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Fracture and Damage Evolution of Fluorinated Polymers

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ABSTRACT

Fluoropolymers are often semi-crystalline in nature, with their linear chains forming complicated phases near room temperature and ambient pressure. The most widely used fluorocarbon polymer for engineering applications is polytetrafluoroethylene (PTFE), due to its extremely low coefficient of friction, outstanding resistance to corrosion, and excellent electrical properties. The phase structure of PTFE is complex with four well-characterized crystalline phases (three observed at atmospheric pressure) and substantial molecular motion well below the melting point. The first-order transition at 19°C between phases II and IV is an unraveling in the helical conformation. Further rotational disordering and untwisting of the helices occurs above 30°C giving way to phase I. The mechanical behavior, including fracture and damage evolution, of PTFE depends on the chain and segment motions dictated by crystalline phase microstructure. The presence of three unique phases at ambient pressure near room temperature implies that failure during standard operating conditions may be strongly dependent on the phase. This paper presents a preliminary study of fracture and damage evolution in PTFE with the effects of temperature-induced phase on fracture mechanisms. The quasi-static fracture of PTFE in the atmospheric pressure regime, over a range of temperatures, was found to be strongly phase dependent: phase II exhibits brittle-fracture, phase IV displays ductile-fracture with crazing and some stable crack growth, and plastic flow dominates phase I. The bulk failure properties are correlated to failure mechanisms through fractography of the fracture surfaces (optical microscopy and scanning electron microscopy (SEM)).

1. INTRODUCTION

Compared with other polymers, those containing fluorine present several advantages for load-bearing structural components including higher strength at elevated temperatures and higher toughness at lowered temperatures [1]. Failure sensitive applications of fluorocarbon polymers include surgical implants, aerospace components, motor seals, and barriers for hazardous chemicals. Fluoropolymers are often semi-crystalline in nature, with their linear chains adopting complicated phases near room temperature and ambient pressure. The most widely used fluorocarbon polymer for engineering applications is polytetrafluoroethylene (PTFE), $-(CF_2)_n-$, which possesses a combination of desirable chemical and physical properties including excellent high temperature stability[2], chemical resistance [3], dielectric properties [4] and extremely low coefficient of friction [5]. The phase behavior of PTFE, as first reported by Bunn and Howells in 1954 [6] and shown in Fig. 1 [7,8], is particularly interesting with two crystalline transitions at 19°C [6] and 30°C [1] and atmospheric pressure. Substantial molecular motion within the crystal is observed well below the melting point (~340°C [9]). The first-order transition at 19°C between phases II and IV is an unraveling in the helical conformation from a well-ordered triclinic structure with 13 atoms/180 degree turn [1,6] to a partially ordered hexagonal phase with 15 atoms/turn [1,7,10]. Further rotational disordering and untwisting of the helices occurs above 30°C giving way to phase I to form a pseudohexagonal structure with dynamic conformational disorder and long-range positional and orientational order [1,2]. The crystalline domains of PTFE form sheets measuring 0.2–1.0 μm thick and several microns in the plane [11] to create a complex composite structure within an amorphous matrix. Interestingly, as for many other polymers, the mechanical characteristics of PTFE including fracture and damage evolution exhibit significant dependence on subtle changes in the polymer structure. The presence of three unique phases at ambient pressure near room temperature implies that failure during standard operating conditions may be strongly dependent on the phase.

