The Fracture Behavior of Phenolphthalein Polyether–Ether Ketone at Elevated Temperature for Long Terms

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SYNOPSIS

The fracture behavior of phenolphthalein polyether–ether ketone (PEK-C) affected by physical aging at 200°C was studied by tensile experiments, scanning electron microscopy, and differential scanning calorimetry observations. The ductile–brittle fracture transition (DBT) caused by physical aging can be considered as a competition between fracture mechanisms of crazing and shear yielding. The aging time required for the DBT is found to be around 400 h, based on the morphological studies and tensile experiments. The shear yielding component of the mechanical deformation could erase the aging effect, thus a deaging phenomenon occurs. We found that the deaging phenomenon has an intrinsic relationship with the extent of aging in the specimen and as a result of the fracture behavior. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Glassy polymers are known to change their physical properties with time when used or stored at temperatures close to but below their glassy transition temperatures. This is because the glassy polymers obtained under normal cooling conditions are thermodynamically unstable. The gradual molecular relaxation toward their equilibrium structure is commonly referred to as physical aging, which was summarized by Struik[1] and extensively studied by other researchers.[1-13] Such studies have been performed in order to develop a better understanding of its molecular origin and to predict approximately changes of physical properties of polymers at extreme conditions. Physical aging has considerable practical importance because it affects all these temperature-dependent properties. In general, with increasing aging time and temperature below T_g, tensile yield strength, density, and excess enthalpy loss of polymers increase, while fracture energy, strain to break, and relaxation rate decrease.

A major problem with ductile polymers is their tendency to undergo transitions to brittle behavior when modified by annealing[2-4] or changing the testing conditions.[6,9] This problem obviously has important implications for the use of glassy thermoplastics in engineering applications. In general, this transition can be considered as being due to a competition between a brittle fracture mechanism such as crazing and a ductile mechanism such as bulk shear yielding.[5-9]

In contrast to chemical aging or degradation, physical aging is a reversible process, i.e., by reheating the aged polymer to a temperature above its T_g, the aging history can be erased.[1] This phenomenon was termed as deaging[1] or rejuvenation.[11] Moreover, it has been found that mechanical deformation can also produce the deaging phenomenon.[3,4,10-12]

High-performance thermoplastics, as engineering plastics or as materials for advanced composites, have been intensively developed in the past decades. Adequate physical properties at elevated temperature, especially under long-term aging, are required to ensure that such thermoplastics can meet high-performance requirements. In this work, phenolphthalein polyether–ether ketone (PEK-C), a novel high-performance thermoplastic developed in this Institute under a Chinese patent,[14] was studied to understand its fracture behavior at elevated temperature during the physical aging process.

EXPERIMENTAL

The PEK-C matrix used in this study was offered by Xuzhou Engineering Plastic Co., China. Its reduced viscosity in chloroform at 25°C is 0.9 dL/g. Owing to the cardo group attached to its main chain, PEK-C is an amorphous polymer with a very high glass transition temperature (220°C), excellent mechanical properties, and exceptional thermal resistance. At room temperature, its tensile modulus is 3.0 GPa and tensile yield strength is 100 MPa.

Powder of PEK-C was compression-molded at 330°C to sheets with thickness of 4 mm. Specimens, in accordance with ASTM D638, type I, machined from these sheets were then quenched, after heat equilibrium, from $T_g + 10°C$ to room temperature in air. Consequently, they were kept at $200 \pm 1°C$ in an air-circulating oven to exposure times up to 1500 h. Results from measurements of intrinsic viscosity and molecular weight distribution showed that there was no chemical degradation during this aging process.

Tensile tests were carried out on an Instron 1121 tensile tester in accordance with the ASTM D638 test procedure. To predict the end-use limits of the material at elevated temperature, these tests were carried out at 199°C.

