

PHASE DEPENDENT FRACTURE AND DAMAGE EVOLUTION OF POLYTETRAFLUOROETHYLENE (PTFE)

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Summary Polytetrafluoroethylene (PTFE) has been described as being in many ways the extreme of known polymers with high stability at elevated temperatures and significant toughness at lowered temperatures. At ambient pressure PTFE transitions between three crystalline phases close to room temperature. This paper presents the fracture and damage evolution of PTFE and elucidates the dependence of mechanical behavior on polymer crystalline structure.

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 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), 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), as shown in Fig 1a [2,3], 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 [4]. The crystalline domains of PTFE form sheets measuring 0.2–1.0 μm thick and several microns in the plane [5] to create a complex composite structure within an amorphous matrix. The mechanical behavior, including failure mechanisms, of PTFE depends on the chain and segment motions dictated by crystalline phase microstructure. The presence of three unique phases near room temperature implies that failure during standard operating conditions may be strongly dependent on the phase. This paper presents a comprehensive and systematic study of fracture and damage evolution of PTFE in relation to the effects of temperature-induced phase on fracture mechanisms.

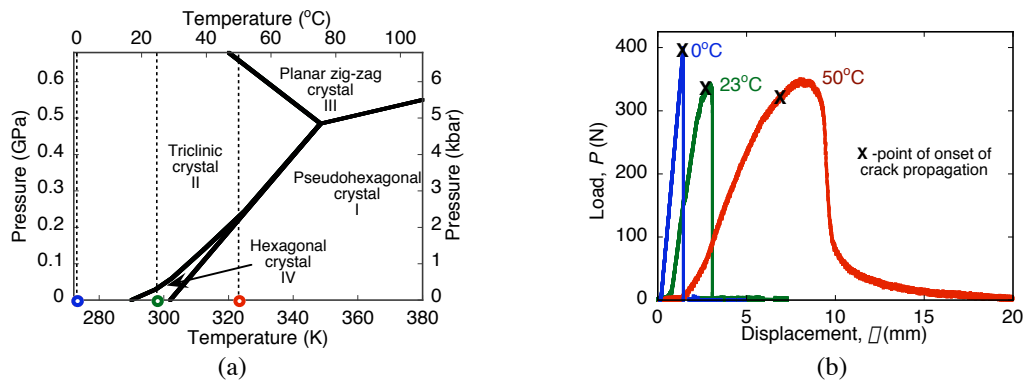


Figure 1. (a) Pressure–temperature phase diagram of PTFE [2,3] and (b) Representative load–displacement curves for double-edge-notched tension specimens tested at 0°C (phase II), 23°C (phase IV), and 50°C (phase I).

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 1b 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 III 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 with the normalization method to obtain fracture initiation properties J_{IC} . 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. 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 [6]. Nominal 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 [7], with rigid domains beneath the microfibril structure.

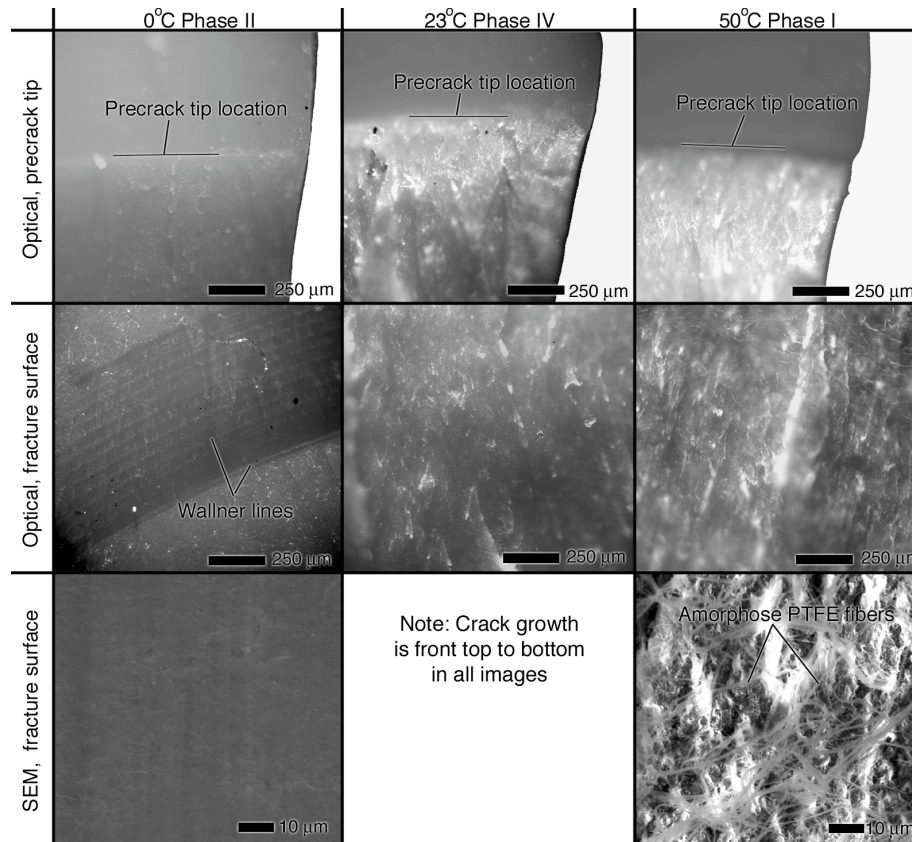


Figure 3. Optical and electron micrographs of the fracture surfaces for samples tested at 0°C, 23°C, and 50°C.

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 is 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 less compliant crystalline structure. Modulated differential scanning calorimetry (MDSC) is utilized to measure changes in the concentration of crystalline domains resulting from plastic deformation in the plastic zone. Helium pycnometry is used in conjunction with MDSC measurements to characterize the increasing orientation of the amorphous polymer chains associated with plastic deformation.

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

References

- [1] Sperati, C. A., Starkweather, H.W., Jr.: Fluorine-Containing Polymers. II. Polytetrafluoroethylene. *Advances in Polymer Science* Springer-Verlag, Berlin, **2**: 465-495, 1961.
- [2] Clark, E.S.: The Molecular Conformations of Polytetrafluoroethylene: Forms II and IV. *Polymer* **40**: 4659-4665, 1999.
- [3] Wu, C.K., Nicol, M.: Raman Spectra of High Pressure Phase and Phase Transition of Polytetrafluoroethylene (Teflon). *Chemical Physics Letters* **21**: 153-156, 1973.
- [4] Kimming, M. Strobl, G., Stuhn, B.: Chain Reorientation in Poly(tetrafluoroethylene) by Mobile Twin-Helix Reversal Defects. *Macromolecules* **27**:2481-2495, 1994.
- [5] Bunn, C.W., Cobbold, A.J., Palmer, R.P.: The Fine Structure of Polytetrafluoroethylene. *J. Poly. Sci.* **28**: 365-376.
- [6] Kerkhof, F.: Bruchmechanische Analyse Von Schadensfallen An Glasern. *Glastechnische Berichte* **48**:112-124: 1975.
- [7] Aglan, H., Gan, Y., El-Hadeki, M., Faughnan, P., and Bryan, C.: Evaluation of the Fatigue Fracture Resistance of Unfilled and Filled Polytetrafluoroethylene Materials. *J. Mater. Sci.* **34**: 83-97:1999.