COMPARATIVE CREEP EVALUATION OF POLYACETAL AND POLYKETONE RESINS

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Abstract

Failures occurred within threaded fasteners used in an outdoor industrial application. Specifically, cracking was observed within fasteners used to terminate a pipe conveying a gaseous chemical product. The parts had been installed leak free as verified through leak testing. However, failures occurred within some of the installations between four and five years, as identified by leakage of the gaseous product. A failure analysis identified that some of the fasteners had cracked though a mechanical short-term overload mechanism in which the stresses applied during installation exceeded the short-term strength of the material. Other parts, however, cracked through creep rupture, whereby the applied service stress exceeded the long-term strength of the material. In both cases, crack propagation and ultimate rupture were associated with the creep properties of the material. A material conversion was considered to increase the creep performance of the fasteners. This paper will review the testing performed to characterize and compare the creep performance of the incumbent and proposed materials.

Introduction

Leakage failure resulting from cracking had been observed within threaded fasteners. The fasteners had been used in hot and dry conditions in above-ground outdoor service in the Southwestern United States, functioning to terminate pipes conveying a gaseous chemical product. The failures were observed after four to five years of service. Leak testing of the pipe/fastener assembly shortly after installation did not reveal any signs of leakage.

A failure analysis was conducted, which identified two different modes of failure. Some of the part failures initiated though a mechanical short-term overload mechanism in which the stresses applied during installation exceeded the short-term strength of the material. Other field failures as well as engineering test parts cracked through creep rupture, whereby the applied stress exceeded the long-term strength of the material. In both cases, crack propagation and ultimate catastrophic splitting was associated with the creep rupture.

The fasteners had been produced from Celcon® M90, a general-purpose, medium viscosity polyacetal copolymer from Celanese Corporation, containing a black colorant. A material review was conducted, and a potential replacement material was identified, Poketone® M630, an unfilled, general-purpose aliphatic polyketone terpolymer from Hyosung Chemical Corporation.

Creep testing was subsequently performed to assess and compare the long-term properties of the two materials. This paper will review that comparative creep evaluation.

Material Background

Polyacetal (POM), also known as polyoxymthylene, is a semi-crystalline thermoplastic resin characterized by relatively high strength and stiffness (modulus), hardness, and low friction properties. Polyacetal is produced through addition polymerization. Two different types of polyacetal resins are available, homopolymers and copolymers. The homopolymer consists of a backbone exclusively made up of alternating CH2 and O functionality. Within polyacetal copolymers, approximately 1.0% to 1.5% of the -CH2O- groups are replaced with -CH2CH2O-.[1,2] The polyacetal copolymer structure is presented in Figure 1.

The presence of the copolymerized oxyethyl segment results in a lower degree of crystallinity, which brings a reduction in strength and modulus, as well as a reduction in the upper limit short-term use temperature. The presence of the additional hydrocarbon linkage in the copolymer backbone provides for improved resistance to oxidation.[3] This corresponds to improved property retention after long-term exposure to elevated temperatures, as well as improved chemical resistance. However, the lower level of crystallinity within the copolymer also translates into decreased bearing properties as well as reduction in fatigue and creep resistance.[3]

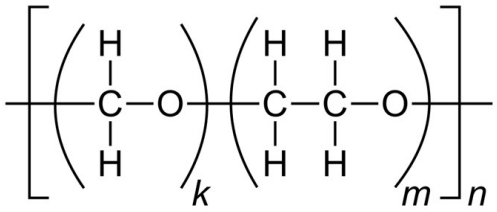

Figure 1. The structure of the polyacetal copolymer is shown.

Similar to polyacetal, aliphatic polyketone (POK) is a semi-crystalline thermoplastic resin. It is known for a balance of processing and performance properties. Polyketone is commercially available as a copolymer, polymerized through the reaction of carbon monoxide and ethylene, or as a terpolymer when propylene is added to the reaction. The polymer backbone consists exclusively of carbon-carbon units with a perfectly alternating structure with the ketone functionality. The polymer

chains are flexible and possess molecular symmetry and cohesive energy resulting in a tough, high-melting-point semi-crystalline structure.[4] The symmetry and chain flexibility promote crystallization with polyketone. The carbonyl structure leads to strong intermolecular attractive interaction between neighboring polymer chains, producing a relatively high melting point and heat of fusion. The polyketone terpolymer structure is presented in Figure 2.