A Perkin-Elmer DSC-7 was used with a heating rate of 10°C/min. Samples cut from the unnecked section and the fractured surface section of the same specimen after the tensile test were subsequently examined by DSC.

The microscopic failure mode was studied on a SEM (Model JAX-840). Prior to the SEM observations, the specimens were sputter-coated with gold.

RESULTS AND DISCUSSION

Effect of Physical Aging on Fracture Behavior

Figure 1 shows the yield strength of PEK-C, plotted against retaining or physical aging time, t_e, at 200°C. To predict the end-use limits of the material at elevated temperature, all tensile tests were carried out at 199°C. The yield strength increases and the elongation at break decreases with increasing t_e. A marked change takes place within the first 10 h. On further aging, only a slow asymptotic approach to equilibrium properties is observed. The yield strength shows a maximum at 589 h. When t_e exceeded this, during tensile testing, the stress increased approximately linearly with increasing elongation up to the breaking point. It then fractured in a brittle manner. On the other hand, necking and cold-drawing were observed in quenched specimens. Necking in specimens with t_e of several decades of hours began to occur at yield but never stabilized. This lack of stabilization resulted in a complete disappearance of stress during which fracture occurred. The yield zone fraction on a fractured specimen, as can be seen later, decreases with increasing t_e. For specimens after prolonged aging, there is no yield
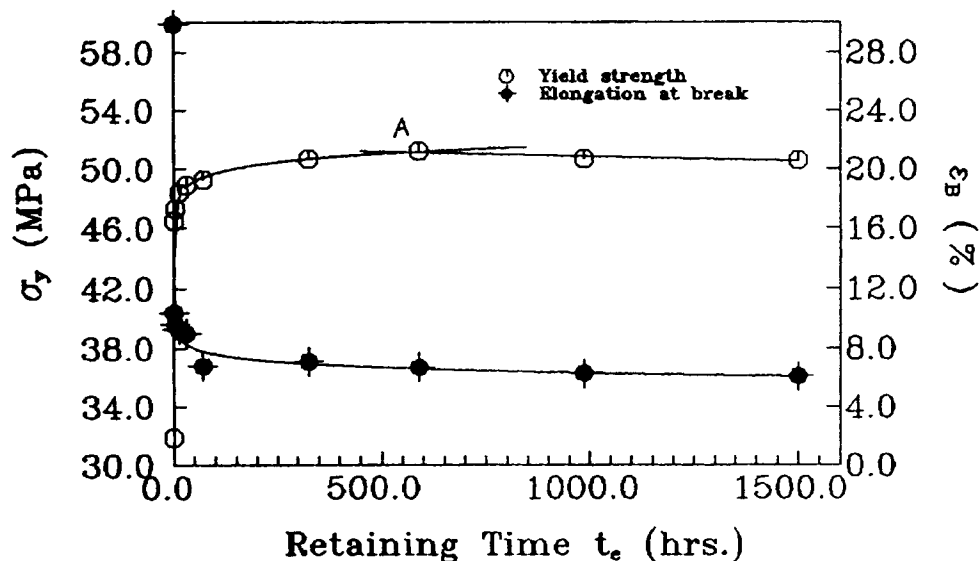

Figure 1   Tensile yield strength and elongation at break of PEK-C as a function of aging time at 200°C.

zone even on the fractured surface. This says that physical aging resulted in a ductile-to-brittle fracture behavior transition (DBT). This DBT phenomenon on progressive aging has been observed previously with polycarbonate (PC),[2] PEEK,[3] PET,[4] etc.

As can be seen from Figure 1, after several hundred hours of aging, the yield stress or fractured stress for aged specimens are almost the same. In agreement with our results, Pitman et al.[5] found that aging led to an increase in the yield strength of PC but did not significantly change the fracture stress. For simplicity, it is assumed that brittle fracture and plastic flow are independent processes, giving separate characteristic curves for the brittle fracture stress and the yield stress as a function of aging time.[6,7] According to this statement, the intersection of the two curves, shown in Figure 1, for yield stress and brittle fracture stress, respectively, may give us the approximate DBT time. The DBT for PEK-C caused by physical aging at 200°C occurred at about 400 h.

