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Authors: Teresa Rodon, DuPont UK
Ernst Poppe, DuPont INTL SA
Alexandra Fabbro, DuPont INTL SA
Tom Baltus, E.I. DuPont Canada Co.

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The effect of common sterilization techniques on the mechanical properties of DuPont Performance Polymers Special Control (SC) and Premium Control (PC) grades

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0. - Summary

DuPont Performance Polymers offer resins for components in medical devices. Certain single-use devices undergo one sterilisation process whilst others designed for multiple-use, must be sterilized several times.

It is vital to ensure that the sterilisation process does not affect the material properties but is successful in destroying microbes. This study was devised in order to predict the behaviour of DuPont Special Control and Premium Control grades following sterilization by methods that are often used in the healthcare industry. Due to their good thermal stability and excellent chemical resistance, engineering polymers can withstand most sterilization processes. An overview is given in the table below:

Sterilization Process Product	Autoclave	Gamma	Ebeam	EtO
Zytel® (PA 66)	+++ <small>Yellowing with > 10 cycles</small>	+++ <small>Yellowing</small>	+++ <small>Yellowing</small>	+++
Zytel® (PA 612)	++ <small>Yellowing with > 10 cycles</small>	- <small>Yellowing</small>	++ <small>Yellowing</small>	+++
Delrin® (POM)	++ <small>Up to 25 cycles, slight discoloration</small>	- <small>Not recommended</small>	- <small>Not recommended</small>	+++
Hytrel® (TPC-ET) soft grades (30-55 Shore D)	++	+++	+++	+++
Hytrel® (TPC-ET) hard grades (63-82 Shore D)	+++	+++	+++	+++
Crastin® (PBT)	+++	+++	+++	+++
Zytel® HTN (PPA)	+++	+++	+++	+++
Polypropylene (unmodified)	++ *)	- *)	n.a.	+++ *)
Polyacrylics (unmodified)	O *) <small>Temperature limited</small>	+ *)	n.a.	+ *) <small>Temperature limited</small>
PVC (unmodified)	O *)	- *)	n.a.	++ *)
PS (unmodified)	O *) <small>Temperature limited</small>	+++ *)	+++ *)	+ *) <small>Potential sticking</small>
PC (unmodified)	++ *)	+ *)	n.a.	+ *) <small>Some EtO gas mixtures can cause microcracks</small>
ABS (unmodified)	O *) <small>Temperature limited</small>	+ *)	n.a.	++ *)

*) source: Sterilisation of Polymer Healthcare Products, Wayne Rogers, Rapra Technology Ltd.

Legend:

+++	Excellent resistance
++	Good resistance, certain limitations require consideration
+	Good resistance, several limitations require consideration
O	Possible, depends on conditions
-	Not recommended

1. – Introduction

Medical devices may be classified into 3 categories as follows:

- A non-critical device where the device has a limited surface contact with non damaged skin,
- A semi-critical device where the device has direct contact with tissues or damaged skin,
- A critical device which penetrates the skin, or the mucosa during use and which gets in direct contact with blood, tissues, organs and trauma

Depending on the above described category, appropriate sterilization of these medical devices will be an essential step in the manufacture of healthcare products to ensure both their shelf-life and reliability when in use. “It is a challenged process of the highest order used to render a product free of all forms of viable micro-organisms.”¹

¹ Wayne Rogers, “Sterilization of Polymer Healthcare Products”, Rapra Technology Ltd.

Sterilization may be defined as the inactivation or destruction of viable micro-organisms. ISO 11135:1994 defines sterility as “State of being free from viable micro-organisms”.

2. - Sterilization Methods

There are few agents capable of sterilizing polymer components. Typical methods are:

- Steam
- Ethylene oxide (EtO)
- Radiation (Gamma, Ebeam)
- Dry Heat
- Plasma

2.1. - Steam Sterilization

Steam sterilization, or autoclaving, is a widely used method. It can be performed with relatively low-cost equipment using saturated steam. The process is robust, easy to control, safe and environmentally friendly.

Typical process conditions are 20 min at 121 °C or 5 min at 134 °C.

The limiting factor for many standard polymers is their heat resistance (T_g, dimensional stability), particularly for single-use devices, and their hydrolytic resistance in the case of multiple sterilisation cycles.

2.2. - Ethylene Oxide Sterilization (EtO)

EtO sterilization is a gaseous method involving the highly diffusive, permeable and toxic EtO gas. This destroys bacteria and other micro-organisms. Due to the nature of the process it is particularly suitable for medical devices containing electronic components.

This technique requires thorough process control to eliminate any residuals on the sterilized components. Well trained personnel and safe practices during operation are required to avoid any leakage of this flammable, explosive, carcinogenic gas.

Typical EtO sterilization processes involve several stages of gas removal; humidification, EtO exposure and air washes. Process pressures are close to vacuum and temperatures used are around 50 °C. Most plastic materials are compatible with EtO sterilization.

2.3. - Radiation

Radiation is a type of “cold” sterilization.

Gamma Sterilization

Sterilization by gamma radiation uses the radioisotope Cobalt 60 as its energy source. Once formed, Cobalt 60 instantly begins to decay, releasing energy in the form of gamma rays. The artificially activated Cobalt 60 pellets are encapsulated in stainless steel “pencils” held in a source rack. To deliver the sterilization dose the source rack is raised from a deep pool of water and the product is passed around this radiation source on a conveyor system. The energy emitted is insufficient to induce radioactivity in any material, irrespective of the length of exposure to the source.

Sterilising products by gamma radiation is a sophisticated process requiring extensive knowledge of the kinetics of microbial inactivation, polymer selection and process controls.

Gamma Irradiation possesses excellent penetrative capability. The unit of absorption is the Gray, expressed in kGy. This absorbed dose is impacted by product density, pack size, dose rate, exposure time and to some degree by part design.

The main disadvantage associated with gamma irradiation concerns the potentially damaging effects of gamma rays on the product, particularly those products that contain polymeric components. Another drawback with this technique is the bulky shielding required to store the radioisotope.

Electron Beam

Sterilization using an Electron Beam involves emitting electrons from a heated tungsten filament gun and accelerating them down an evacuated tube. This beam then passes through an oscillating magnetic field which “scans” it back and forth across the sample ensuring a uniform dose of radiation.

The e-beam process achieves lethality using ionising radiation which acts on cellular constituents in a similar manner to Gamma radiation.

E-beam sterilization has a number of advantages over gamma irradiation including its ability to be switched on and off at will, greater product compatibility and potentially very high throughput. Disadvantages include higher machine complexity and poor material penetration. In addition, validation and control of this technology is more demanding.

