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Failure analysis of aging in polyoxymethylene fuel valves using fractography and thermal-FTIR analysis

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ABSTRACT

Polyoxymethylene (POM), a thermoplastic polymer used in precision parts, is popular for its high stiffness, low friction, and resistance to various working fluids. The polymer also presents unique chemical degradation and aging mechanisms. An investigation into commercial POM-made fuel valves (commercial, heat-stabilized copolymer), which failed in similar ways after over a decade of service in an aviation system, is presented and compared to an unused valve of the same type and material, with failures induced by overload. A comparison between fracture surfaces imaged by SEM microscopy, of POM failure as a result of overload or as result of ten years aging is shown for the first time. No definitive differences were found between aged and new POM material based on Differential Scanning Calorimetry (DSC) and direct Fourier Transfer Infra-Red (FTIR) measurements. However, a significant difference in decomposition profiles was found according to Thermogravimetric Analysis coupled with FTIR (TGA-FTIR), accompanied by release of formaldehyde, indicative of depolymerization in the decade-aged POM. Other mechanisms, such as overpressure failure, effects of exposure to gasoline, increased crystallinity, intermolecular rearrangements or internal hydrolysis were refuted. The failure mechanism is attributed to aging depolymerization in the bulk, accompanied by static stress.

1. Introduction

Polyoxymethylene (POM) is an engineering thermoplastic used in precision parts requiring high stiffness, low friction and reliable dimensional stability. Typical applications for injection-molded POM include high performance engineering components such as gear wheels, ball bearings, ski bindings and fasteners. The material is widely used in the automotive, aviation, and electronics industries. A particularly attractive feature of POM is its excellent resistance against swelling or attack by most chemicals, including hydrocarbon solvents [1], making it useful in fuel systems.

POM was discovered by Staudinger in the 1920's [2] and patented by DuPont as high molecular weight POM [3], and heat-stable (and therefore useful) POM homopolymer obtained by reacting the hemiacetal ends with acetic anhydride. The anhydride converts the readily depolymerizable hemiacetal into a thermally stable, melt-processable polymer [4]. The exploitation of POM as a commercial polymer has created a great deal of interest although it is a relatively unstable material. The two methods that have been used to achieve stabilization of POM are either 'end-capping' or copolymerization with small concentrations of a second monomer

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containing adjacent −C−C− bonds. The degradation behavior of these two types of the polymer is different [5–8]. Despite this improvement, stabilizers against other environmental influences have to be added to ensure a feasible service lifetime.

Polymer degradation is a frequent problem during extrusion and compounding, during the shelf life of the product in storage and, more commonly, during the service of the POM part. Degradation in processed POM is often the result of more than one type of mechanism: a combination of processes such as thermal degradation, oxidation and other chemical reactions, mechanical stresses, and UV-irradiation taking place during its shelf life and service life [9]. The resistance against thermal degradation depends on the inherent thermal stability of the polymer backbone. Thermal degradation can appear in three main forms: depolymerization, random chain scission, and unzipping of side groups [10–13]. Chemical degradation refers to processes induced by chemicals in contact with the polymer. These chemicals can be acids, bases, solvents, reactive gases, etc. In many cases, a significant conversion is only observed at elevated temperatures because of the high activation energy for these processes [14–16]. In addition, hydrolysis can occur by protonation of the backbone oxygen or hydrolysis of the ester end-groups. These processes result in the release of formic acid (from formaldehyde) and acetic acid, which facilitate further degradation, and can lead to “hollowing-out” [17]. These processes often occur together, and quantifying all the various aspects and their effects on polymer performance is necessary for assessment of the effectiveness of stabilizer systems and phenomena in aged POM. A sequence of publications reporting POM degradation by thermal, thermal-oxidative, UV-irradiation, aging and recycling effects was published by Archodoulaki et al. [18–21]. Oxidation Induction Time/Temperature (OIT), TGA/MS, GPC and other methods were applied for determining the degree and rate of degradation. Ramirez et al., reported quantification of such degradation through FTIR spectroscopy and color spectrophotometry methods [22]. They suggested IR bands which are a reliable indicator during the initial conditions of degradation. However, after more aggressive processes, even leading to carbonization, spectrophotometric methods are preferred [22]. Rajan et al. offer a method for FTIR on line monitoring during melt extrusion [23].