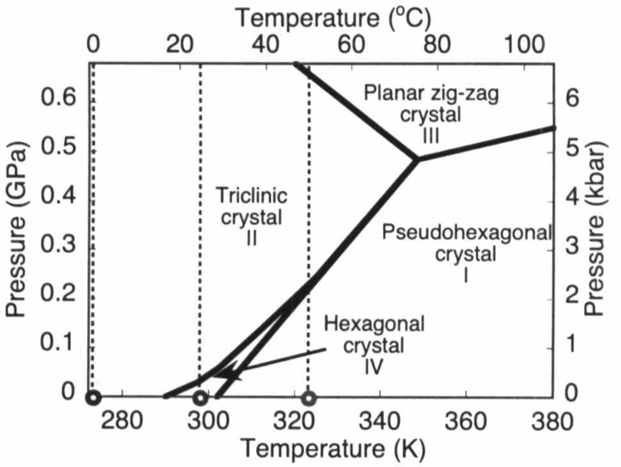
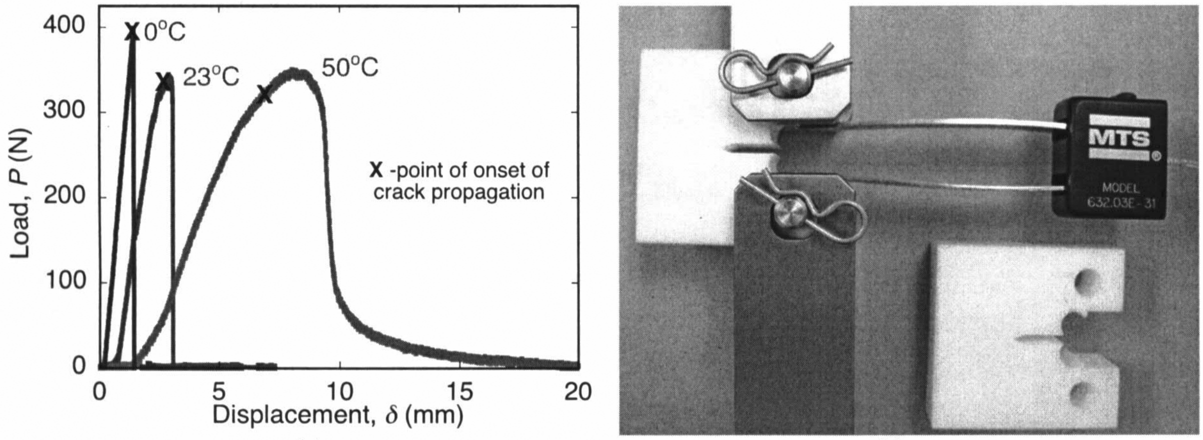


Figure 1. Pressure–temperature phase diagram of PTFE [6,7].

Despite an extensive body of work in the literature investigating aspects of the chemical structure of PTFE, such as the crystalline phase transitions and the percent crystallinity, these studies have focused on virgin, as manufactured—pressed and sintered—material. Conversely, most studies of the mechanical behavior of PTFE have either focused on a single temperature [12–14] or disregarded the occurrence of phase transitions over the temperature range investigated [15–17]. Notable exceptions include work by McCrum [18] and Kisbenyi [19] measuring the temperature dependence of modulus and loss factor to correlate changes in mechanical behavior with phase transitions. Moreover, the mechanical and chemical characteristics of PTFE are strongly dependent on the grade of molding powder and method of processing used to manufacture the polymer, yet the majority of work in the literature reports on generic samples tested without sufficiently communicating the specifics of the polymer being measured. To illustrate the process dependent variation, the crystallinity of PTFE prepolymer resin ranges from 93–98%, which is reduced to 40–80% crystallinity in the final product due the melting and recrystallization that occurs during sintering and cooling of the polymer [19,20]. An interdisciplinary team at Los Alamos National Laboratory has been pursuing a comprehensive investigation of the mechanical properties of pedigreed PTFE 7A and 7C polymer. This paper focuses on the systematic study of fracture and damage evolution of PTFE in relation to the effects of temperature induced crystalline phase of fracture mechanisms.