The crystallinity, melting point and glass transition temperature are influenced by the introduction of the third monomer, propylene, within the terpolymer. A 6 mole% propylene is typical and reduces the melting point from 257 °C to 222 °C.[4]

Typical characteristics of polyketone include high tensile strength and stiffness, as well as good impact strength. They are noted for exceptionally high abrasion resistance with minimal wear characteristics. The terpolymer is noted for outstanding chemical and hydrolysis resistance.[5]

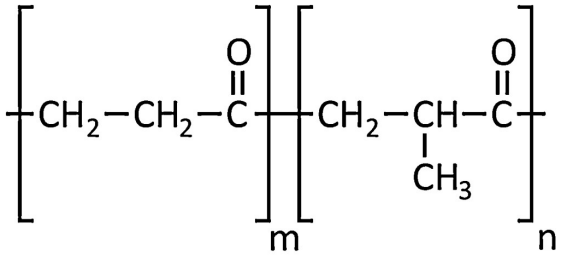

Figure 2. The structure of the polyketone terpolymer is shown.

Testing

Sample Preparation

For the creep evaluation, the supplied Celcon® M90 and Poketone® M630 resins were molded into ASTM D638 Type I tensile bars using resin supplier recommended conditions. The tensile bars were molded without knit lines using a mold configured with a single injection molding gate design.

Temperature-Dependent Behavior

The materials were evaluated for temperature-dependent behavior by dynamic mechanical analysis (DMA). The samples were evaluated from -50 °C at a heating rate of 2 °C/min. to an upper temperature based upon each material's thermal response. The center portion of the ASTM D638 Type I tensile bar was tested under an oscillatory stress at a frequency of 1 Hz in accordance with ASTM D4065. The storage modulus (E'), loss modulus (E"), and tan delta (E"/E') were plotted as a function of temperature. Glass transition temperatures (T_g) were determined as the localized maxima in the loss moduli. The resulting DMA thermograms are shown in Figures 1 through 3.

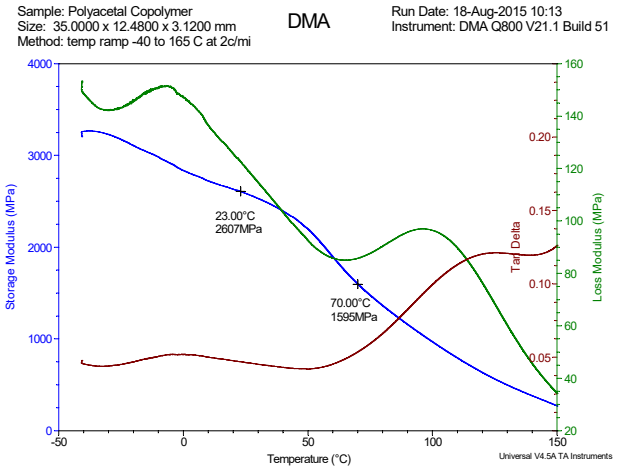

Figure 1. The DMA temperature sweep for the polyacetal copolymer is presented.

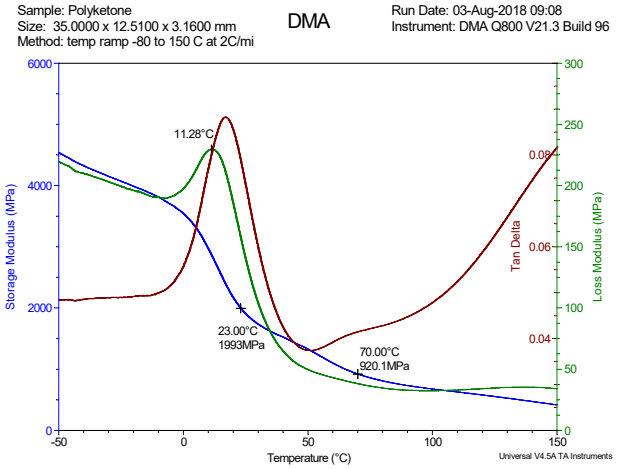

Figure 2. The DMA temperature sweep for the polyketone is presented.

