

Mechanical Properties of Polymer Composites Used in Oxidizing Environments: A Review

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ABSTRACT

Polymer composites have been increasingly used for high temperature applications such as engine components. Exposed at elevated temperature for prolonged time, the polymer composites will undergo thermo-oxidative degradation, which is distinctive from the conventional physical degradation. The present paper reviews recent progress on studying the thermo-oxidative degradation and resultant mechanical properties of polymer composites.

INTRODUCTION

Polymer matrix composites (PMCs) have been increasingly used for high temperature applications in automotive and aerospace industries. Example applications include the automotive engine covers and turbine engine exhaust structures. The matrix systems in the high temperature PMCs are predominantly thermoset polymers. These polymers are chosen since they have highly cross-linked structures that form during the curing process. Typical thermosets include polyimides, epoxies, unsaturated polyesters, vinyl esters, etc. One of the major concerns in using polymer matrix composites at high temperature environments is the thermo-oxidative degradations of the polymer matrix and the matrix-fiber interfaces. Exposed to elevated temperature, the free surfaces of PMCs are susceptible to oxidation. When exposed to thermo-mechanical loading, the result is accelerated degradation and ply cracking which in turn introduces new free surfaces. Ultimately, the thermo-oxidative degradation reduces the life and durability of the composite system. Thus, the ability to fully understand and characterize the physical and mechanical responses resulting from thermo-oxidative processes is paramount to the continued development and increased use of high temperature PMCs in the industry.

The present paper reviews briefly recent progresses on studying the thermo-oxidative degradation of polymer composites used in high temperature applications. Numerous polymer material systems have been used for high temperature application; the most widely used is a polyimide-based resin, namely, the polymerization of monomeric reactants (PMR-15). Originally developed by the NASA Lewis Research Center, PMR-15 offers stable performance at high temperatures in addition to low cost and ease in processing [1-2]. In addition, this material has been used extensively to study the thermo-oxidation process of polymers. The present review focuses on the PMR-15 material, with emphases placed on: (1) the overall mechanism of thermo-oxidative degradation and (2) the mechanical properties of the material as a result of oxidation.

MECHANISM OF THERMO- OXIDATIVE DEGRADATION OF PMCS

The degradation of polymer matrix composites (PMCs) used in high temperature applications can be a result of either physical aging or chemical aging, or both. The physical aging is a thermodynamically reversible volumetric response due to slow evolution toward thermodynamic equilibrium. The decreased molecular mobility and free-volume reduction lead to strain and damage development in the material. The chemical aging is a nonreversible volumetric response due to chain-scission reactions and/or additional cross-linking, hydrolysis, depolymerization, and plasticization. A dominant chemical aging process for high temperature PMCs is thermo-oxidative aging. According to Schoeppner, et al. [3], the thermo-oxidative aging of polymers is “a nonreversible, surface diffusion response in which chemical changes occur during the oxidation of a polymer, [where] oxidation leads to a reduction in molecular weight as a result of chemical bond

breakage and weight loss due to out-gassing of low-molecular weight gaseous species.”

A three-region model has been proposed by Tandon, et al [4], to explain the mechanism of the thermo-oxidative degradation in polymers. According to this model, the surface oxidative layer is separated from the unoxidized polymer with an active reaction zone (Figure 1). The oxygen (O_2) in air diffuses through the polymer and then consumed by the oxidation reaction. The parameter ϕ shown in Figure 1 is called the polymer availability state variable and the parameter ϕ_{ox} characterizes the completely oxidized polymer. Once a region is fully oxidized (called the Oxidized Layer), the oxidation reaction is terminated and oxygen can diffuse through it. Then, oxygen begins to react in the adjoining region (called the Transition Region), where $\phi_{ox} < \phi < 1$. In the region far from the exposed surface (called the Unoxidized Interior), no polymer has been oxidized ($\phi=1$).