2. FRACTURE BEHAVIOR

The quasi-static fracture of PTFE in the atmospheric pressure regime, over a range of temperatures, was found to be strongly phase dependent. Representative load–displacement curves are given in Fig. 2a for double-edge-notched tension specimens tested at 0°C, 23°C, and 50°C corresponding to phase II, phase IV, and phase I respectively. The specimens were notched with a razor blade. The load for initiation of crack propagation is indicated with an "X". Phase II exhibits linear-elastic brittle-fracture, phase IV displays ductile-fracture with some stable crack growth, and plastic flow dominates phase I with continuous stable crack extension. Analysis is performed for compact tension specimens (Fig. 2b) with the normalization method to obtain fracture initiation properties J_{IC} as outlined by ASTM E-1820 and Joyce [17]. The initial elastic modulus and yield stress of PTFE are both measured to decrease with increased temperature, which supports the observed increase of plasticity in the higher temperature phases [21]. The bulk failure properties are correlated to failure mechanisms through fractography of the fracture surfaces. As shown in Fig. 3, the fracture plane morphology changes significantly with the different phases. For each sample types tested, low magnification optical micrographs of the region of the precrack tip and of a representative region from the center of the fracture surface were acquired. High magnification micrographs of the center of the fracture surface were also acquired using a scanning electron microscope (SEM). The fracture surface of the phase II PTFE is indicative of brittle fracture; the fracture surface morphology is glassy down to micron length scales with regions of Wallner lines [22]. Minimal Poisson contraction or plastic zone are observed in the region of the crack tip. Phase IV PTFE exhibits the onset of hackle features and increased Poisson contraction at the crack tip. The size and prevalence of hackle features increases in phase I PTFE indicative of ductile tearing, as well as localized deformation at the crack tip. At higher magnification the fracture surface features a strong interlaced structure of microfibrils [23], with rigid domains beneath the microfibril structure. Similar transitions are observed for the mechanical behavior and fracture plane morphology for tensile dogbone specimens, as shown in Fig. 4. These tests showed a pronounced phase and temperature dependent complex convolution of visco-elastic and visco-plastic deformation. Phase II PTFE 7C (–50°C) exhibits brittle fracture morphology, with minimal plastic deformation and low strain to failure (76 MPa ultimate true strain, 0.55 ultimate true strain [21]). The maximum ultimate properties are obtained in Phase IV PTFE 7C (25°C) (190 MPa ultimate true stress, 1.75 ultimate true strain [21]). The residual plastic true strain is 1.01 and the fracture plane morphology is ductile with extensive drawing but with out localized fibril formation. Phase I PTFE 7C (50°C) failure is dominated by localization leading to extensive fibril formation followed by ductile fracture. The ultimate properties decrease slightly (137 MPa ultimate true stress, 1.65 ultimate true strain [21]), while the residual plastic true strain (0.97) remains significant.



(a) (b)

Figure 2. (a) Representative load–displacement curves for double-edge-notched tension specimens tested at 0°C (phase II), 23°C (phase IV), and 50°C (phase I). (b) Compact tension specimens with load line mounted CTOD gage.