2.4. - Dry Heat

Dry Heat Sterilization is generally conducted at 160°C-170°C for a minimum of two hours. Specific exposures are dictated by bioburden concentrations and temperature tolerances of the products. Appropriate conditions will enable complete sterilization of the material. The equipment required is forced-air type ovens with temperature monitoring capabilities. This type of sterilization is highly dependent on the temperature resistance of the polymer.

2.5. - Plasma

Plasma is a gas in which a certain portion of the molecules are ionized.

Different gases can be used, but Hydrogen Peroxide is most commonly used in this methodology.

The process is easy to use, is safe, and can be considered as an alternative to the EtO method but it is more expensive.

It is typically used where devices cannot handle high sterilization temperatures.

3. - General Considerations of Polymers for Sterilization

Designers of medical devices require multiple skills to ensure safe and reliable components for healthcare applications. In addition to their medical engineering capabilities they need to be experts in function integration to enable component cost to be minimized and they also require advanced material knowledge for the appropriate polymer selection.

In most projects the sterilization method is already known at an early stage. Therefore, it is necessary to check the polymer material candidates' resistance to the selected sterilisation method upfront, which will help avoid any surprises during the later stages of device development.

4. - Results of Sterilization on DuPont Engineering Polymers

For the purpose of the study, ISO 2BA tensile bars (thickness = 2mm) were moulded and submitted to sterilization.

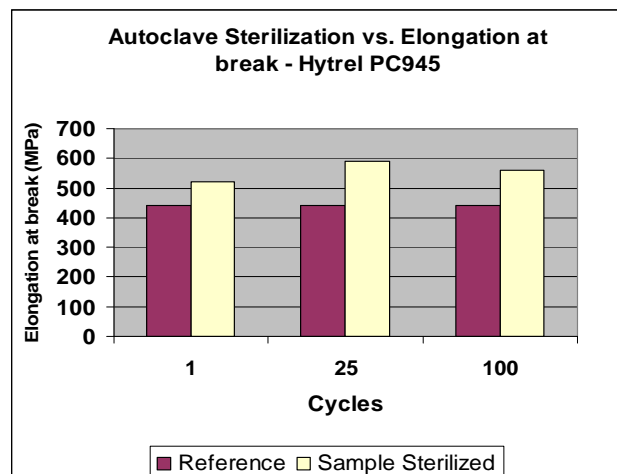
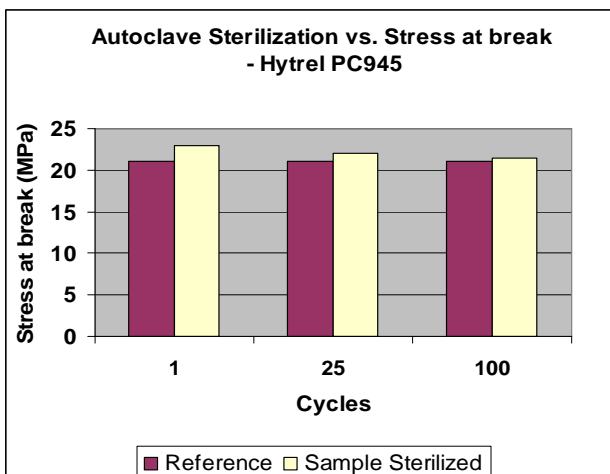
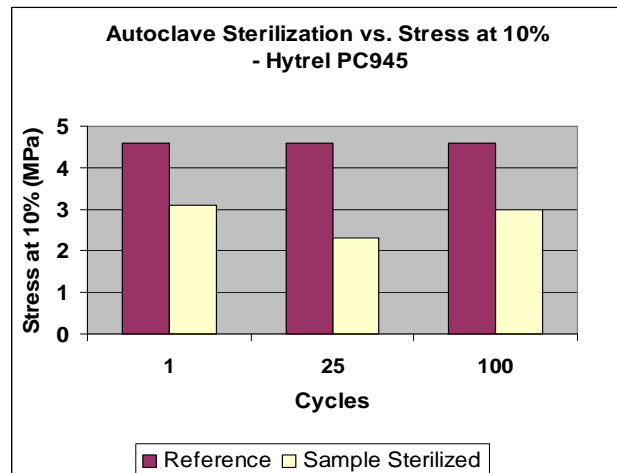
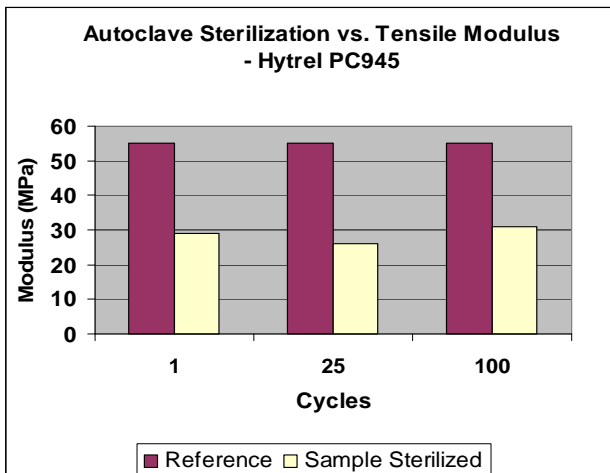
All recordings were made through tensile testing.