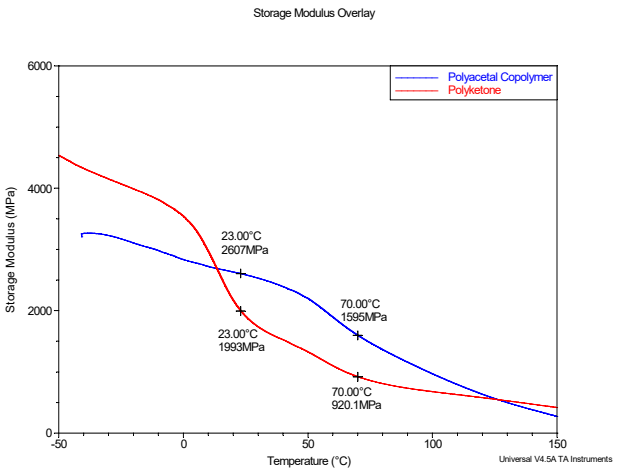

Figure 3. Overlay comparing the storage moduli of the two materials.

Both materials demonstrated a continuous decline in modulus with increasing temperature. The storage moduli were determined for the two materials at two temperatures, 23 °C and 70 °C.

The polyacetal copolymer displayed a steady modulus reduction over the analysis temperature range. A minor inflection was noted at approximately 50 °C, above which the rate of decline was slightly higher. The DMA results were in agreement with a semi-crystalline resin above the glass transition temperature (T_g), and specifically the observed behavior was consistent with that expected for a polyacetal resin.

The polyketone terpolymer presented a variable decline in modulus with increasing temperature. The subambient modulus was greater than that of the polyacetal copolymer. A major inflection in the polyketone terpolymer storage modulus was noted at approximately 10 °C. This was accompanied by maxima in the loss modulus and tan Delta responses. This event represented a glass transition within the material and a glass transition temperature (T_g) of 12 °C was determined. The modulus of the polyketone was lower than that of the polyacetal copolymer above this temperature. However, the rate of decline was lower, and the two modulus curves crossed over at approximately 125 °C. The polyketone terpolymer DMA results were in agreement with a semi-crystalline resin passing through glass transition, and the observed behavior was consistent with that expected for a polyketone resin.

Tensile Properties

Tensile tests were performed on samples representing the two materials in accordance with ASTM D638 at 23 °C. Injection molded Type I tensile bars were tested using a universal mechanical tester equipped with a contact extensometer. The testing was performed using crosshead speeds of 0.2 in./min. and 2 in./min. for the polyacetal copolymer and polyketone terpolymer respectively, based on their observed tensile properties and compliance with the test standard. The average results of five specimens are presented below in Table 1, and the stress – strain curves are illustrated in Figure 4 through 6.

Table 1. Tensile Test Results – 23 °C

Parameter	Polyacetal Copolymer	Polyketone
Modulus, MPa	2,837	1,630
Tensile Strength at Yield, MPa	61.1	59.8
Elongation at Yield, %	8.51	22.2
Tensile Stress at Break, MPa	55.2	55.7
Elongation at Break, %	31.9	243
Proportional Limit, %	0.625	0.719
Linear Equivalent of Yield, %	2.144	3.555