Decomposition studies using TGA-FTIR (Thermogravimetric Analysis coupled with Fourier Transform Infrared Spectrometry) are expected to provide a simple and sensitive chemical characterization of gases or volatile compounds generated during thermal decomposition. POM releases formaldehyde during thermal decomposition [24,25]. Formaldehyde is an infrared active molecule [26], and therefore FTIR spectroscopy is one of the best techniques for its detection. The FTIR spectrometer provides real time measurement of formaldehyde over various concentration ranges while POM is decomposed in the TGA oven. Lüftl [21] investigated degradation of POM with a TGA-MS coupled system. The main problem of formaldehyde detection by MS is the difficulty in distinguishing formaldehyde (main ions: 29, 30, 28 m/z) from other gases involved in POM decomposition [21]: CO_2 (44, 28 m/z), H_2O, formic acid (29, 46 m/z), and N_2 (28 m/z) – inert sample TGA gas. The FTIR gas spectrum, on the other hand, contains numerous absorbent peaks that allow differentiation between the spectrum of formaldehyde and that of other gases which may be released from the sample during FTIR-TGA analysis.

Fractographic features in POM were reported by Dziadur [27], the microstructure of the basic POM was changed by the addition (by injection) of a thermoplastic elastomer (ionomeric ethylene copolymer - Surlyn). It was observed that the additive strongly affected the mechanical properties and fracture topography of the investigated polymers. Beguelin and Kausch reported the observation of the specimen tested at different opening velocities to characterize a zone of microscopic yielding in the early stages of crack growth [28].

This paper presents a study of the failure of fuel valves, from similar aviation systems, all made of commercially available heat-stabilized POM copolymer. All failed valves involved did so after more than a decade of service in an aviation gasoline (Avgas ASTM D910) fuel system. A combination of methods such as fractography using stereomicroscopy and high-resolution scanning electron microscopy (SEM) along with a range of thermal analysis methods were used to characterize changes and degradation occurring throughout long-term usage. A fracture surface analysis of the failed POM valves compared to specimens from new and old (ten years in service) POM valves with induced failures under overload experiments is presented for the first time. Scientific exploration and publication in this field is limited and thus far to the best of our knowledge, no information is available on the possible correlation between fracture mode and degradation level.

Although degradation mechanisms of different POM types have been published and some of them are referenced above, only a handful of these case studies utilize these techniques to report on degradation of POM products in-situ over ten years of service.

2. Materials and methods

The investigation included microscopic inspection and chemical characterization of various samples made from POM, that were retrieved from the fuel valves. Stereo microscopy and SEM examinations were carried out on fracture surfaces belonging to the failed aviation gasoline valves, and on a fracture surface from a new valve that was laboratory overloaded. Samples for thermal and spectroscopic analyses were taken from old (ten years in service) and new items and from internal shielded areas and external areas exposed to fuel and air, respectively. The analyses included FTIR-ATR (Attenuated Total Reflection) with diamond and germanium crystals, Differential Scattering Colorimetry (DSC) and combined TGA-FTIR methods.

2.1. The valves

The valves, P/N PA201-001P were manufactured by Staiger GmbH & Co. KG. During their ten-year service, the valves experience periodic contact with flowing Aviation Gasoline fuel (Avgas 100LL, ASTM D910).

Seven different valves were examined during the investigation. All the valves were examined for leakage using water at low pressure. Five of the valves (referred to as “failed”) experienced a decade of use in the fuel system, and were found to be leaking. One