4.1. - Steam Sterilization

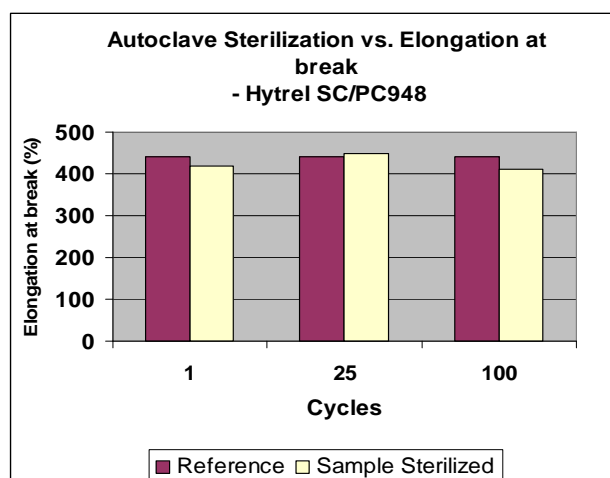
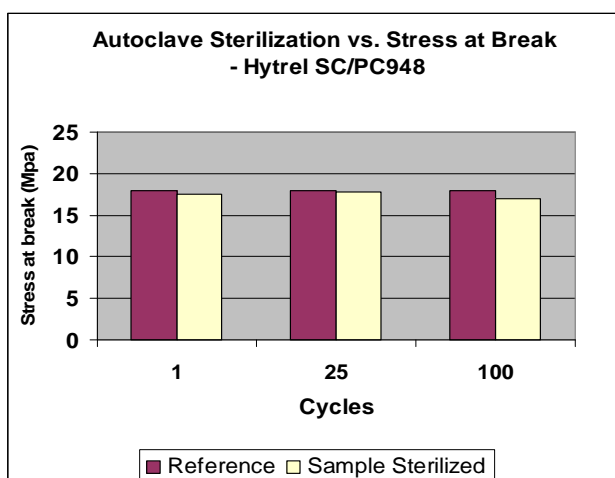
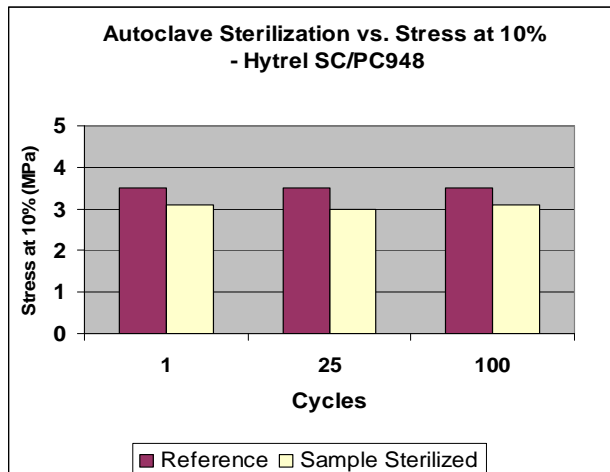
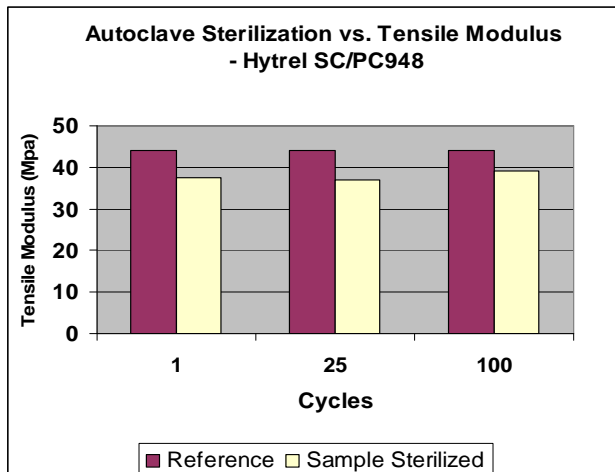
Conditions: 1 cycle = 1 wash in ultrasonic bath at 87°C + 3 min. at 134°C

Hytrel® SC/PC Grades

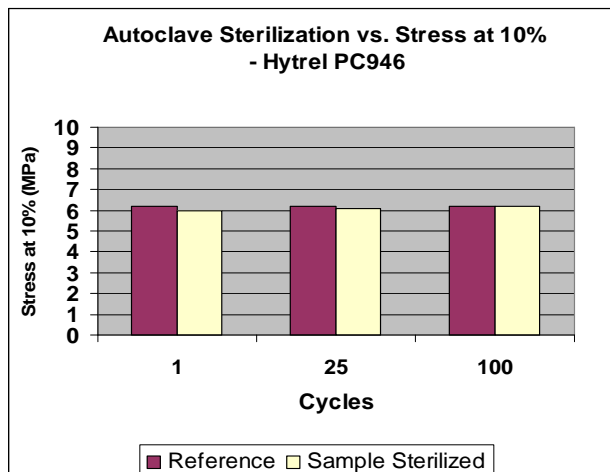
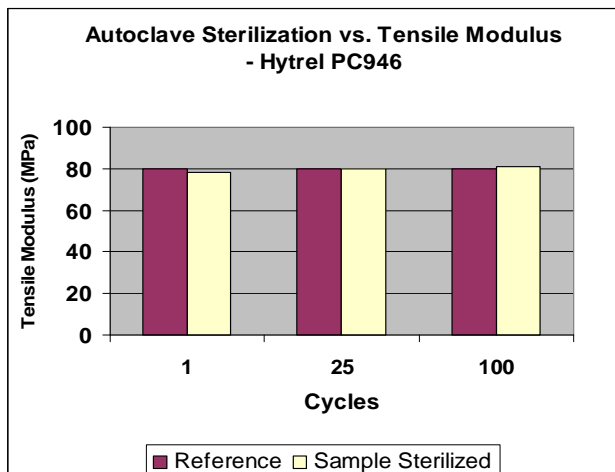
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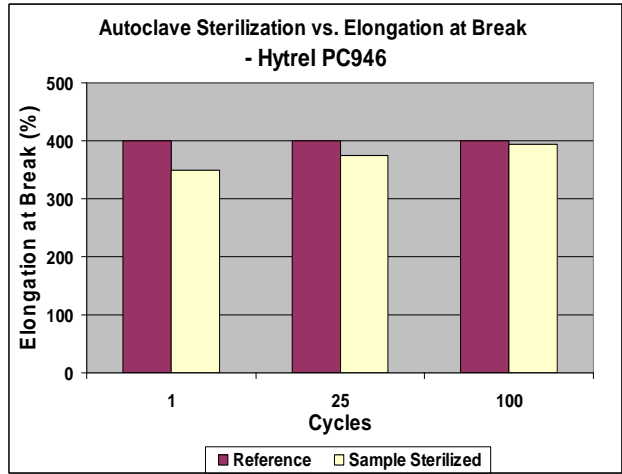
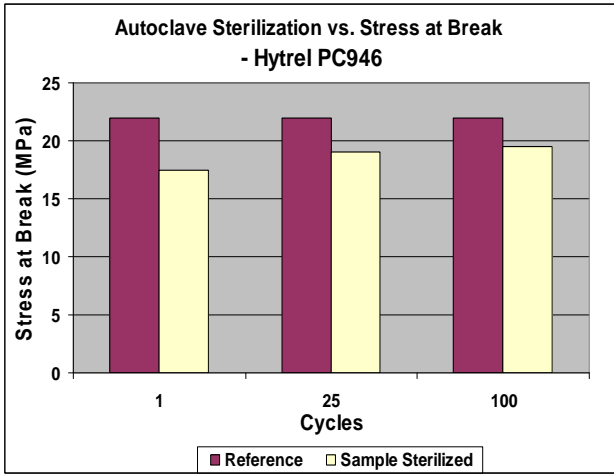


