

Thermal decomposition and micropore formation in PEK, PEEK and PES

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At strain rates greater than about 10 the deformation of polymers is an adiabatic process which can lead to the generation of very high localized temperatures. These may be well in excess of the temperatures required for thermal decomposition of the polymer to occur. It is speculated that gaseous products arising from such decomposition may act as the source of microcavities and craze initiators. Experiments are described in which the thermal decomposition reaction parameters of polyetherketone, polyetheretherketone, and polysulphone are measured using differential scanning calorimetry and thermogravimetric analysis, and the decomposition products analysed by mass spectrometry. The results indicate that the proposed mechanism could act as a source of micropores with total pore volumes amounting to several per cent of the material volume.

1. Introduction

Crazing ahead of propagating cracks in amorphous and semi-crystalline polymers is commonly observed and is believed to be initiated by the formation of micropores [1]. Theories for the formation of the pores attribute the formation to stress concentrations ahead of the crack [2]. However, previous work has shown that very high temperatures can be reached in the crack zone of a running crack in many polymers. Temperature rises of up to 500°C have been recorded in polymethylmethacrylate and similar rises have been recorded in polycarbonate, polyetherketone (PEK), polyetheretherketone (PEEK) and polyethersulphone (PES) [3,4]. These high temperatures are restricted to an area of ~1 µm on either side of the crack and their duration is of the order of tens of microseconds. Nevertheless, they greatly exceed the thermal decomposition temperatures for these materials and it would, therefore, be probable that the formation of the pores could be assisted by the presence of gaseous decomposition products in the heated region. In order to assess the possibility of such a pore-formation mechanism, we conducted thermal decomposition experiments on PEK, PEEK, and PES. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) have been used to evaluate the decomposition rate parameters, and mass spectrometry (MS) to identify the decomposition products. The kinetic parameters can be used to deduce by extrapolation the likely fractional decomposition ahead of a crack and the MS results to estimate the percentage of pore volume resulting from the decomposition.

2. Experimental procedure

2.1. Decomposition kinetics

DSC measurements were carried out in a Mettler DSC-20 system, on 10 mg samples heated in an argon atmosphere at 2–100 K min⁻¹, to a maximum of 600°C. The sample under study was sealed in an aluminium pan with a hole in the lid, which permitted decomposition products to escape. Each experiment was repeated at least three times to check for reproducibility. The activation energies E were calculated from the reaction peak rate temperatures, T_{\max} , corresponding to various heating rates, H , because

$$E = - \frac{R}{0.457} \frac{d(\log H)}{d(1/T_{\max})} \quad (1)$$

(R being the gas constant) by the Ozawa method [5], which is similar to those of Flynn and Wall [6], Duswalt [7] and Jones *et al.* [8]. The pre-exponential factor, A , was obtained by a method based on the work of Rogers and Smith [9], as

$$A = HE \exp\left(\frac{E}{RT_{\max}}\right) / RT_{\max}^2 \quad (2)$$

This method is sensitive to errors in E and T_{\max} but not to errors in H and thus excels in the treatment of DSC data, for which H will not be accurately known at the reaction rate maximum.

PES did not yield sufficiently reproducible results for reliable calculation of E and A . For it, separate TGA experiments were carried out in a SETARAM TGA-92 system, at 5, 10, 30 or 80 K min⁻¹ in a dynamic

TABLE I Decomposition rate parameters

Material	$E(\text{kJ/mol})(\pm 10\%)$	$A(\text{s}^{-1})(\pm 10\%)$
PEK	230	4.6×10^{11}
PEEK	220	1.3×10^{11}
PES	280	2.7×10^{13}

argon atmosphere. The gravimetric data were differentiated with manufacturer-supplied software.

Table I summarizes our derived rate parameters, where the mole refers to the molecular weight of the monomer. It should be emphasized that their significance is strictly phenomenological; the methods of data analysis we have adopted are insensitive to the form of the governing kinetic function $f(1 - \alpha)$, to be discussed below [10], which may only be identified with confidence from isothermal experiments [11]. However, they suffice for our present purpose, namely extrapolation of the decomposition rate to a higher temperature rather than elucidation of the underlying reaction mechanism.

2.2. Mass spectrometry

Experiments were carried out in a UHV (10^{-9} torr; 1 torr = 133.322 Pa) system equipped with a ULVAC MSQ-400 quadrupole mass spectrometer, which has been modified to become capable of scanning up to 500 a.m.u. Its electron energy was set at 70 eV. A furnace situated in the centre of the system was heated to 500 °C and, after equilibrium had been reached and the background mass spectra recorded, the sample under study was introduced into the furnace using an externally driven arm. The sample temperature before introduction into the furnace region was monitored to ensure that the background did not contain decomposition products, which could therefore be identified via a comparison of the mass spectra before and after sample heating. The former, background spectrum had no peaks of mass > 50. Table II sets out the main peaks observed of mass > 50 in spectra scanned after heating the respective materials, the molecular structures of which are illustrated in Fig. 1.

Fission of any of the three molecules along the bonds between the CO or SO₂ groups and the benzene rings would lead to the production of C₁₂OH₁₀ (170 a.m.u.). This is evident in all spectra which contain mass 168 corresponding to the above before the addition of hydrogen to each of the benzene groups. Other major components are C₆H₆ (78) and C₆H₆OH (94). SO₂ (64) accounts for a large peak in the PES decomposition spectrum, and H₂C₄O, produced by

TABLE II Main decomposition peaks above 50 a.m.u.