Morphological Analysis

The fracture surfaces of the specimens with various aging times were examined and photographed by SEM subsequent to the tensile testing. Some typical morphologies that can reveal the microscopic failure mode are shown in Figure 2. The quenched specimen and specimens aged for several decades of hours show typical ductile fracture morphology with clear evidence of ductile tearing on the fracture surface, as shown in Figure 2(a) and (b). In addition, there exist different extents of necking and cold-drawing on these samples. The fracture process was governed by a shear yielding mechanism. As a comparison, after prolonged aging, typical brittle fracture morphology, with a flat surface and no surface deformation signs, is shown in Figure 2(e) and (f) for specimens with t_e of 986 and 1500 h, respectively. The crazing mechanism is considered to be the microscopic failure mode for these samples. For a specimen aged 326 h [Fig. 2(c)], the fracture surface, which was slightly narrowed by tensile testing, shows evidence of localized shear deformation that dispersed in many regions. For this situation, the fracture might be initiated by some microcracks and then these microcracks propagated in the form of shear deformation. The shear yielding mechanism is dominant. For a specimen aged 589 h [Fig. 2(d)], the fracture surface is rougher than those shown in Figure 2(e) and (f) and shows a mixing failure mode. The fracture might be initiated by many microcracks that propagate in the form of multiple

crazing and/or shear yielding, but the crazing mechanism plays a leading role.

In agreement with our results, the ability of shear deformation is decreased by physical aging.[5,8] Hence, the aged polymer is brittle because it tends to undergo localized crazing rather than extensive shear yielding under an applied load. In general, the DBT can be considered as being due to a competition between a brittle fracture mechanism such as crazing and a ductile mechanism such as bulk shear yielding.[5-9] In the viewpoint of this competition concept, we may estimate the DBT time of PEK-C caused by physical aging at 200°C to be within 326–589 h.

Deaging Phenomena

The glass transition of aged specimens exhibit a marked endothermic process, as measured by DSC. The endothermic peak area, which reflects the recovery process of the structure relaxation, indicates the extent of aging. If the mechanical deformation could erase the aging effect, as many researchers have reported,[3,4,10] it must also erase the endothermic peak area between the unnecked section, which is cut from outside the yielded zone, and the fractured surface section, which is cut from the fractured surface on the same specimen.

The DSC curves for specimens aged 32 and 986 h are shown in Figure 3(a) and (b), respectively. For the 32 h-aged specimen, the endothermic peak for the deformed section disappeared and its DSC curve shows little difference from the quenched sample. In this situation, complete deaging occurs. In Figure 3(b), the endothermic peaks for undrawn and fractured section are almost the same. In this situation, the deaging phenomenon does not occur.

