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Shelf Life and Sterilization Study

KetaSpire® PEEK KT-820

KetaSpire® polyetheretherketone (PEEK) is part of Solvay's family of Spire® Ultra Polymers, a line of ultra-high performance materials offered for use in short-term contact medical devices, specifically those that are in contact with bodily tissue or fluids for less than 24 hours. KetaSpire® PEEK is available in high viscosity (KT-820) and low viscosity (KT-880) grades, as well as modified compounds which incorporate additives such as glass fiber, carbon fiber, and color pigments.

This document presents test results showing that KetaSpire® KT-820 is highly resistant to changes in mechanical, thermal, and chemical properties after being exposed to gamma, steam, and ethylene oxide (ETO) sterilization procedures. In addition, thermally accelerated aging studies spanning three years show that KetaSpire® KT-820 possesses a shelf-life in excess of 100 years at 23 °C.

Standard and Accelerated Aging

Aging Procedures

Test samples were prepared by injection molding KetaSpire® KT-820 from production lot Y9143. Standard published injection molding parameters for KetaSpire® PEEK resin were used to prepare ASTM Type I tensile bars and ASTM flexural bars. Samples had a nominal 3.12-mm thickness and were not annealed prior to testing.

For both non-sterilized and gamma-sterilized testing, the standard aging test samples were stored in a climate-controlled area kept at 23 °C and 50 % relative humidity. The accelerated aging test samples were placed inside a calibrated oven set to 100 °C with a constant air flow rate. Samples pulled at 3, 6, 12, 24, and 36-month intervals were tested in Solvay's Alpharetta, GA, laboratories, which have ISO 9001 and A2LA certifications and are ISO 17025 compliant. Test method details are provided in the Equipment References section at the end of this document.

Gamma Sterilization

Gamma Sterilization Procedures

Samples for gamma sterilization were submitted to the Sterigenics Facility in Charlotte, NC. Sterilization was conducted using Sterigenic's procedures per requirements of the submitted packaging and material load. Actual radiation dosage conditions for all mechanical and physical test specimens are documented in Sterigenic Dose Map 6944 run on Aug. 6, 2010. Test samples submitted for biocompatibility testing were gamma sterilized, and radiation levels were documented in Sterigenic Dose Map 6956 on Sept. 12, 2010.

Samples radiated on Aug. 6, 2010, were exposed to 4 cycles with a nominal dosage level of 30 kGy per pass for a total minimum exposure of 116.3 kGy and maximum exposure of 143.0 kGy. Samples radiated on Sept. 12, 2010, were exposed to 3 cycles with a nominal dosage level of 37 kGy per pass for a total minimum exposure of 107.5 kGy and maximum exposure of 117.8 kGy. After exposure, samples were returned to Solvay for property evaluation and inclusion in the standard and accelerated aging study.

Shelf Life and Gamma Sterilization Results

Standard and accelerated aging results, both with and without gamma radiation exposure, are presented in Table 1.

Test results indicate that KetaSpire® KT-820 is highly resistant to significant changes in its mechanical, thermal, and chemical properties when exposed to both standard and accelerated aging conditions. Samples maintained at 100 °C for three years experienced a slight increase in strength and modulus, along with a slight decrease in elongation.

Table 1 Shelf life and effects of gamma sterilization on KetaSpire® KT-820 at 3 years

		No Gamma Treatment		100 kGy Gamma Treatment		
Property	**As-Molded**	**3 years at 23 °C**	**3 years at 100 °C**	**Post-Treatment**	**3 years at 23 °C**	**3 years at 100 °C**
Color – CIE L*A*B						
Color change, ΔE	Nominal	0.3	1.3	2.6	3.5	3.7
Characteristic Temperatures – DSC – ASTM D3418						
Glass transition, T_g	Nominal	0.0 %	0.4 %	0.0 %	−0.1 %	0.0 %
Recrystallization, T_c	Nominal	0.0 %	0.1 %	−0.4 %	0.2 %	0.1 %
Melt temperature, T_m	Nominal	−0.3 %	−0.3 %	0.4 %	−0.3 %	−0.3 %
Molecular Weight – GPC – Solvay Method						
Number average, M_n	Nominal	−7.2 %	−4.8 %	−0.7 %	−1.2 %	−0.6 %
Weight average, M_w	Nominal	−4.8 %	−3.3 %	0.4 %	−0.3 %	−0.3 %
Tensile Properties – ASTM D638						
Strength at yield	Nominal	0.0 %	5.1 %	0.7 %	0.7 %	4.4 %
Elongation at yield	Nominal	1.9 %	−11.5 %	0.0 %	1.9 %	−11.5 %
Modulus of elasticity	Nominal	1.5 %	5.7 %	0.9 %	1.7 %	3.9 %
Biocompatibility						
Cytotoxicity	Pass	Pass	Pass	Pass	Pass	Pass
Physiochemical testing	Pass	Pass	Pass	Pass	Pass	Pass

This is believed to be caused by an annealing effect resulting from the samples being kept at high temperatures. Samples irradiated with 100 kGy of gamma radiation displayed a small color shift. Please refer to the Explanation of Color Change section for a description of ΔE values. While slight changes were observed in other testing conditions, they were all within the confines of expected testing error.