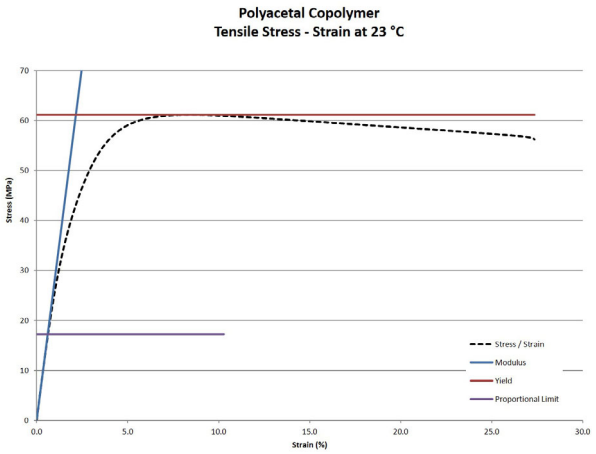

Figure 4. The tensile stress-strain curve is shown for the polyacetal copolymer.

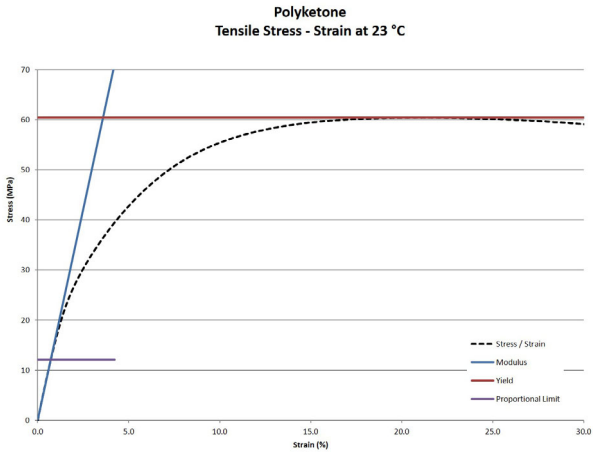

Figure 5. The tensile stress-strain curve is shown for the polyketone.

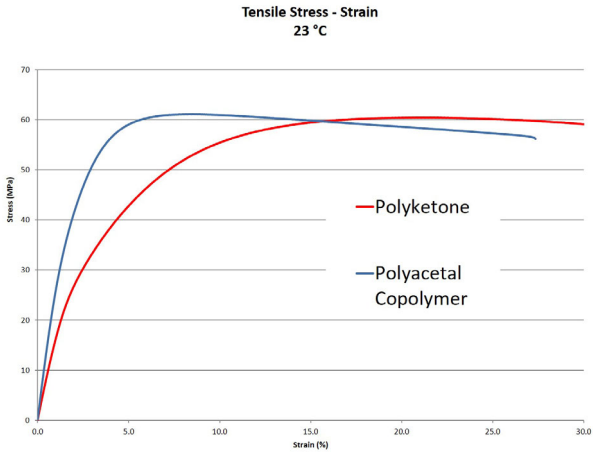

Figure 6. Overlay showing the stress-strain curves for the two materials.

The results obtained for the two materials, were consistent with those expected based upon their respective technical

data sheets. The two materials showed very similar tensile strength at yield and tensile stress at break values. However, a significant difference was noted in the elongation properties. The polyketone demonstrated substantially higher elongations for both yield and break. This correlated with the markedly elevated modulus of the polyacetal copolymer, consistent with comparative results from the DMA temperature sweep. In summary, the tensile test results indicated that the polyacetal copolymer was stiffer, but the polyketone was more ductile.

Creep Properties

The assessment of creep properties was conducted via dynamic mechanical analysis (DMA) by running multiple determinations for fifteen-minute periods at isothermal conditions ranging from 10 °C to 150 ° C in increments of 5 °C. The evaluations were conducted using a dual cantilever configuration. The polyacetal copolymer and polyketone were tested using stresses of 1.5 MPa and 1.9 MPa, respectively, based on their room-temperature modulus values. These data were used to develop master curves for the materials that extended to 200,000 hours at a reference temperature of 23 °C. These are illustrated as semi-log plots of apparent modulus as a function of time in Figures 7 through 9. A review of the creep response of the materials showed very good correlation to the temperature dependent behavior demonstrated by each during the DMA temperature sweep.

