-memory effect* (SME).[4]

A typical SME cycle for a heating-responsive SMM includes two parts, namely, programming and shape recovery. As illustrated in Figure 1, in the first step a, a piece of SMM was strained to the maximum compression strain (ε_m) at high or low temperatures. Subsequently, with or without the step of cooling back to room temperature, the SMM was unloaded (curve b), and a residual strain (ε_u) resulted. The shape fixity ratio (R_f), which is normally defined as follows:

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \quad (1)$$

R_f is one of the key parameters in characterizing the shape-memory phenomenon of an SMM. This ends the programming process.

In the following shape-recovery process, the material is heated (Figure 1, curve c), and the final strain after recovery is abbreviated as ε_h. The shape-recovery ratio (R_r) is normally defined as follows:

$$R_r = \frac{\varepsilon_u - \varepsilon_h}{\varepsilon_u} \quad (2)$$

It is another key parameter in the characterization of SMMs.

Now, the family of SMMs has expanded greatly to include alloys (known as *shape-memory alloys*), polymers (shape-memory polymers), hybrids (shape-memory hybrids), and their composites.[5–14] In addition to the response to temperature variation (thermoresponsivity, including both heating and cooling), chemoresponsivity and photoresponsivity have been realized in polymeric SMMs.[15–20]

In recent days, alongside with continuous efforts to develop new SMMs, new features, such as the multiple SME and temperature-memory effect, have been identified.[21–23] According to ref. 24, on the basis of different underlying mechanisms for SME, most polymers, if not all, naturally have both thermoresponsive (heating) and chemoresponsive SMEs, whereas the exact shape-memory performance varies from material to material and is also very much dependent on the exact working mechanism and programming method/conditions.

At present, many engineering polymers have become part of our daily life. Some of them, such as acrylonitrile butadiene styrene, polycarbonate, acrylonitrile butadiene styrene/polycarbonate, ethylene vinyl acetate, poly(ethylene terephthalate), polytetrafluoroethylene, poly(methyl methacrylate), and silicone,

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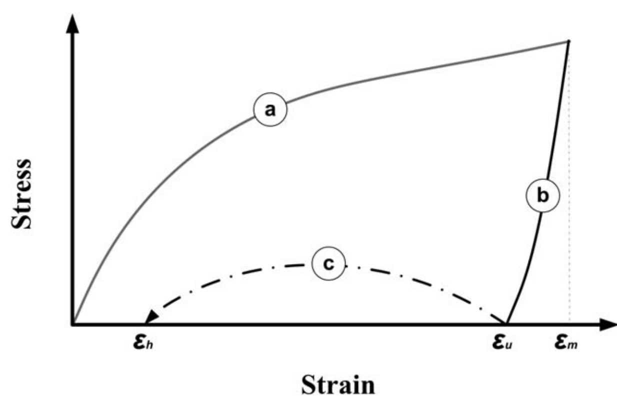

Figure 1. Illustration of a typical SME cycle in heating-responsive SMM.

have been investigated to reveal their shape-memory performance.[24–26]

Poly(ether ether ketone) (PEEK) is a widely used engineering polymer, in particular, for high-temperature applications. It is a homopolymer in which with ether ether ketone as a repeating unit. In addition to its high Young's modulus and excellent mechanical and chemical resistance and flame retardance, it is also highly biocompatible and is regarded as an advanced biomaterial in medical implants.[27–31] Well-documented experimental results of its standard properties are now available in the literature.[32,33]

PEEKshrink, heat-shrinkable tubing, was developed by ZEUS for challenging environments, where extreme heat or cold, intense pressure, chemicals, water, or dielectric interference pose a threat. According to ZEUS's PEEKshrink recovery guide, the triggering temperature for shrinkage is around 343°C, which is actually the melting temperature (T_m) of PEEK.

The purpose of this study was to systematically investigate the SME in a commercial PEEK. The focus was on the influence of the programming conditions and heating temperature for shape recovery on R_r, particularly on the feasibility of low-temperature heating for shape recovery.

EXPERIMENTAL

Material

Thermoplastic Vestakeep PEEK (L4000G, virgin-grade) sheets were purchased from Evonik Degussa through Professional Plastics Pte, Ltd. (Singapore). Rectangular-shaped samples (9.5 × 9.5 × 6.5 mm^3) were prepared by means of laser cutting from the PEEK sheet for mechanical and shape-recovery tests. Small sample pieces were also prepared for thermal tests.