Accelerated Aging Equivalency

Thermal aging was used to accelerate the shelf-life aging study of KetaSpire® PEEK. There are multiple approaches commonly used with plastics to estimate the equivalency of accelerated thermal aging.

Method 1: Every 10 °C Doubles the Rate of Aging

A standard rule in the plastics industry, outlined by Hukins et al. (2008), is that increasing the temperature by 10 °C doubles the rate of aging, as illustrated by Equation 1, where *f* is the accelerated aging factor.

Equation 1 $$f = 2^{\frac{\Delta T}{10}}$$

KetaSpire® KT-820 is undergoing a five-year aging study at 23 °C and 100 °C. At the three-year mark, all test results indicate that there is no measurable thermal decomposition. Plugging ΔT = 100 – 23 = 77 °C into Equation 1 estimates that KetaSpire® KT-820 aging at 100 °C for three years is equivalent to 23 °C for 623 years.

Method 2: Arrhenius' Equation

The Arrhenius' equation is commonly used to estimate the acceleration factor caused by thermal-oxidative accelerated aging (Equation 2), where *k* is the chemical reaction rate, *A* is the pre-exponential factor, E_a is the activation energy, *R* is the universal gas constant, and *T* is the absolute temperature.

Equation 2 $$k = Ae^{-\frac{E_a}{RT}}$$

A modification of Arrhenius' equation (Equation 3) can be used to estimate the increase in reaction rate brought about by an increase in temperature, where k_2/k_1 is the acceleration factor brought about by the increase in temperature from T_1 to T_2.

Equation 3 $$\frac{k_2}{k_1} = \frac{Ae^{-\frac{E_a}{RT_2}}}{Ae^{-\frac{E_a}{RT_1}}} = e^{-\frac{E_a}{R} * \left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

This simplification assumes that the pre-exponential factors for each temperature are approximately equivalent when both temperatures fall within the same phase. In this case, both 23 °C and 100 °C are well below PEEK's glass transition temperature of approximately 150 °C. In order to solve for k_2/k_1, an activation energy must be determined for thermal-oxidative degradation.

To estimate a thermal-oxidative activation energy for PC, a thermogravimetric analysis (TGA) outlined in ASTM E1641[2] was performed by Kang, et al.[3]. The observed activation energy was approximately 241.87 kJ/mol. Plugging this activation energy into Equation 3 estimated an acceleration rate of 636,000,000x. If the goal was only to demonstrate that 100 °C for three years is equivalent to 23 °C for 100 years (acceleration factor of 33.3x), the thermal-oxidative activation energy required would be approximately 41.84 kJ/mol, or 17.3 % of the activation energy estimated by Kang, et al.. Therefore, based on the test results and experimental calculations, it is believed that the stability of KetaSpire KT-820 at 100 °C for three years is equivalent to a minimum of 100 years at 23 °C.

Steam Sterilization

Steam Sterilization Procedures

KetaSpire® KT-820 samples were exposed continuously in a Pre-Vac sterilizer for 500 cycles using the following conditions:

- Unit: Amsco Century Sterilizer SV-136H
- Cycle: Pre-Vac
- Temperature: 134 °C to 136 °C
- Pressure: 35 to psig to 37 psig
- Vacuum: 27 in. Hg
- Sterilization Times: 18 min. sterilization, 10 min, dry, 36 min. total

The unit uses a dedicated steam generator supplied by filtered, deionized water, which is chemically balanced per the sterilizer unit manufacturer's recommendations. Testing method details are provided in the equipment references section of this document. Relative results of the effects of 500 cycles of steam sterilization on KetaSpire® KT-820 are presented in Table 2.

Steam Sterilization Results

Extensive testing indicates that KetaSpire® KT-820 can resist significant changes in mechanical, thermal, and chemical properties after 500 cycles of steam sterilization. A slight increase in strength and modulus along with a slight decrease in elongation was observed due to an annealing effect of the high temperatures used during steam sterilization. Please refer to the Explanation of Color Change section in this document for a description of ΔE values.

While slight changes were observed in other testing conditions, they were all within the confines of expected testing error. With no significant changes resulting from aging or steam sterilization, it is believed that samples can be stored for an indefinite time after exposure to steam sterilization without any adverse effects on properties.