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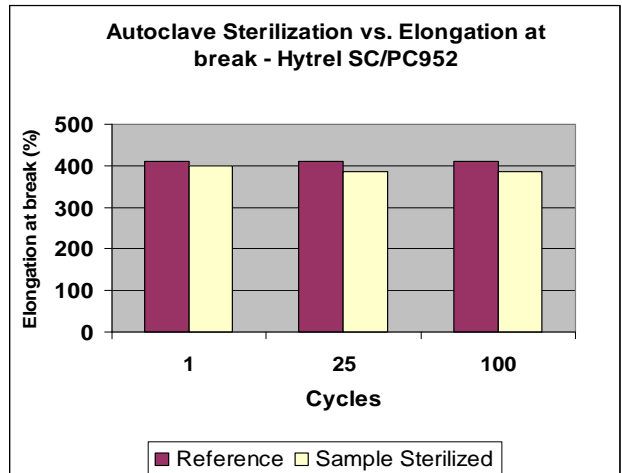
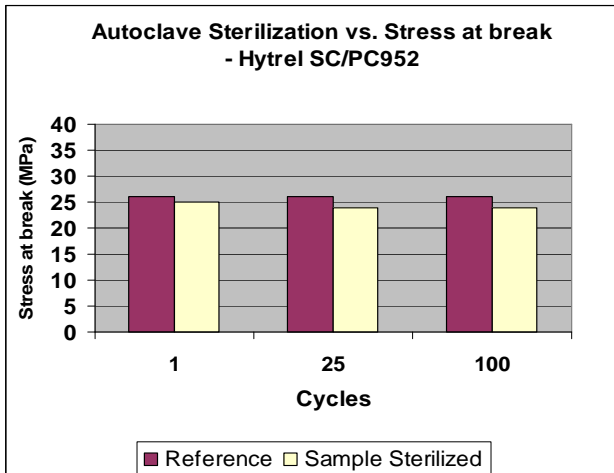
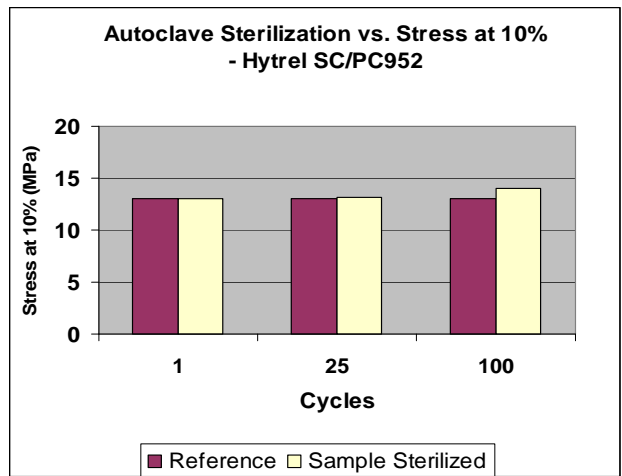
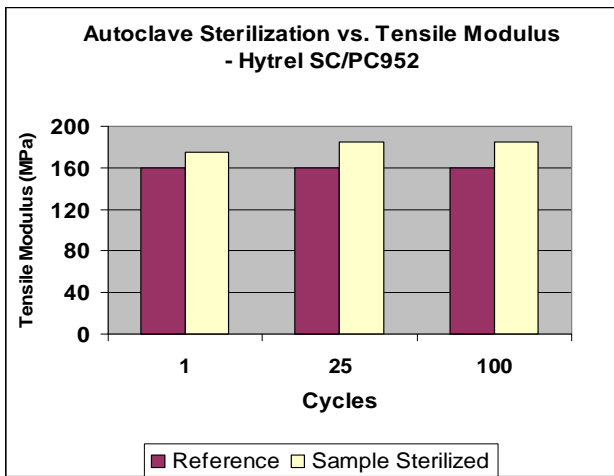


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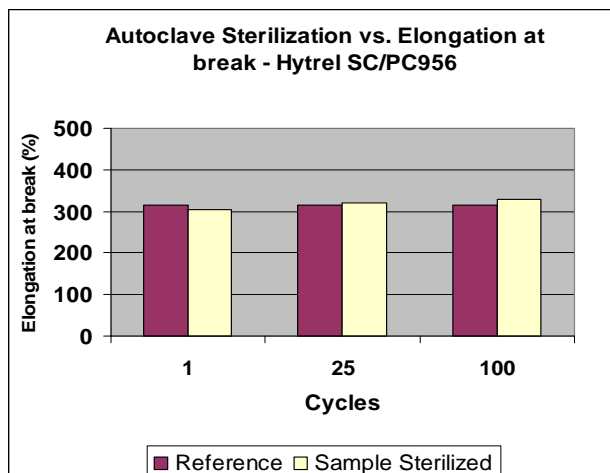
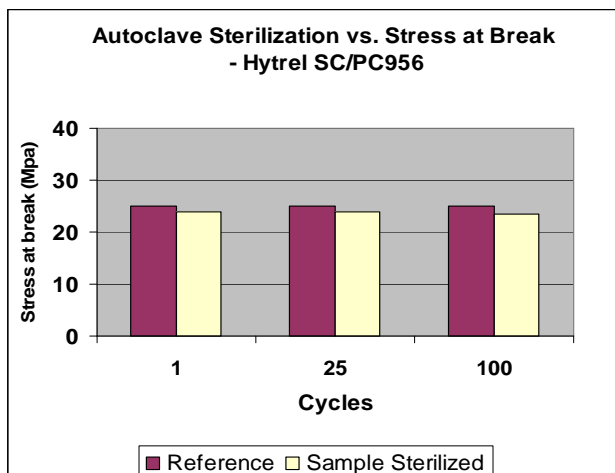
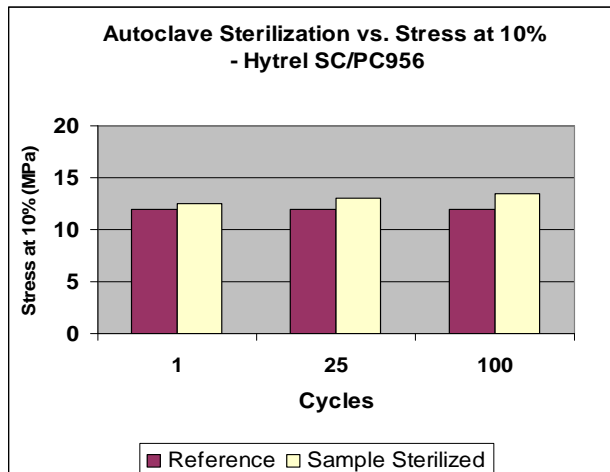
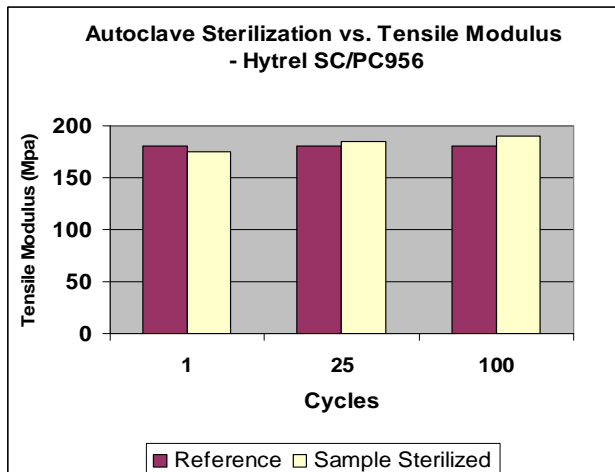