Thermal Tests

Thermogravimetric analysis (TGA; TGA 2950, Surplus Solutions, Inc.) was conducted from 25 to 850°C with a ramp rate of 10°C/min. Differential scanning calorimetry (DSC; DSC Q200, TA Instruments) tests were carried out between 25 and 400°C at a heating/cooling rate of 10°C/min. Dynamic mechanical analysis (DMA) was conducted in tension mode (DMA Q800, TA) at a heating ramp of 1°C/min.

Characterization of the SME

In theory, both the glass transition and melting in polymeric materials may be used for the thermoresponsive SME.[5,24] It should be pointed out that only in the presence of a crosslinked structure can a semicrystalline polymer recover its original shape when it is heated above T_m for shape recovery.[19]

In this study, the focus was on the glass transition only because the required corresponding heating temperature for recovery was lower, and thus, this would lower the energy costs in real engineering practices.

A series of uniaxial compression tests were conducted to program PEEK samples (9.5 × 9.5 × 6.5 mm^3) at two different temperature conditions with an Instron 5565, which had a temperature-controllable chamber for high-temperature tests. A constant strain rate of 0.1%/s was applied in both loading and unloading in all of the tests we conducted. The reason we applied uniaxial compression in programming was to prevent possible necking and propagation phenomenon, which causes significant uneven deformation, in uniaxial stretching glassy polymers.[13,34]

Note that for simplicity, the strain and stress in this study are the engineering strain and stress.

For the first condition, the samples (first group) were compressed at room temperature (ca. 22°C, so that the samples were in the glassy state according to the DSC results, shown later in Figure 3) to some prescribed ε_m's, which ranged from 10 to 50% with a 10% interval, and were then unloaded. Note that according to ZEUS's data sheet, the recoverable strain in its PEEKshrink tubing was about 35%.

For the second condition, samples (second group) were heated inside the temperature-controllable chamber for 15 min at prescribed temperatures (e.g., 120, 130, 140, 150, or 160°C; the temperature were measured with a thermocouple attached to the tested sample) and were then compressed to a maximum strain of 10 or 30%. Subsequently, the samples were cooled back to room temperature and unloaded.

Subsequent shape-recovery tests were carried out in two different ways according to the exact programming conditions.

For the first group of samples, which were programmed at room temperature, they were gradually heated in a furnace to 180, 200, 250, 300, and then 310°C in a step-by-step manner.

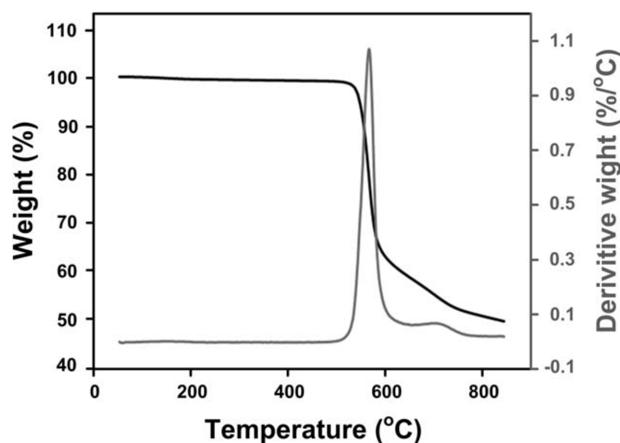

Figure 2. TGA results.

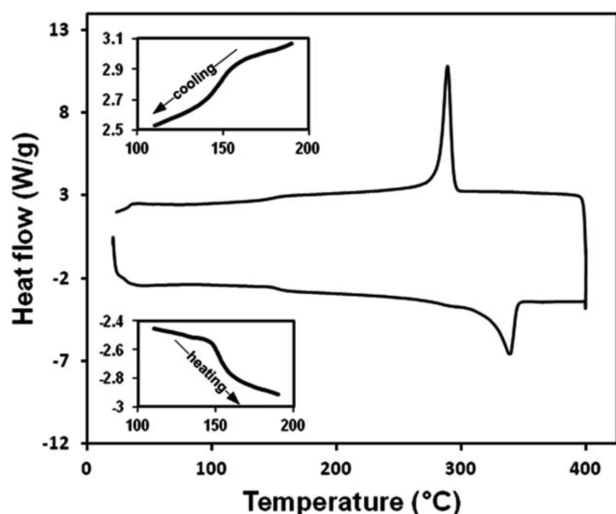

Figure 3. DSC results. The insets show zoom-in views of the glass-transition range in heating and cooling.

