Proactive Mitigation of Polychlorotrifluoroethylene-Related Ignition Hazards in Oxygen Systems

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Revelations of dimensional instability in polychlorotrifluoroethylene (PCTFE) semifinished articles and finished parts raised concerns that leaks or part failure could occur during service, leading to catastrophic component or system failure, especially in high-pressure gaseous oxygen systems where flow friction, flow resonance, or kindling chain ignition mechanisms are operative. These concerns, coupled with the occurrence of a series of leaks and fires in regulators, cylinder valves, and station valves, as well as a fire at Kennedy Space Center (KSC) involving a compressed oxygen trailer discharge valve, raised concerns about the design limitations of PCTFE in compressed gas componentry. These concerns culminated in the release of an internal NASA-KSC Problem Advisory and a Government Industry Data Exchange Program Problem Advisory on PCTFE.

Release of the advisories coincided with an American Society for Testing and Materials (ASTM) G04-sponsored task group study examining the factors contributing to PCTFE property variation. Specifically, it determined the effects of two resin grades, two processing routes, three annealing conditions, and three machine shops on dimensional stability and crystallinity. Use of a D-Optimal design of experiment and Analysis of Variance (ANOVA) techniques allowed the total number of runs to be reduced from 36 (full factorial) to 21 without biasing main factor effects and two-factor interactions (figure 1). Thermomechanical analysis (TMA) showed that Neoflon M300P resin was easier to anneal than M400H, and the 2.5-h annealing time was not long enough to impart complete stress relief. TMA found poorer dimensional stability in finished valve seats after machining compared to the starting rod stock, and poorer dimensional stability on average for extruded, unannealed M300P valve seats (up to 3.1% axial contraction upon heating was observed). Also, improved dimensional stability was observed for unannealed valve seats that were allowed to sit on the shelf for an additional 6 months. Molecular weight (resin grade), process, and annealing at 175°C all had significant effects on the specific gravity; hence, the percent crystallinity of semifinished rod stock and finished valve seats (figure 2).

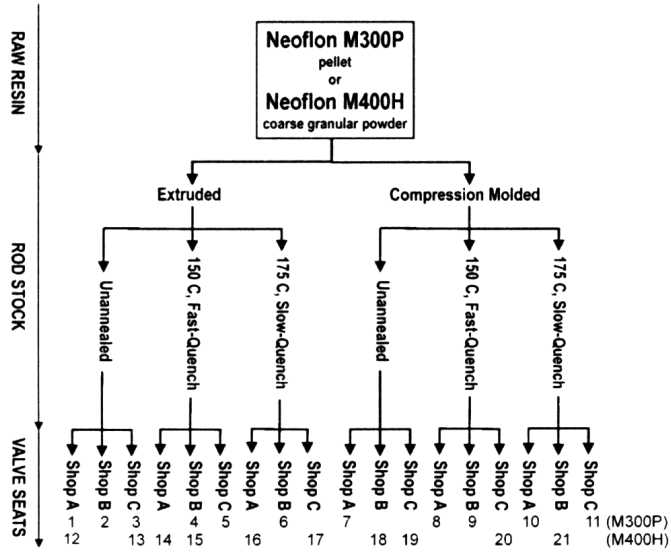

Fig. 1. D-Optimal design of experiment (numbers at bottom denote run number).

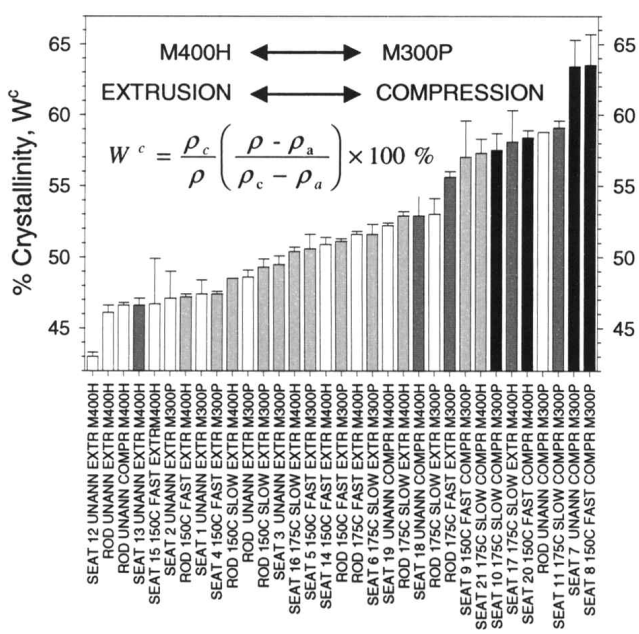

Fig. 2. Weight percent crystallinity variation for PCTFE rod stock, and valve seat specimens.

Although only two lots were used, percent crystallinities ranging from 43 to 63% were observed in finished valve seats. In general, M400H and extruded specimens tended to be less crystalline.

Since good valve seat performance is predicated, in part, on minimal shift in valve regulator droop and creep, one of the questions that arose was if the fourfold goal of dimensional stability, crystallinity control, high molecular weight, and minimal shift in droop and creep could be satisfied. ANOVA-derived significance levels of single-factor effects showed that valve regulator droop, for example, was governed primarily by annealing method. Machining history also played a significant but less prominent role. Resin grade and processing history were found to be insignificant. On the basis of present data, however, it does not appear the fourfold goal can be simultaneously met.