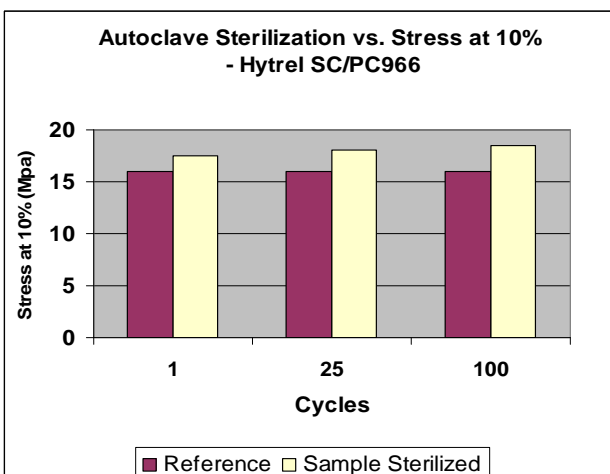
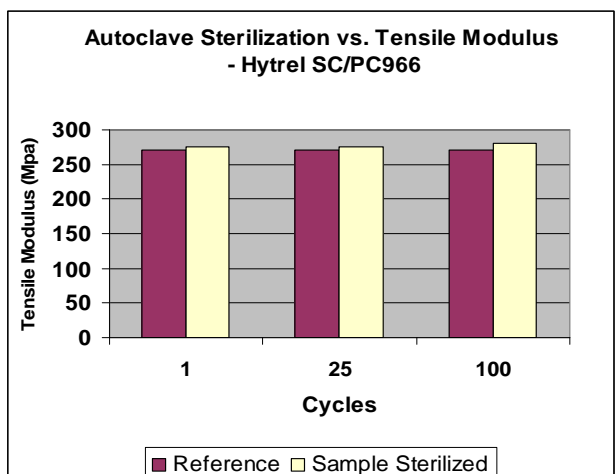
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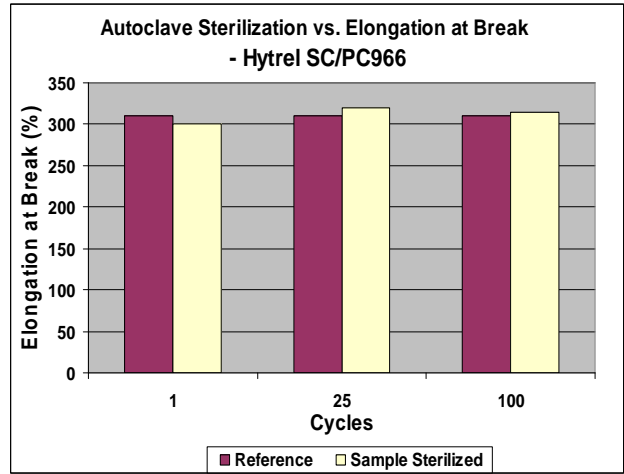
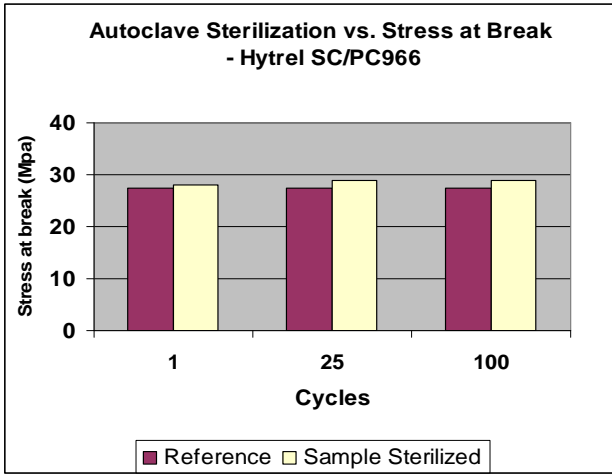


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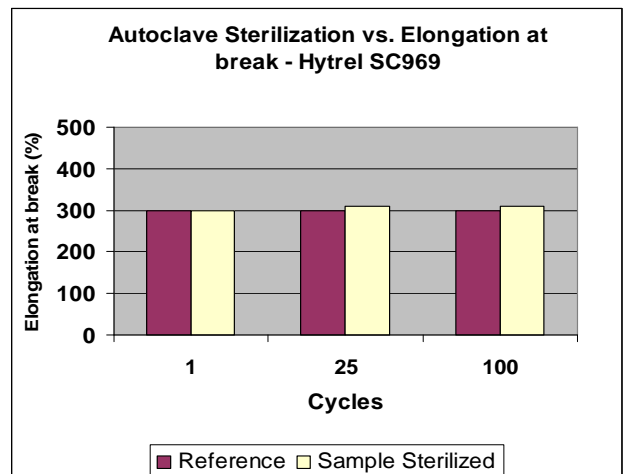
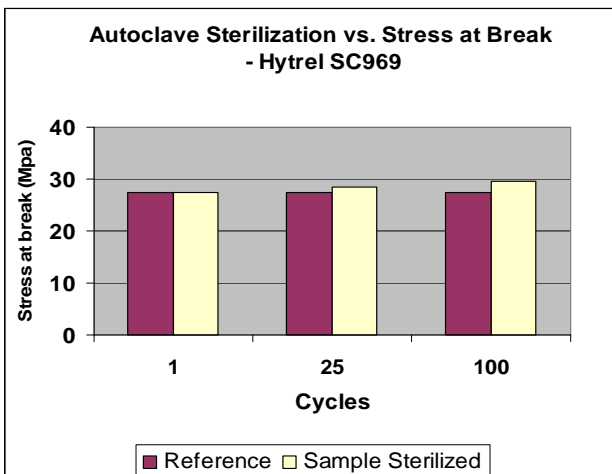
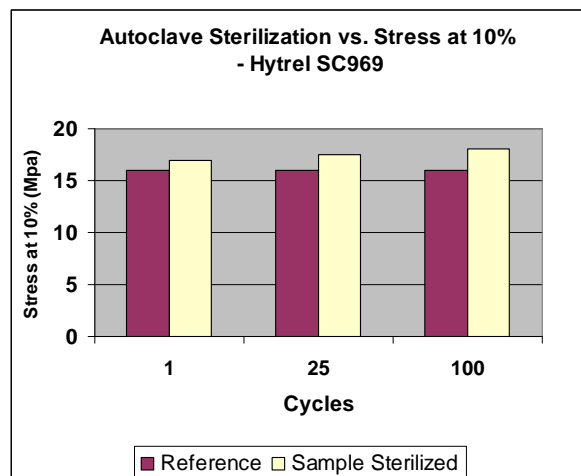
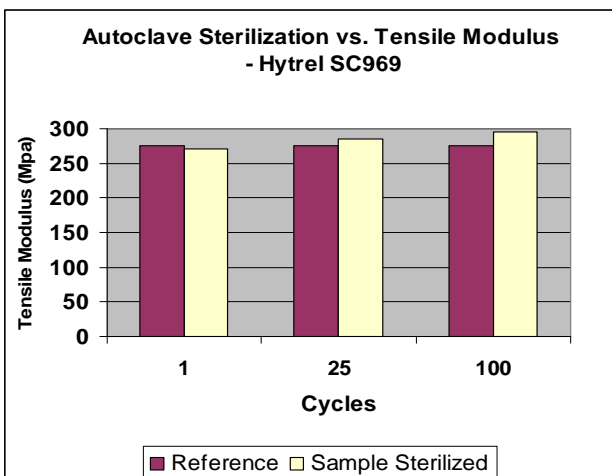