After a holding period of 15 min at the prescribed temperature, they were cooled to room temperature. The sample height was measured before the sample was heated to the next prescribed temperature in the following heating step.

For the second group of samples, they were gradually heated in a furnace to their respective programming temperatures first (viz., 120, 130, 140, 150, and 160°C). After a holding period of 15 min at the programming temperature, they were cooled to room temperature. The sample height was measured before the sample was reheated to 180°C for 15 min. After cooling, the sample height was remeasured again.

RESULTS AND DISCUSSION

Thermal Properties

Figure 2 presents the TGA curve of PEEK. According to Figure 2, there was virtually no weight loss before 500°C; this confirmed the high thermal stability of this PEEK.

Figure 3 is the DSC result of PEEK. As shown in Figure 3, there were two types of transitions in PEEK during thermal cycling between 25 and 400°C. The transition at the lower temperature range was the glass transition, and the glass-transition temperature (T_g) was about 155°C. The other transition at the higher temperature range was melting. A close look revealed that its T_m was about 340°C, whereas the crystallization temperature was about 285°C.

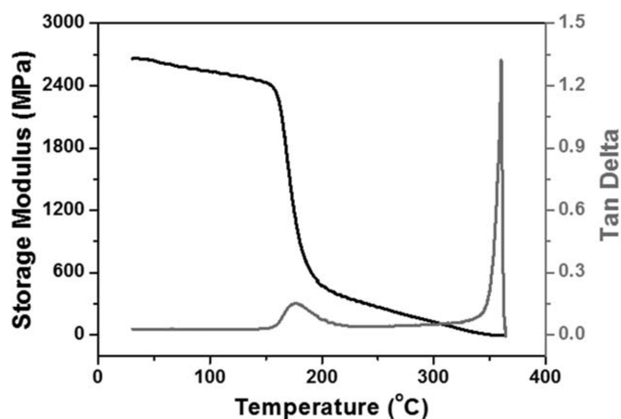

Figure 4. DMA results.

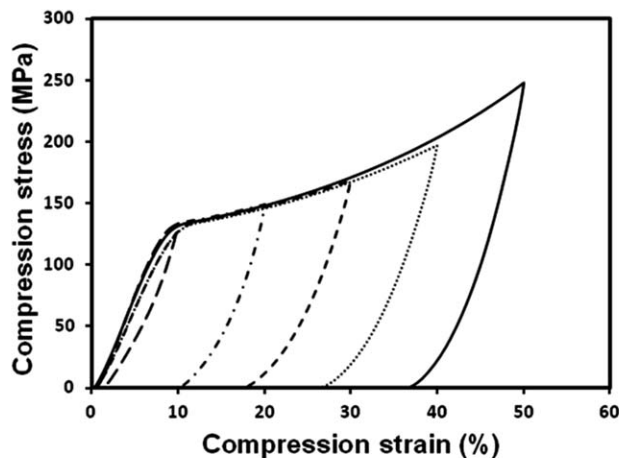

Figure 5. Typical stress–strain relationships of PEEK in uniaxial compression to different maximum strains at room temperature.

The relationships of the storage modulus and tan δ against temperature are plotted in Figure 4. It was clear that the storage modulus only started to drop significantly when it was heated to above about 160°C. As we observed, there were two peaks in the tan δ curve. The corresponding peak temperatures were about 175 and 355°C, respectively; these were slightly higher than T_g and T_m defined according to the previous DSC results. The diffidence was mainly due to the fact that different material properties were measured by DSC and DMA.

Shape-Memory Behaviors

Influence of the Maximum Strain (Room-Temperature Programming). Figure 5 presents the typical strain-versus-stress relationships of PEEK upon loading to five different maximum strains, namely, 10, 20, 30, 40, and 50%, followed by unloading at room temperature. As shown, during compression, PEEK experienced elastic deformation and then quasi-plastic deformation with apparent strain hardening. After unloading, a significant ε_u was observed, particularly when the applied maximum strain was high. Figure 6 plots the variation of the elastic modulus at unloading as a function of ε_m. It was apparent that the elastic modulus at unloading monotonically increased with increasing maximum strain. However, even for the 50% ε_m case, the variation of elastic strain due to the increase in the elastic modulus at unloading was less than 4%.