The endothermic peak area (ΔH), which indicates the extent of aging, with various aging times for both unnecked and fractured surface sections, are shown in Figure 4. As can be seen, when aging time exceeds 32 h, the ΔH increases with increased aging time for both sections. The low value of ΔH for the unnecked section with aging time below 13 h implies that the broad shear yielding that spread along the testing specimen had erased the aging effect. It is very interesting to note that the difference between the aging and deaging effect, i.e., the extent of deaging remains almost constant for the range of aging times of 32–589 h. The above results indicate that the deaging effect has an intrinsic relationship with the extent of aging and, as a result, with the fracture behavior. Only the shear yielding component of mechanical deformation could erase the aging effect.
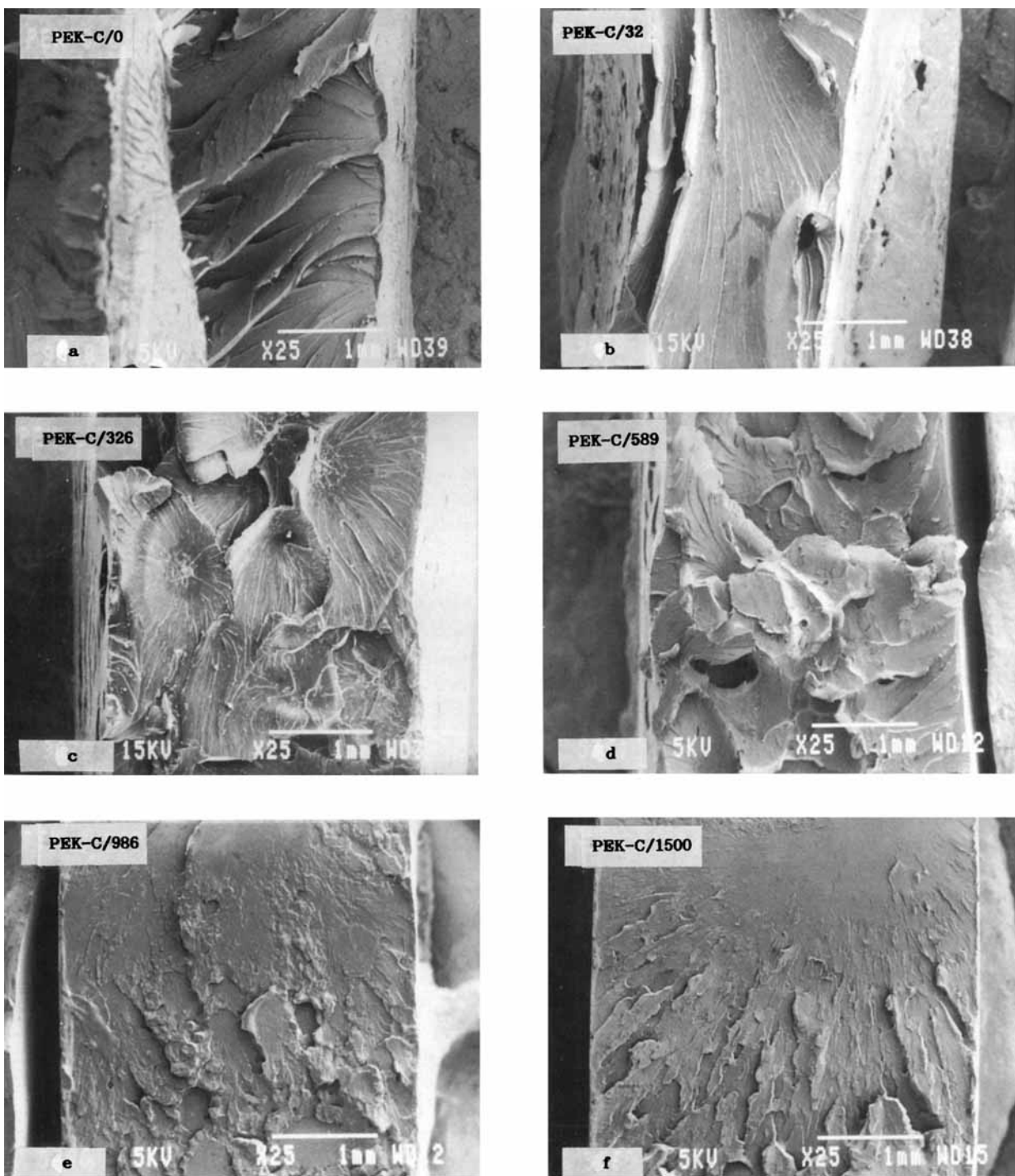
Figure 2   SEM micrographs of the fracture surface of quenched and aged PEK-C fractured by tensile tests: (a) quenched; (b) 32 h; (c) 326 h; (d) 589 h; (e) 986 h; (f) 1500 h.