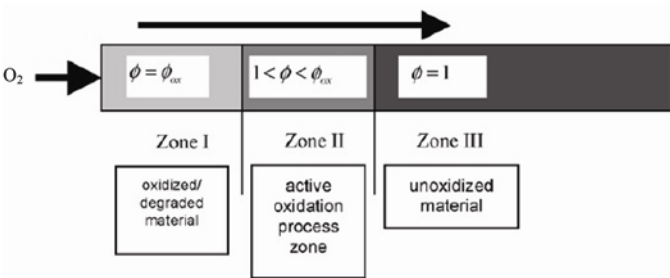


Figure 1. Schematic of the three-zones in thermo-oxidation of polymers (Tandon, et al [4]).

The experimental evidence of thermo-oxidative degradation in a polymer can be seen in Figure 2 [22]. Due to the diffusion-reaction occurred, the surface layer near the specimen edges is seen to exhibit different optical characteristics than the interior of the specimen. Using bright-field light microscopy, the oxidized material is found to have a different appearance than the unoxidized interior. Between the outer oxidized layer and the interior unoxidized region is a transition region. The oxidized surface thickness has been found to be affected by the aging conditions (aging time, aging temperatures, and aging pressures). Figure 3 shows the oxidized surface thickness at various aging conditions for PMR-15. Initially, the thickness of this oxidized layer increases rapidly with aging time and then the rate of change starts to decrease. This is because the oxidation growth rate decreases with time over longer aging time periods, and eventually approaches an auto-retardation state. There is a small increase in the oxidation growth with increasing aging temperature (Figure 4). The aging pressure has also affected the size of the oxidized layer. The increase in pressure can result in a substantial increase in oxidation layer thickness since the pressure generally increases the rate of diffusion of the oxygen into the polymer specimen [20,21,22].

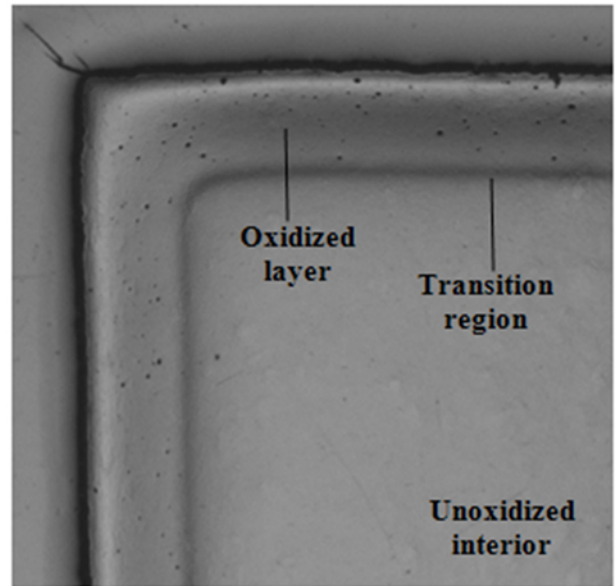


Figure 2. Optical micrographs of thermal-oxidized PMR-15 neat resin aged at 288 °C for 1518 hrs (Lu, Y.C. et al [22]).