Figure 7 (gray line) presents the relationship of R_f versus ε_m on the basis of the experimental results. With the decrease in the fraction of the elastic strain in the total compression strain when the sample was compressed to higher maximum programming strains, the quasi-plastic strain became more significant. Consequently, R_f increased with increasing ε_m, from less than 10% at a 10% maximum programming strain to over 70% at a 50% maximum programming strain. Upon heating to 180°C, which was above the glass-transition range according to the DSC result in Figure 3), significant shape recovery did happen,

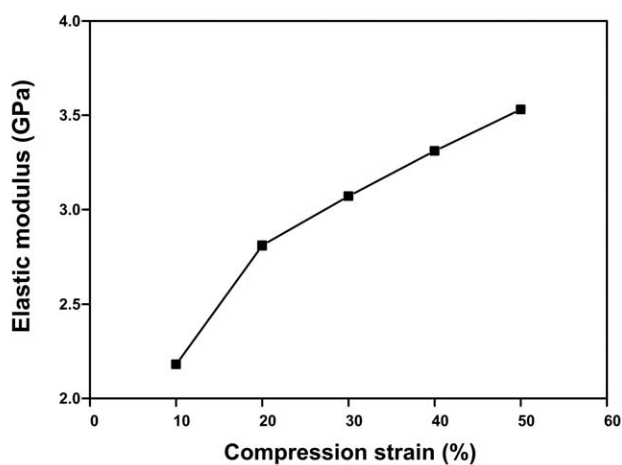

Figure 6. Elastic modulus at unloading as a function of ε_m.

as revealed in Figure 7 (solid black line). However, the exact recovery ratio decreased with increasing ε_m in programming, from about 100% at a 10% ε_m to about 82% at a 50% ε_m. Upon further heating to higher temperatures (the highest was 310°C, which was about the melting starting point in the heating process according to the DSC result in Figure 3), the increase in R_r was only slight, in particular at small ε_m's.

It was clear that this PEEK did have a good SME, even when they were programmed at room temperature, particularly when the applied programming strain was small. On the other hand, instead of heating to T_m as recommended in ZEUS's practice for its PEEKshrink tubing, heating to above its T_g was more or less good enough for shape recovery.

Influence of the Programming Temperature. Figure 8 presents typical strain versus stress relationships of PEEK upon compression to 10 or 30% at five different programming temperatures, namely, 120, 130, 140, 150, and 160°C, respectively. According to the DSC result in Figure 3, these five temperatures were around the lower half of the T_g range of this PEEK. Apparently, even at 160°C, the yield start stress of the material was still about 100 MPa; this confirmed the DMA result in Figure 4 and

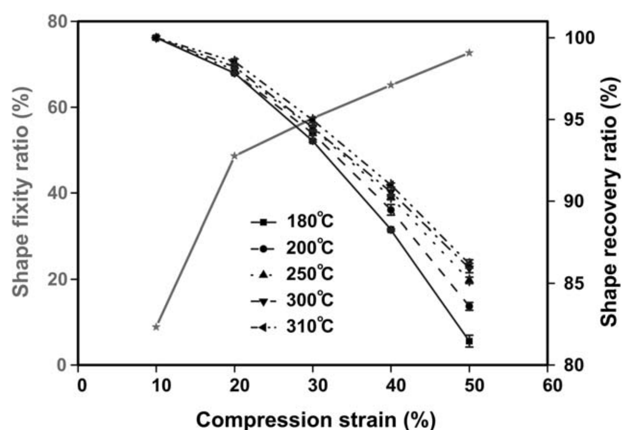

Figure 7. Evolution of R_f (gray line) and R_r (black line with deviation marked) against the programming strain (and heating temperature).

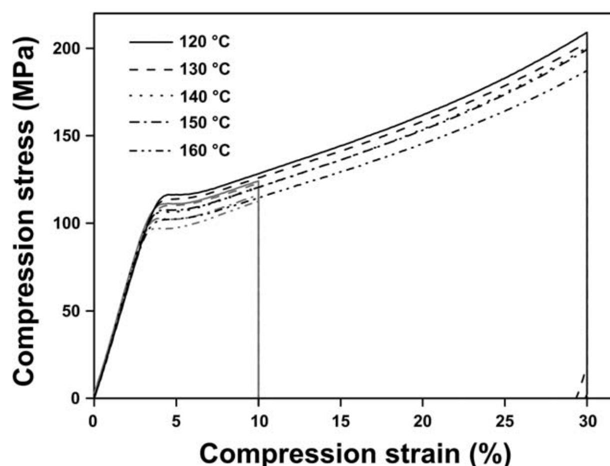

Figure 8. Typical stress–strain relationships in uniaxial compression at different temperatures to 10 and 30% maximum strains (gray and black lines, respectively).

demonstrated the high performance of PEEK as an important engineering polymer in high-temperature applications.