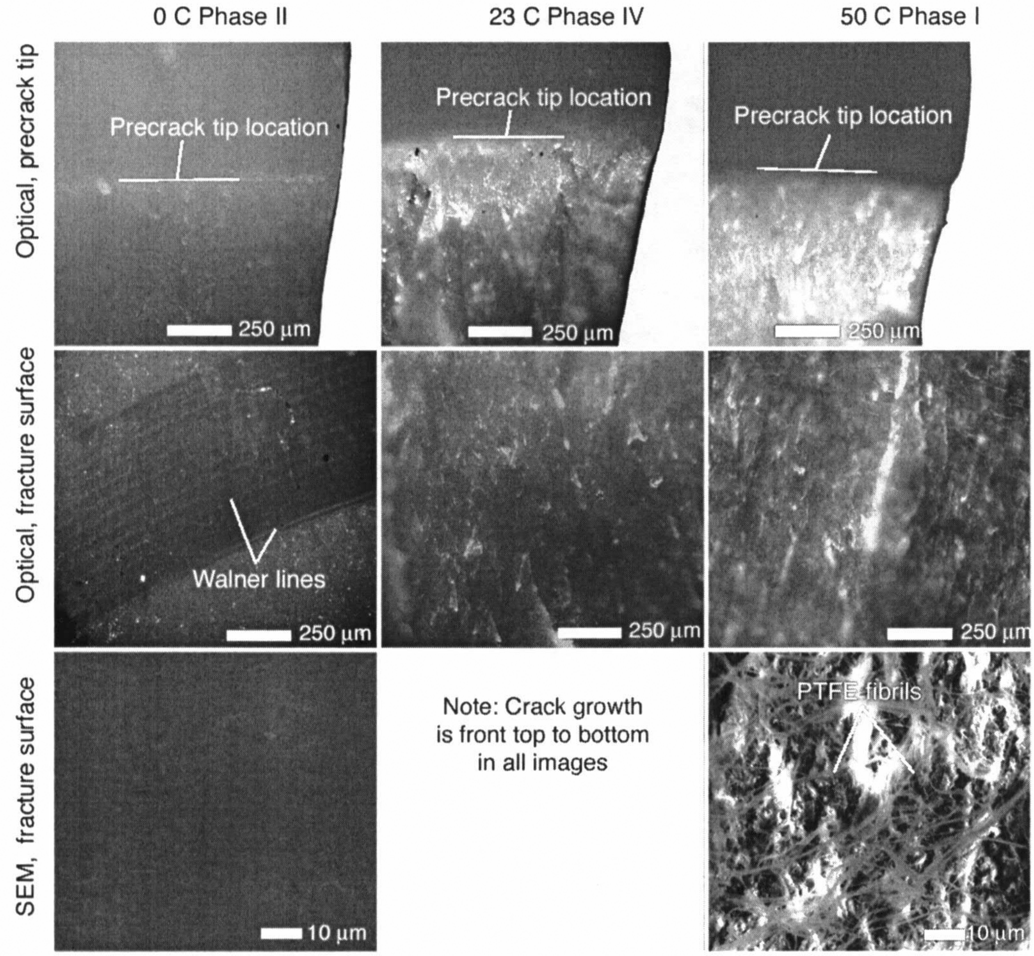


Figure 3. Optical and electron micrographs of the fracture surfaces for samples tested at 0°C, 23°C, and 50°C.