It has been reported previously that the endo-thermic process observed in the DSC measurement of the glass transition on aged specimens is removed entirely after yielding.[1,3,10] This phenomenon could be explained by the free volume concept[1] for mechanical deformation, probably re-creating the free

volume in the aged specimen. Based on a comparison of normalized additional mechanical work, which is the work difference required to deform the aged and quenched specimen, and the excess enthalpy loss, Afref-Azor et al.[4] and Kemmish and Hay[13] found that the additional mechanical work was four to five
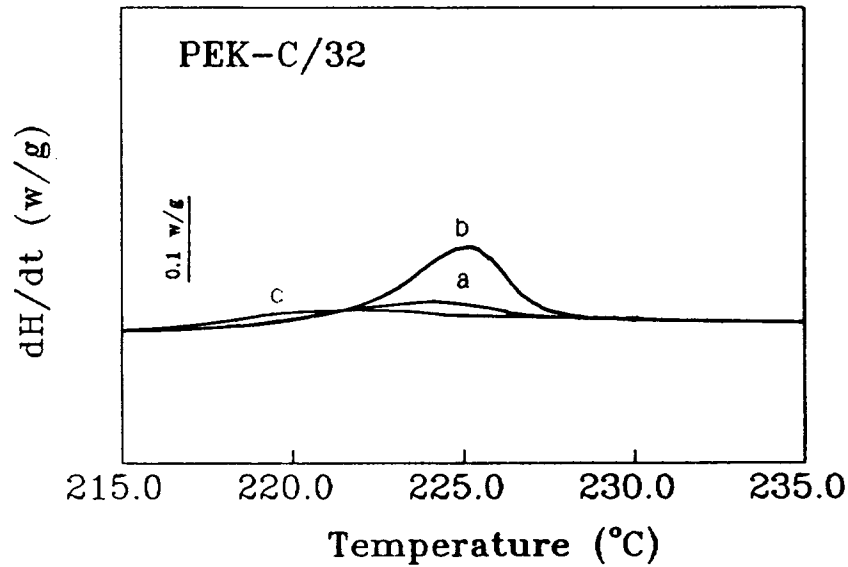
Figure 3   (a) DSC curves for specimen of aged 32 h. Curve (a) is for the fractured surface section; (b) for the unnecked section, and (c) for the quenched specimen.

times the ΔH and suggested that the endothermic process was eliminated by only part of the additional mechanical work involved in yielding. This suggestion could be reasonably explained by Maher's work with the use of an infrared camera which showed that at least 85% of the mechanical work done on the specimen during necking was converted into heat in the necking region.[13] Moreover, in the narrow zone of necking, the generation of heat is a consecutive process, leading to a consecutive softening of the material and is enough for heating the material above its glass transition temperature.[15]

In fact, the ability to deform and absorb energy under an applied load depends on the ease with which its molecular chains can slide past each other or change conformations via in-chain rotations. This ability and, as a result, the bulk shear deformation under tensile testing decreased markedly with increasing aging time. So, the deaging effect caused by shear deformation decreases with aging time. On the other hand, the rate of energy dissipation of localized heat, generated during the yielding process, slows down due to the lower mobility of molecular segments. Therefore, the localized temperature in-
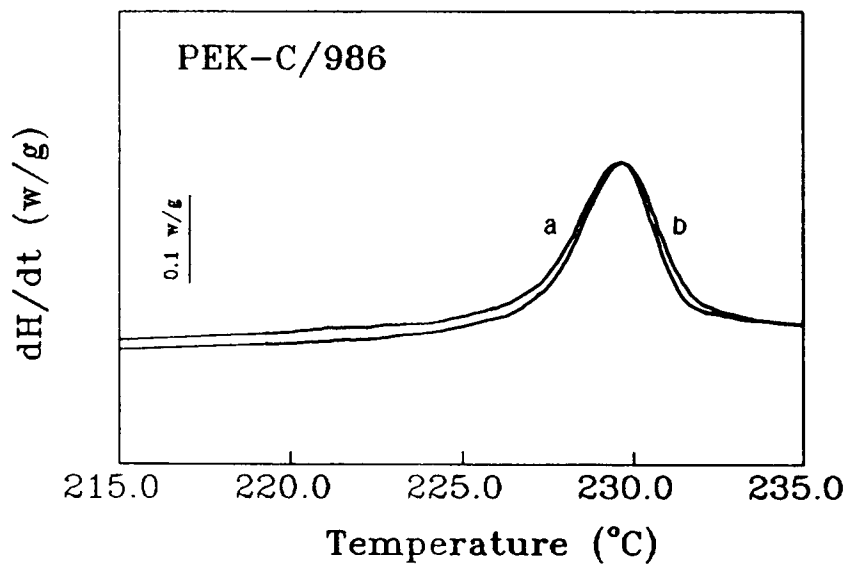