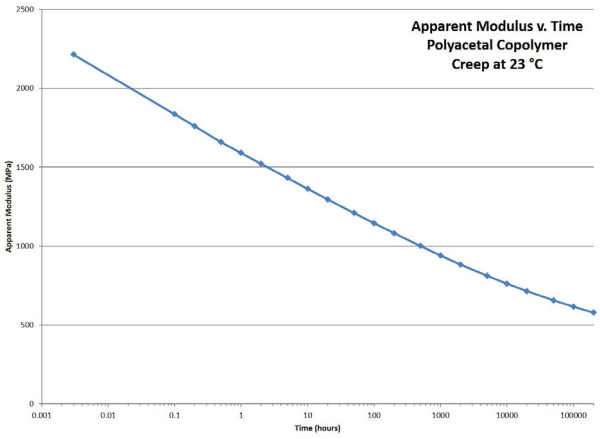

Figure 7. The plot of apparent modulus over time is shown for the polyacetal copolymer.

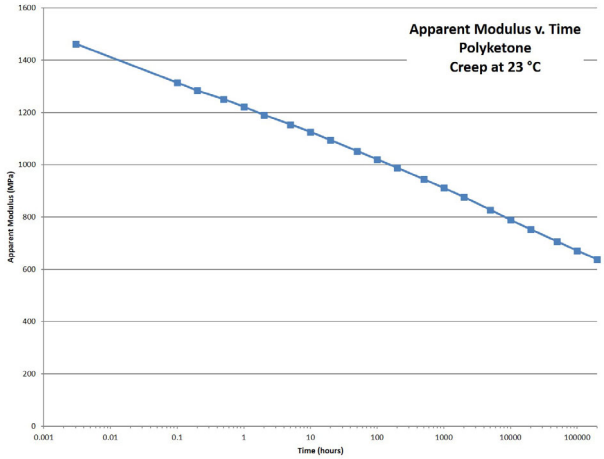

Figure 8. The plot of apparent modulus over time is shown for the polyketone.

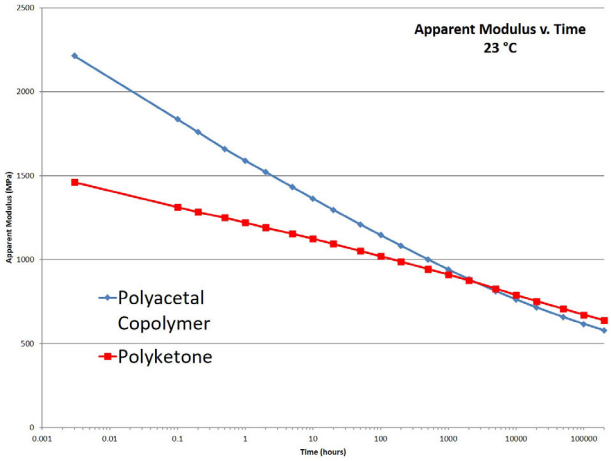

Figure 9. Overlay of the creep master curves for the two materials.

A comparison of the master curves representing the two materials showed that the polyacetal copolymer exhibited a higher apparent modulus at time zero. This was in agreement with the DMA temperature sweep and the tensile test data. Over time, the two apparent moduli converged, with the polyketone terpolymer have a slightly higher apparent modulus above and beyond 50,000 hours. Again, this was consistent with the comparative temperature-dependent data.

Dynamic mechanical analysis (DMA) creep data is generated at very low stress levels; therefore, the behavior documented by this method tends to be in the portion of the stress-strain curve that is below the proportional limit. Consequently, the apparent modulus data represented by the DMA results assumes linear elastic behavior throughout. However, apparent modulus behavior is translated into strain versus time behavior by applying various stresses. These stresses frequently result in plastic deformation that extends into the non-linear portion of the stress-strain profile. The actual stress-strain data presented

by the tensile tests is used to correct the DMA data to include the non-linear response.

Strains were calculated for the two materials for a constant applied stress level of 14 MPa, the nominal stress identified for the fastener in field service. The results of these calculations were plotted versus time and are illustrated in Figure 10.