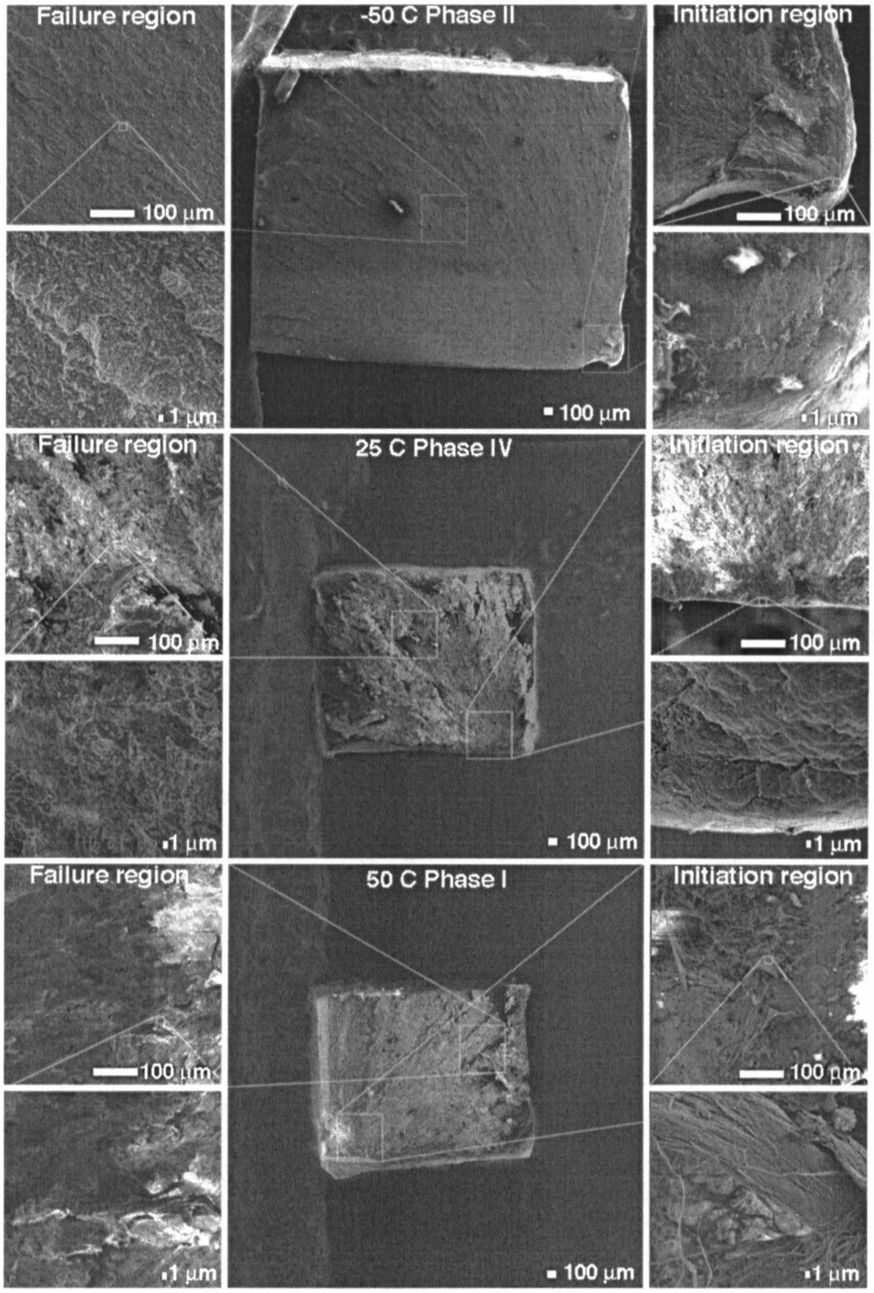


Figure 4. Scanning electron micrographs of the failure surface for PTFE 7C dogbone specimens tested as –50, 25, and 50°C.

3. STRUCTURAL ANALYSIS

The mechanical behavior and failure of PTFE is correlated to changes in the polymer microstructure associated with plastic deformation. Transmission polarized optical microscopy and atomic force microscopy (AFM) are performed on microtomed samples of deformed and undeformed PTFE to characterize the crystalline domains and the residual stresses in the deformed amorphous polymer resulting from constraint at the boundary with the less compliant crystalline structure. Modulated differential scanning calorimetry (MDSC) and Helium pycnometry are utilized to measure changes in the concentration of crystalline domains resulting from plastic deformation in the plastic zone. Crystallinity measurement in PTFE has been reviewed extensively in the literature (see for example [1,20,24]). The percent crystallinity can be estimated as the ratio of the area of the melt endotherm (heat of fusion ΔH^S_f) measured from MDSC with the theoretical heat of fusion for a 100% crystalline sample ΔH^0_f. Values of ΔH^0_f for PTFE in the literature range from 57–104 J/g [24]. In the current work, ΔH^0_f is taken to be 80 J/g and calculated the weight fraction of crystallinity by

$$X_c = \Delta H^S_f / \Delta H^0_f \tag{1}$$

Alternately, the percent crystallinity can be determined from a simple rule-of-mixtures argument using the measured density ρ for PTFE of unknown crystallinity and known density values for pure amorphous PTFE ρ_a (X_c = 0%) and pure crystalline PTFE ρ_c (X_c = 100%),