Material	Product masses (a.m.u.)
PEK	66 ^a , 93 ^a , 141, 168, 170 ^a , 197, 242
PEEK	78 ^a , 94 ^a , 133, 140, 168, 170 ^a , 207 ^a , 281 ^a
PES	64 ^a , 78, 94 ^a , 143, 168, 170, 246

^aPeaks of high intensities.

Repeat unit

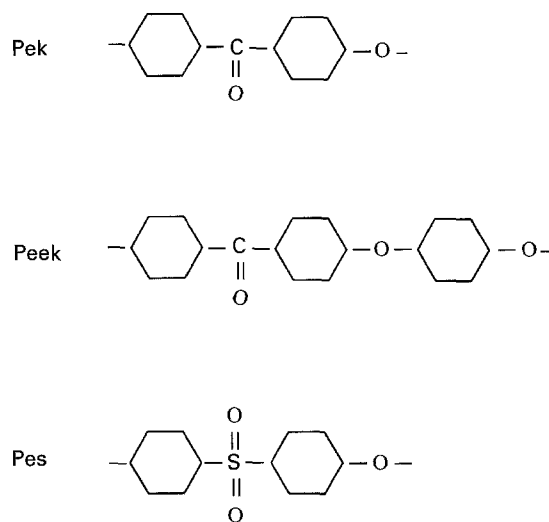


Figure 1 Repeat units for PEK, PEEK and PES.

opening the rings, can be assigned to the observed 66 in the PEK spectrum.

Decomposition products of mass < 50 were determined by subtracting the background from respective spectra. For PES the main increases are seen at mass numbers 28, 40, 44 and 48, attributable to CO, C₃H₄, CO₂, SO, respectively. For PEK (and PEEK) the major increases are for species of mass numbers 28, 40 and 44. Their peaks are at least a factor of 10 bigger than those of higher (> 50) masses. The indication is, therefore, that decomposition (mainly thermal) at these temperatures leads predominantly to the production of low molecular weight species CO, C₃H₄, CO₂, and for PES, SO and SO₂, in addition to C₆H₆, C₆H₆OH and C₁₂OH₁₀.

3. Discussion

The aim of this work was to estimate the void volume generated ahead of a running crack in a polymer. Therefore, from the measured kinetic parameters we now calculate the extrapolated decomposition rate at the maximum temperature, 1000 K, expected to arise during fracture of the polymers. Because the decomposition rate

$$\dot{\alpha} = Ae^{-E/RT}f(1 - \alpha) \quad (3)$$

but the degree of conversion, α , is nearly zero in the present situation, we may put $f(1 - \alpha)$ equal to 1. This approximation holds for all standard decomposition models when α is very small (< 0.01). This leads to values of $\dot{\alpha} \approx 0.63, 0.53$ and 0.07 s^{-1} for PEK, PEEK and PES, respectively. Let us take $\dot{\alpha} = 1 \text{ s}^{-1}$. The time of decomposition (ahead of the crack) is estimated as the time it takes for a crack to traverse the heated zone ahead of a running crack. Measured crack velocities during catastrophic failure of PEK, PES and PEEK are $\sim 200 \text{ m s}^{-1}$. The crazed zones ahead of cracks in a range of polymers extend up to 1 mm [12] and imply a duration of decomposition about 5 μs . Thus one would expect a fraction of $\sim 5 \times 10^{-6}$ of the polymer

ahead of the crack to have decomposed. The main decomposition products have been shown to be CO, CO₂ and low molecular-weight hydrocarbons which will be gaseous and therefore tend to produce bubble-like pores. Although the distribution of pores volumes is unknown, the aggregate fractional volume taken up by the products can be calculated if they are treated as perfect gases. The fractional volume occupied is given by $(\alpha\rho/M) 22.4 \times 10^3$, where ρ is the specific gravity of the polymer and M the average products molecular weight. Inserting the values for α and putting ρ equal to 1.2 and M to 50 yields $\sim 6 \times 10^{-3} \text{ m}^3 \text{ m}^{-3}$. However, this is at STP. In the tensile region ahead of the crack, $T \sim 1000 \text{ K}$, and the pressure falls into vacuum levels. It is therefore not unreasonable to expect an increased value for gaseous product volume to several per cent of the polymer volume. The results of these experiments indicate that during rapid localized deformation of polymers, at strain rates such that the process is adiabatic, temperatures, decomposition rates and products are likely to cause a significant amount of void generation.

Theories of craze extension are often dependent on the meniscus instability mechanism developed by Argon and Salama [13] who rejected the concept of repeated generation of pores ahead of the craze tip. Repeated nucleation is, however, the favoured mechanism of other workers [12]. The work described here suggests a mechanism for the generation of micropores which does not require any inhomogeneities in the material to act as stress concentrators, but derives solely from the thermal stability of the polymer. Although we have concentrated on high strain rates, where processes are adiabatic, the thermal mechanism for micropore formation may also contribute at lower strain rates, because strains within the craze zone are high and, on a local level, the strain rates may still suffice to produce localized high temperatures. Strains of 200% are common in crazed material and this

strain occurs over a craze length of $< 1 \text{ mm}$. Thus, even if a constant strain rate is assumed, the rate would be $\sim 2 \text{ s}^{-1}$ for a craze elongation rate of 1 mm s^{-1} and this would be sufficient for the process to be adiabatic.

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