Figure 3   (b) DSC curves for specimen of aged 986 h. Curve (a) is for the fractured surface section; (b) is for the unnecked section.
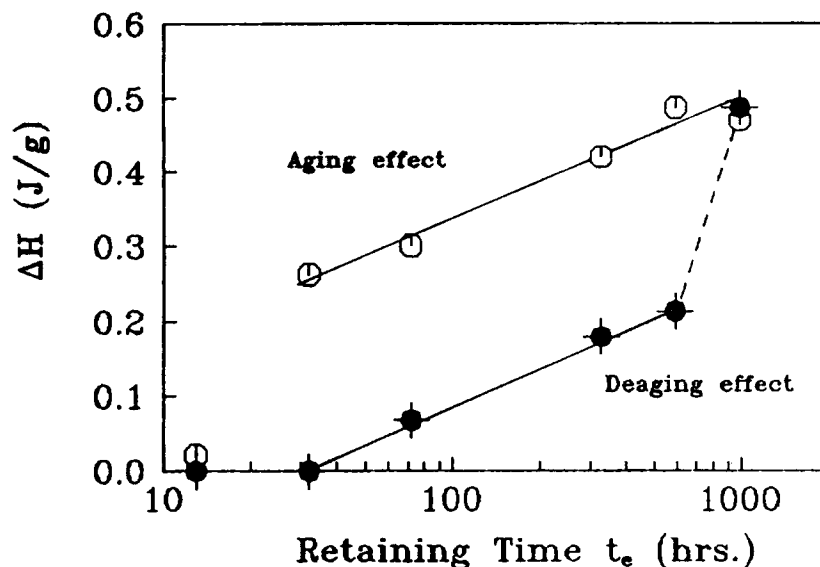
Figure 4 The endothermic peak area for both the unnecked and fractured surface sections on the same specimen with various aging times.

creased and the deaging effect caused by heat generation increased with aging time. As a whole, the deaging effect may not change for a long period time, as shown in Figure 4. It is concluded that the shear deformation and heat generation during yielding and cold drawing help each other forward and the cooperative effect results in the deaging phenomenon.

CONCLUSIONS

To predict the end-use limits of a material at elevated temperature, we studied the fracture behavior of PEK-C. It is found that a marked increase in tensile yield strength and decrease in elongation at break take place within the first 10 aging hours. On further aging, only a slow asymptotic approach to equilibrium properties are observed. The ductile-to-brittle fracture transition (DBT), caused by physical aging, can be considered as a competition between fracture mechanisms of crazing and shear yielding. Based on observations of fracture morphology and the assumption proposed by Ward,[6] the aging time required for DBT is found to be around 400 h.

Based on the DSC measurements, we observed that the deaging phenomenon was caused by the shear yielding component of mechanical deformation. We found that the deaging phenomenon had an intrinsic relationship with the extent of aging in the specimen and, as a result, with the fracture behavior.

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