$$X_c = \frac{\rho_c}{\rho}\frac{\rho - \rho_a}{\rho_c - \rho_a}. \tag{2}$$

However, pure amorphous and pure crystalline PTFE cannot be experimentally isolated requiring extrapolation of values for ρ_a and ρ_c, as shown in Fig. 5. A range of crytallinities was achieved by using the PTFE molding powder, the as pressed and sintered PTFE, and sintered PTFE that was heat treated by either quenching to obtain reduced crystallinity or slow cooling to obtain increased crystallinity. For the two pedigreed PTFE materials under investigation, the extrapolated pure crystalline density ρ_c is 2.302 g/cm^3 in good agreement with the literature [24], including IR measurements [25] and calculations based on the crystallographic unit cell [26]. However, the data for 7A and 7C PTFE fall on slightly different lines yielding extrapolated pure amorphous densities ρ_a of 2.086 g/cm^3 and 2.069 g/cm^3 respectively. While these are slightly higher than the commonly references value for ρ_a of 2.060 g/cm^3 [24,27], values of up to 2.080 g/cm^3 have been reported [24]. The literature for PTFE has focused entirely on changes in crystallinity due to thermal history, and, as illustrated in Fig 5, the relationship given by Eq. (2) accurately captures the resulting behavior. In relation to the current work, deformation is known to cause changes in polymer crystallinity, as reported for polyethylene [28], polyethylenenaphthalate [29], polyethyleneterephthalate [30], and polyvinylidenefluoride [31]. In each case, crystallinitity was calculated from changes in density and was reported to increase with increased uniaxial deformation. Plastically deformed PTFE also exhibits increased density, as shown in Fig. 4 for quasi-statically (tensile dog bone with plastic true strain of ~1) and dynamically deformed material (Taylor Anvil specimen and impacted dynamic deformed specimens), which from Eq. (2) indicates an increase in crystallinity. However, the heat of fusion decreases with increasing deformation, suggesting that in reality deformation leads to decreased crystallinity in PTFE. In part, the divergence of density/heat of fusion data from the linear relationship (Fig. 5) may result form the simplicity of the model, which assumes a composite of only purely crystalline domains in a purely amorphous matrix, when in reality an interphase exists between the amorphous and crystalline domains introducing a third set of properties. Moreover, Eq. (2) assumes two fixed end values, when in reality the densities will be depend on changes in polymer chain orientation and free volume associated with plastic deformation. The crystalline density is greater than amorphous density due to high degree of orientation of the polymer chains and associated tighter packing. Amorphous domains can be oriented resulting in polymer chain packing that is more efficient than the unoriented polymer, with a dense that approaches the density of the crystalline polymer.

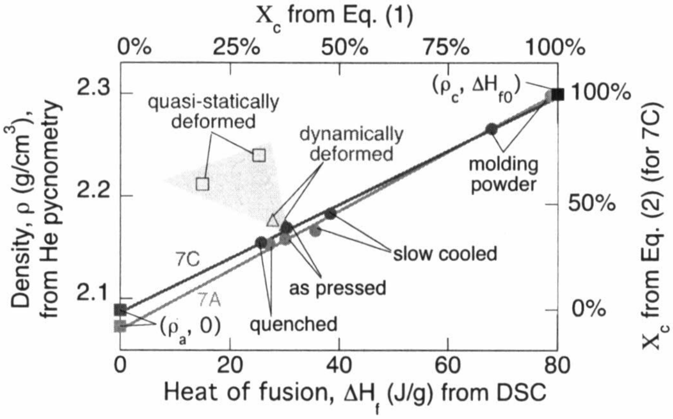


Figure 5. Density versus heat of fusion for undeformed PTFE 7A and 7C with varied crystallinity and deformed material.

4. CONCLUSIONS

The fracture behavior of polytetrafluoroethylene is characterized with consideration for dependence on temperature induced phase transformations. Mechanical behavior is correlated to the fracture plane morphology, changes in the crystalline concentration, and orientation of the amorphous polymer chains. The quasi-static fracture of PTFE in the atmospheric pressure regime, over a range of temperatures, was found to be strongly phase dependent: phase II exhibits brittle-fracture, phase IV displays ductile-fracture with crazing and some stable crack growth, and plastic flow dominates phase I. Crystallinity values from DSC and density measurements show good agreement for samples of varied thermal histories, but deviate significantly following mechanical deformation.

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