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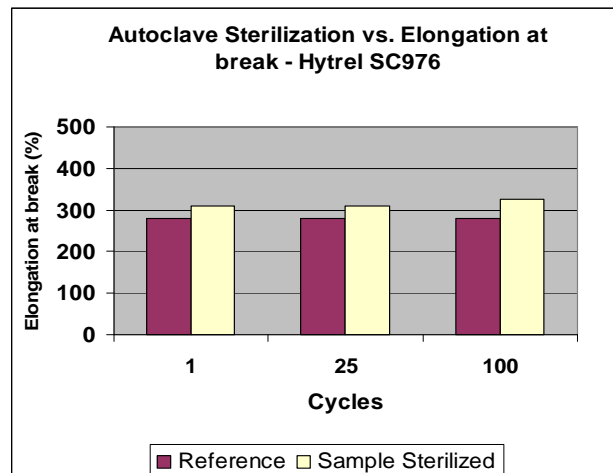
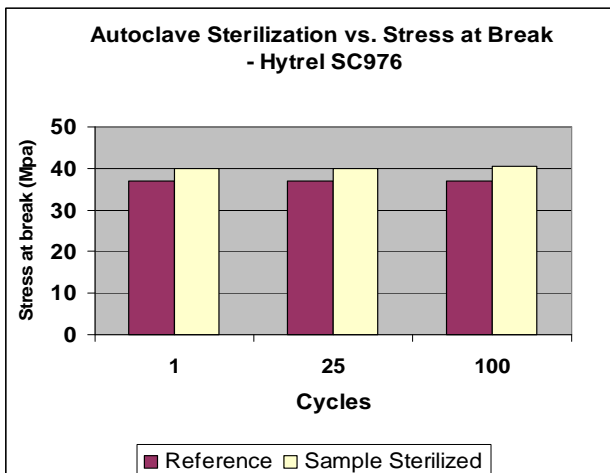
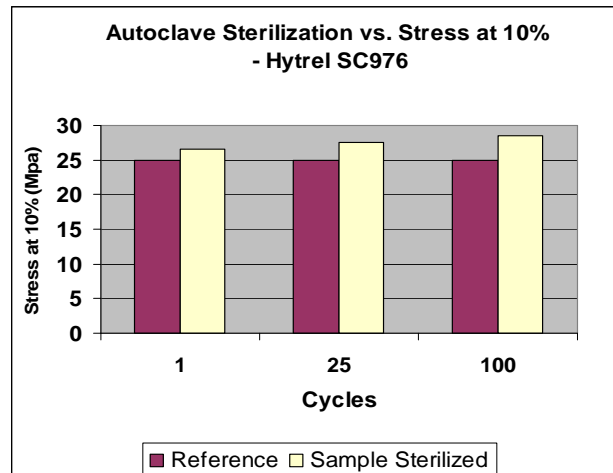
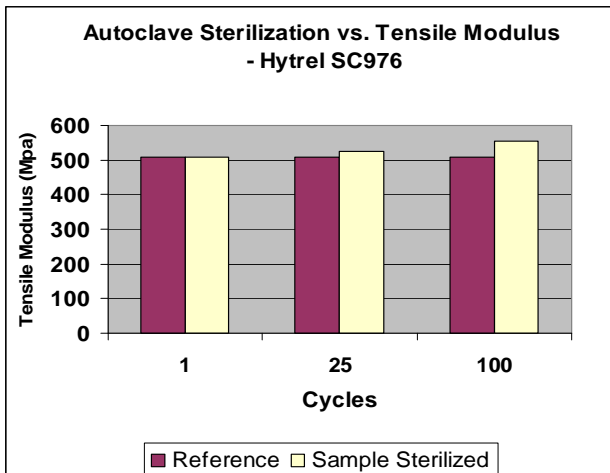