Table 2 Effects of steam sterilization results on KetaSpire® KT-820

Property	As-Molded	KT-820 at 500 Cycles
Color – CIE L*A*B		
Color change, ΔE	Nominal	3.0
Characteristic Temperatures – DSC – ASTM D3418		
Glass transition, T_g	Nominal	+0.1 %
Recrystallization, T_c	Nominal	No change
Melt temperature, T_m	Nominal	No change
Molecular Weight – GPC – Solvay Method		
Number average, M_n	Nominal	+4.9 %
Weight average, M_w	Nominal	+3.0 %
Tensile Properties – ASTM D638		
Strength at yield	Nominal	+1.0 %
Elongation at yield	Nominal	–13.5 %
Modulus of elasticity	Nominal	+2.7 %
Biocompatibility		
Cytotoxicity	Pass	Pass
Physiochemical testing	Pass	Pass

Ethylene Oxide (ETO) Sterilization

ETO Sterilization Procedures

KetaSpire® KT-820 samples were submitted to the Sterigenics Facility in Smyrna, GA, for ethylene oxide (ETO) sterilization, which was conducted using Sterigenics procedures per requirements of the submitted packaging and material load. Actual conditions are documented in Sterigenic work orders 542504, 544611, 547965, 552296, and 556340 from Nov. 14, 2010 to Dec. 9, 2010.

The average gas exposure time for 50 ETO cycles was 12.3 hours. Samples and supporting Certificates of Processing were returned to Solvay for property evaluations and documentation. Details of testing methods are provided in the Equipment References section of this document. Relative results of KetaSpire® KT-820 exposed to 50 cycles of ETO sterilization are presented in Table 3.

ETO Sterilization Results

Test results indicate that KetaSpire® KT-820 is resistant to mechanical, thermal, and chemical changes after ETO sterilization. While slight changes were observed in some testing conditions all were within the confines of expected testing error. With no significant changes resulting from aging or ETO sterilization, it is believed that samples can be stored for an indefinite time after exposure to ETO sterilization without any adverse effects on properties.

Explanation of Color Change

LAB color space was used for evaluation of color change. Color space is tracked using three values: L (brightness), a (red/green), and b (blue/yellow), representing a three-dimensional color space. A single numerical value, ΔE, can be used to estimate the degree of overall color change using Equation 4. Color changes as seen by the naked eye are summarized in Table 4.

Equation 4

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b)^2}$$

Table 3 Effects of ETO sterilization on KetaSpire® KT-820

Property	As-Molded	KT-820 at 50 Cycles
Color – CIE L*A*B		
Color change, ΔE	Nominal	1.1
Characteristic Temperatures – DSC – ASTM D3418		
Glass transition, T_g	Nominal	+1.0 %
Recrystallization, T_c	Nominal	–0.1 %
Melt, T_m	Nominal	No change
Molecular Weight – GPC – Solvay Method		
Number average, M_n	Nominal	+1.1 %
Weight average, M_w	Nominal	+2.8 %
Tensile Properties – ASTM D638		
Strength at yield	Nominal	+1.0 %
Elongation at yield	Nominal	+1.9 %
Modulus of elasticity	Nominal	No change
Biocompatibility		
Cytotoxicity	Pass	Pass
Physiochemical testing	Pass	Pass

Table 4 Typical ΔE significance to the naked eye

ΔE Value	Color change as seen by the naked eye
$\Delta E < 1$	Unable to distinguish
$1 \leq \Delta E < 2$	Noticeable by some upon a close inspection
$2 \leq \Delta E < 3$	Noticeable upon inspection
$\Delta E \geq 3$	Obvious change in color

Equipment References

Tensile testing was conducted on an Instron® 5569 Load Frame at 2 in/min test speed per the ASTM D638 standard.

Thermal properties were tested using a TA Instruments® Q20 Differential Scanning Calorimeter per ASTM D3418 standard. Analysis used 1st and 2nd heat with a 20°C/min ramp rate.

Color Change was measured on the wide end of a Type I tensile bar using a BYK Gardner® Colorsphere Instrument; Reflectance mode, CIE L*a*b* scale with a D65 – 10° illuminant and observer.

Molecular weight was determined by Size Exclusion Chromatography using a Waters Alliance 2695 separation module and 2487 detector.

FTIR was run on a Perkin-Elmer® Spectrum 2000 FT-IR instrument using a DATR (Direct Attenuated Total Reflectance) probe. Surface is read directly, no preparation is needed.

Cytotoxicity (ISO 10993-5) and Physio-Chemical analysis (ISO 10993-18) were conducted by the NAMSA laboratories in Northwood, OH.

Literature References

[1] D. W. L. Hukins, et al., "Accelerated Aging for Testing Polymeric Biomaterials and Medical Devices," *Medical Engineering & Physics*, Vol. 30, pp. 1270-1274, 2008.

[2] *Annual Book of ASTM Standards, E1641, Standard Test Method for Decomposition Kinetics by Thermogravimetry*, pp. 1041-1045 (1994).

[3] P. H. Kang, et al., "Radiation and Thermal Effects on the Dielectric Relaxation Properties of PEEK," Korea Atomic Energy Research Institute, Korea, Sept. 2006.

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