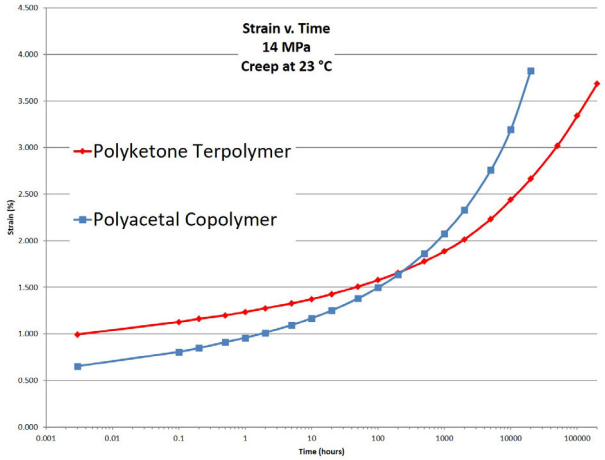

Figure 10. Plot of strain over time for the polyacetal copolymer and polyketone terpolymer.

Failure is defined as the point at which the calculated strain equals the yield strain, at which time cracking is expected. The anticipated lifetimes for the two materials were determined at 23 °C and a stress level of 14 MPa.

At 23 °C the polyacetal copolymer is projected to result in failure at approximately 50,000 hours (5.7 years). The polyketone terpolymer is predicted to provide performance beyond 200,000 hours (22.8 years) at 14 MPa.

It should be noted that since the polyacetal copolymer, and to an even great extent the polyketone terpolymer, exhibit an ultimate strain limit that is considerably greater than the yield strain, the actual time to catastrophic failure at the stress level evaluated may be somewhat greater than those predicted by the model. This technique cannot quantify the timeframe associated with the tertiary creep that immediately precedes complete failure. However, since tertiary creep is characterized by an increase in strain that does not require the application of additional stress, the time frame is expected to represent a relatively small percentage of the time required to reach the yield strain.

Conclusions

It is the conclusion of this work that the Poketone® M630 polyketone terpolymer displayed superior creep rupture resistance properties compared with the Celcon® M90 polyacetal copolymer under the controlled parameters of this evaluation. Specifically, the modeling was conducted using a temperature of 23 °C and a stress level of 14 MPa. The creep study indicated that the polyacetal copolymer was projected to result in failure at approximately 50,000 hours (5.7 years), while the polyketone terpolymer was predicted to provide performance beyond 200,000 hours (22.8 years). Given the creep testing outcome, the enhanced performance of the polyketone terpolymer appears to be primarily related to the substantially higher elongation at yield value, in sprite of a lower modulus at the modeling temperature. This study suggests that the polyketone terpolymer may be a good candidate for material replacement in this fastener application. It should be noted that the stress level of 14 MPa would be expected to reduce overtime due to stress relaxation. This would increase the time to failure to a degree. However, stress relaxation would affect both materials, and the comparative performance results obtained during this study remain applicable.

It is significant to remember that the tensile bar specimens used for the evaluation were injection molded using an end-gated tool. Such specimens afford the optimal geometry and flow for mechanical properties. The mechanical properties, including tensile strength and creep resistance, will likely be lower in injection molded parts. Any environmental conditions that can produce structural changes in the polymer, such as, molecular degradation or environmental stress cracking, will reduce the predicted time to failure.

In the application, specifically the installation locations where failure was observed, the service temperatures would be expected to exceed that used to model this evaluation. Further work should include addition testing to account for this variation in service conditions.

With any material conversion, it is recommended that adequate performance testing be conducted to assure the intended performance. Sufficient information cannot be obtained from material property data sheets, and final performance should be evaluated through testing. In this application, additional recommended testing includes:

- Impact testing to account for high strain rate loading during assembly and installation.
- Weather testing to evaluate outdoor exposure performance.
- Short-term burst testing to test the pressure rating of the molded fasteners in service.

Keywords

creep, dynamic mechanical analysis, time-temperature superposition, failure analysis, polyacetal, polyketone,

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