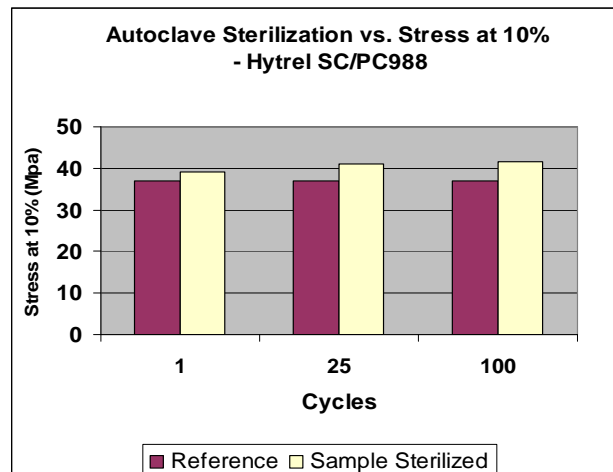
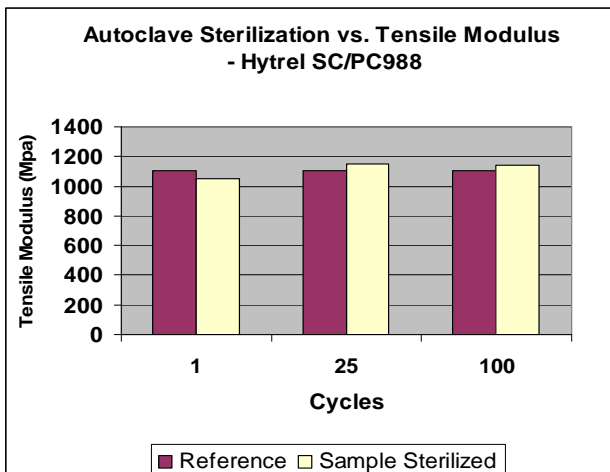
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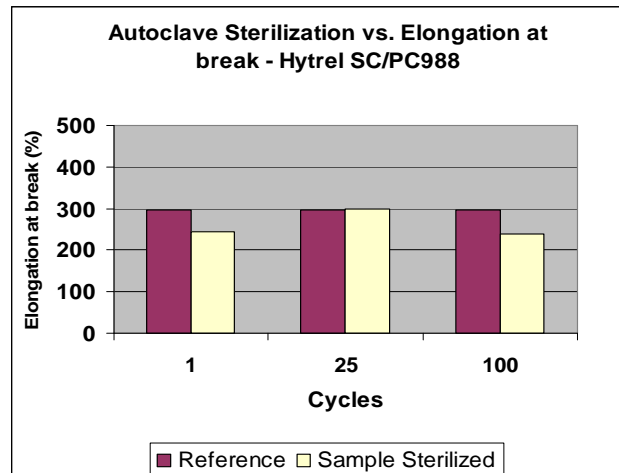
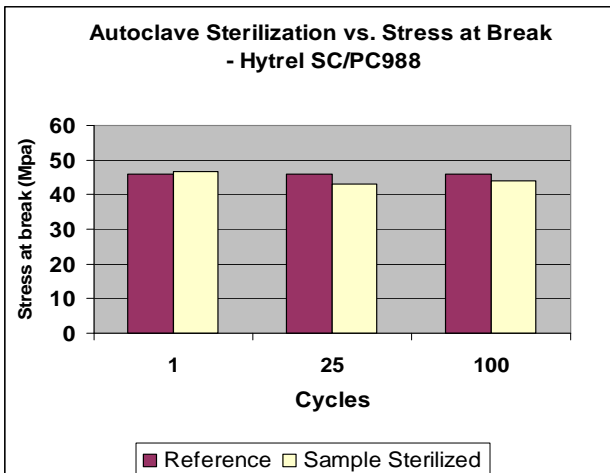


Hytre SC976 (TPC-ET)



Hytre SC/PC988 (TPC-ET)

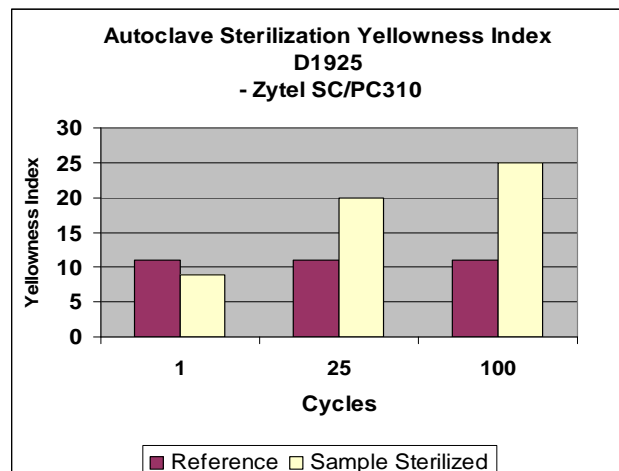
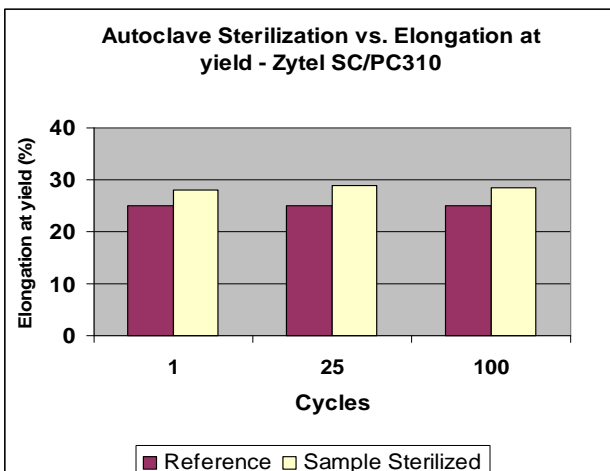
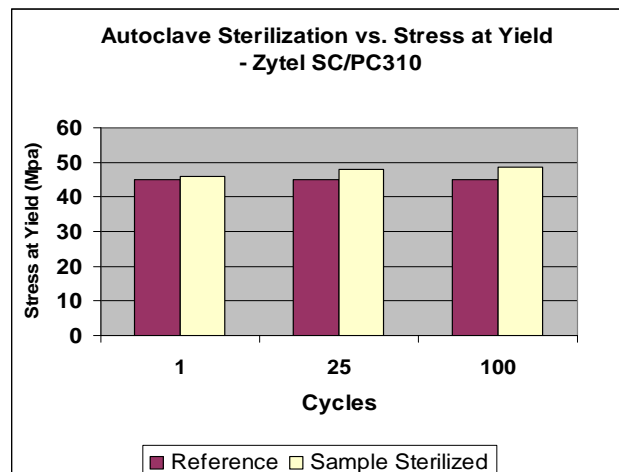
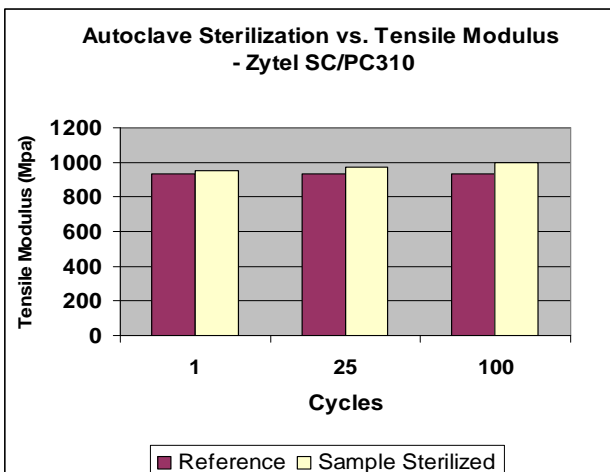