Molded plastics such as PCTFE contain internal stresses. The magnitude of these stresses is not uniform and will change with the size and thickness of the molded part, and it can result in dimensional changes when parts cut therefrom are heated or machined. Annealing may relieve some of the stresses. However, no amount of annealing will ensure complete stress relief and, thus, dimensional stability of the finished part. This limitation notwithstanding, experience shows that annealing is best performed after all machining operations are complete (best dimensional stability), or immediately before final machining operations are complete (best engineering tolerances). By comparison, annealing on as-molded semifinished rod and sheet stock will produce a partially annealed finished article.

Effective annealing also requires selecting the appropriate temperature and time. Annealing should be carried out well above (e.g., ~ 50°C) the glass transition temperature, at a temperature above the highest temperature the polymer encounters during service, but below any temperature that causes significant property loss (due to oxidation, depolymerization, decomposition, etc.).

As for selecting the best annealing time, the method (oven heating or immersion in a thermally conductive, inert media), oven type (radiant vs. convective), placement relative to the heater elements, and sample geometry and thickness must be considered. Since stress relief is a time-dependent process in polymers, reaching thermal equilibrium is a necessary but insufficient condition for proper annealing. To be sufficient, enough time must elapse after thermal equilibrium is reached for adequate internal stress relief to occur. No recommendations are made as to how much time should elapse after thermal equilibrium is reached; however, available specifications for PCTFE suggest an upper limit of 48 h.

Since polymers such as PCTFE are poor conductors of heat, the time it takes to reach thermal equilibrium will be longer than for metals. For the ideal case of heat conduction through simple shapes (e.g., rod or sheet) with free convection at the outer surface, a Biot Fourier approach can be used to calculate the time, τ, for samples to reach thermal equilibrium. Radiation and improved convection from forced convective flows were not considered when estimating the maximum time required. In the case of an infinite cylinder or sheet, the heat conduction equations are:

$$\frac{\partial\theta}{\partial\tau} = \alpha\left(\frac{\partial^2\theta}{\partial r^2} + \frac{1}{r}\frac{\partial\theta}{\partial r}\right)\text{(rod) and } \frac{\partial\theta}{\partial\tau} = \alpha\left(\frac{\partial^2\theta}{\partial x^2}\right)\text{(sheet)} \quad (1)$$

Here, θ is the temperature excess of a point at distance r or x from the centerline over the environment temperature t_e, while α is the thermal diffusivity of PCTFE. Using appropriate boundary conditions gave a series solution to (1) where the centerline temperature excess θ_o is given by series summation of Bessel functions, which can be conveniently represented in a Heisler chart. The calculated annealing time was determined by calculating the Biot number for each rod diameter, using the chart to establish when the centerline temperature excess was 1% of the

initial temperature excess (thermal equilibrium), and then calculating the time τ to reach this temperature from the corresponding Fourier number. Results for common rod diameters and sheet thicknesses (figure 3) show that sheet will take about two times longer than rod to reach thermal equilibrium.

To better control properties in finished PCTFE parts used in aerospace applications, a new voluntary consensus standard specification (ASTM D7194-05) was developed. The new specification ensures that: a) all machined PCTFE parts shall be in an annealed condition; b) annealing shall be performed immediately before (best tolerances) or after final machining (best dimensional stability); c) the drop in the zero strength time (ZST), which correlates with the molecular weight drop, shall not exceed 20% after processing; d) the ZST of the as-molded semifinished article shall be 300 to 450 s (Grade 3 ASTM D1430-03 material); and e) the specific gravity variation for finished parts shall not exceed ± 0.01 (i.e., percent crystallinity shall not vary more than ± 10%).

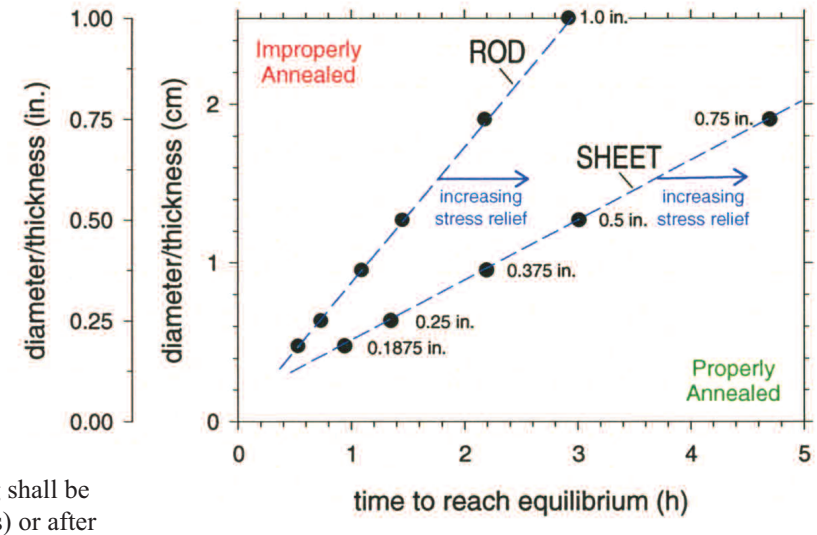

Fig. 3. Time to reach thermal equilibrium for selected PCTFE rod and sheet (dashed lines).