As shown in Figure 8, in both the 10 and 30% maximum strain cases, the strain during unloading seemingly did not change at all; that is, R_f of this material was about 100%. The thermal expansion/contraction of the whole experimental setup and PEEK sample (the coefficient of linear thermal expansion of this PEEK was about 0.6×10^{-4}/°C) during heating and cooling in programming were the major factors for this seemingly 100% R_f phenomenon. We will explore the precise reasons in future work.

Figure 9 reveals the evolution of R_r upon heating to the previous programming temperature and subsequent further heating to 180°C. For the 10% programming strain, R_r was always over 95% with a rough trend in which higher programming temperatures resulted in a higher R_r when the sample was heated to the previous programming temperature. This followed the same trend reported in refs. 24 and 34. Upon further heating to 180°C, R_r increased further and reached around 100%. The

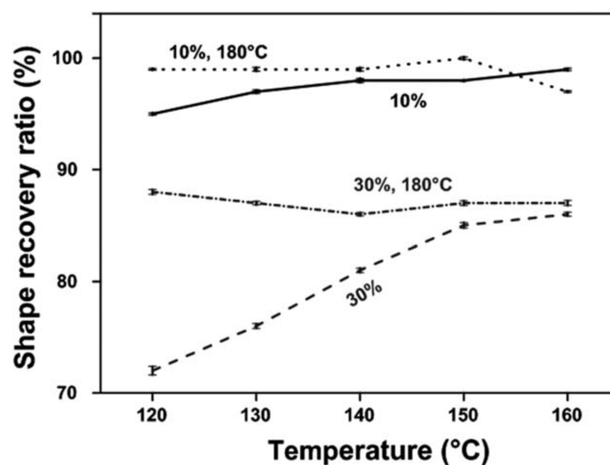

Figure 9. R_r (with deviation indicated) as a function of the programming temperature and strain.

seemingly abnormal case of a 160°C programming temperature was most likely due to a small experimental error during measurement. In the case of a 30% programming strain, the general trend in R_r upon heating to the previous programming temperature was similar. In the case of the 10% programming strain, the actual R_r was much lower, from 72% for the programming temperature of 120°C to 86% for the programming temperature of 160°C. After further heating to 180°C, the shape recovery values improved in all of the samples, and all of them reached about 88%.

Now, we concluded that around the lower half of the T_g range, with increasing programming temperature upon heating to the programming temperature, the corresponding R_r increased. However, the exact level of R_r was apparently not only programming-temperature-dependent but also programming-strain-dependent; that is, higher programming strains resulted in lower R_r's. On the other hand, R_r, upon further heating to higher temperatures, was virtually only dependent on the programming strain; that is, a lower programming strains resulted in higher R_r's. More importantly, R_r after heating to 180°C was about a constant; this was determined by the maximum programming strain but was independent on the programming temperature.

CONCLUSIONS

A systematic investigation was conducted to study the thermoresponsive SME in a commercial PEEK under the stress state of uniaxial compression. The following conclusions were obtained:

- This PEEK was a good high-temperature thermoresponsive SMM. In the case of lower shape-recovery strains, R_r was very high (ca. 100% for a maximum programming strain of 10%, above 95% for a maximum programming strain of 20%, and close to 90% for a maximum programming strain of 30%).
- At higher programming temperatures (ca. the lower temperature half of the glass transition), R_f was high, whereas at lower programming temperatures (i.e., room temperature in this study), R_f increased with increasing maximum programming strain.
- In the case of high-temperature programming to a fixed maximum programming strain, R_r upon heating to the programming temperature increased with increasing programming temperature.
- It was practically feasible to program PEEK at room temperature to save the energy used in processing.
- Instead of heating to around its T_m for shape recovery, which is recommended for PEEKshrink tubings, it was feasible to significantly lower the heating temperature to around its T_g (i.e., from about 340 to 180°C or even lower), whereas R_r was still around 80%, even for 30% maximum compression in programming.

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