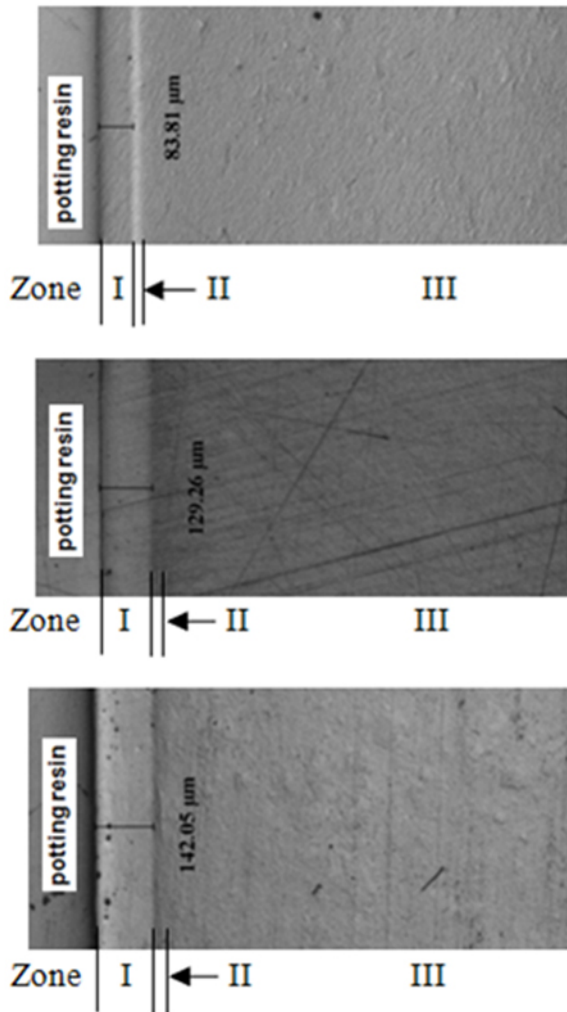


Figure 3. Evolution of oxidized surface thickness as a function of aging time. Specimens are isothermally aged at 316°C for a time period of a) 215 hr, b) 500 hr, and c) 1315 hr (Lu, Y.C. et al [20]).

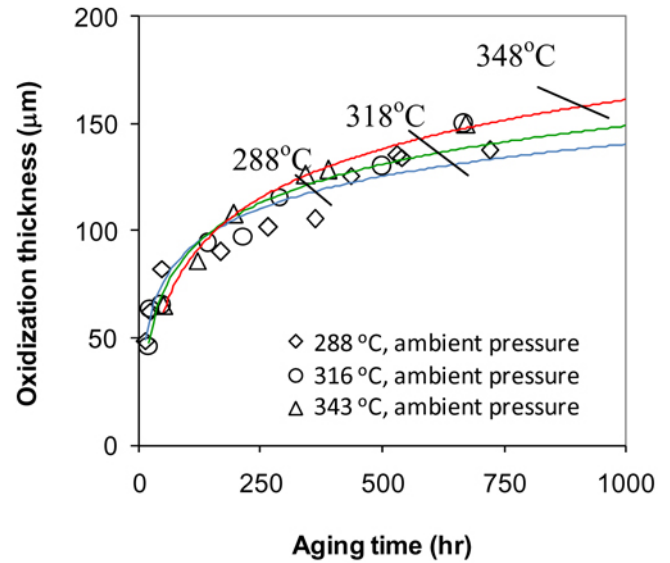


Figure 4. Evolution of oxidized surface thickness as a function of aging time. Specimens are isothermally aged at 288°C, 316°C, 343°C (Lu, Y.C. et al [22]).

At longer aging time, small voids are seen to develop in the oxidized regions (Figures 2 and 3). The occurrence of voids can be interpreted as the Kirkendall effect [7,8,9]. The Kirkendall effect refers to the migration of atoms in a solid at an interface. In the oxidation process, the inward diffusion of oxygen is slower than the outward diffusion of degradation products, therefore, the small voids form. Voids can increase in size and density over time, which act as starter points for microcracks.

The changes in chemical structures in the oxidized surface layer have also been studied [7,8,9, 16-17]. Meador et al [7,8,9] have studied the chemical structures of oxidized PMR-15 using nuclear magnetic resonance (NMR) spectroscopy. It was found that the end-caps of the molecular chain in PMR-15 have changed after thermo-oxidative aging (Figure 5). Xie et al [16] and Patekar [17] have used the Fourier-Transform Infrared (FTIR) spectrometer to study the aged PMR-15 and found that many by-products are released from PMR-15 as a results of thermo-oxidation, including H₂O, CO, CO₂, CH₄, and NH₄. These chemical structural changes are believed to account for much of the weight loss of the resin aged in air at elevated temperatures.