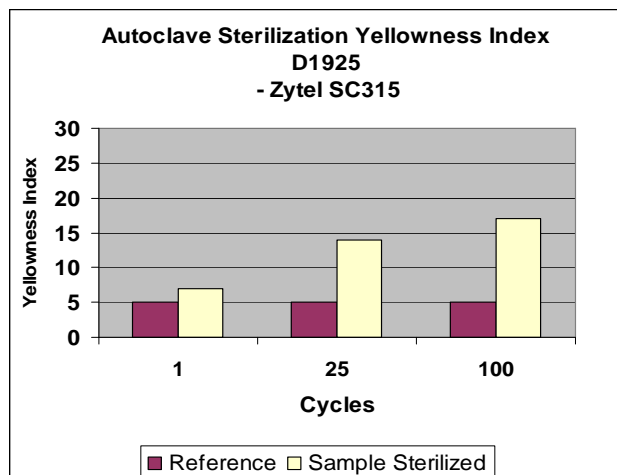
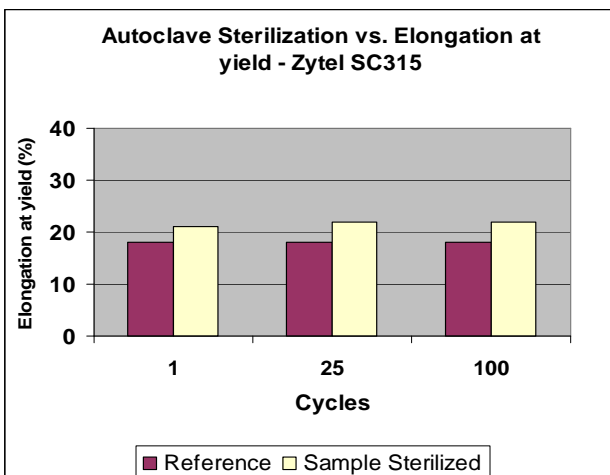
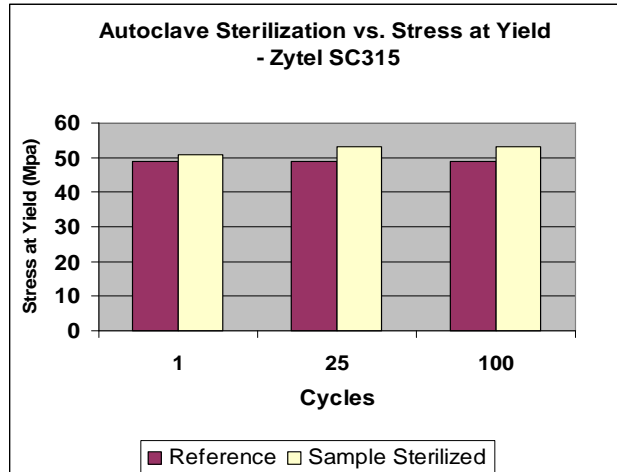
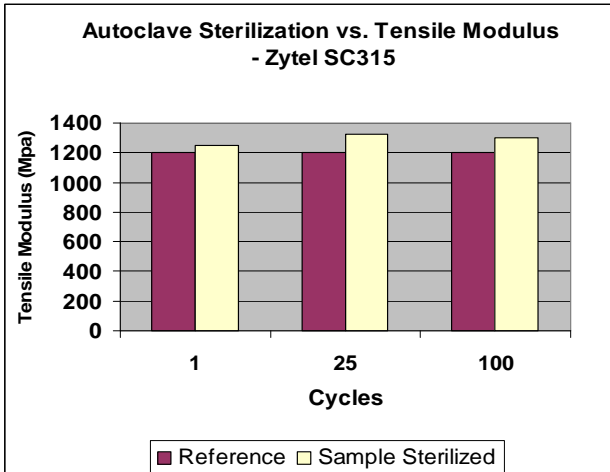
Zytel®

Due to the hydrophilic behaviour of nylons (PA), test samples naturally pick up moisture during the steam sterilization process. In order to minimize the effect of the moisture all test samples were conditioned at 23°C, 50%RH.

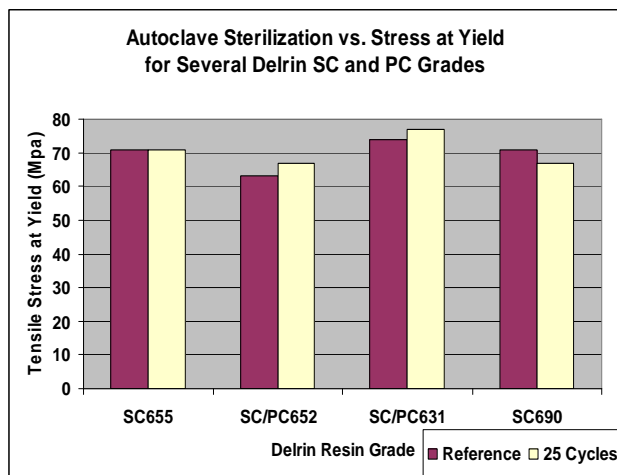
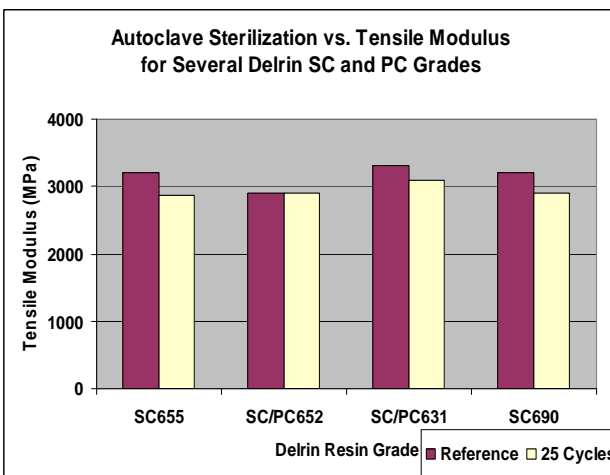
Zytel® SC/PC310 (PA 66)

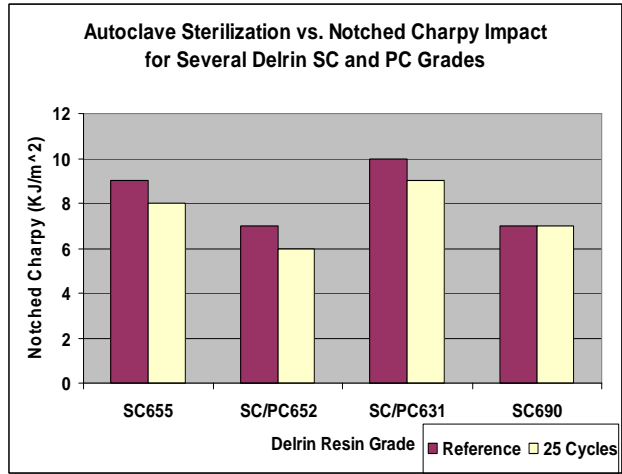
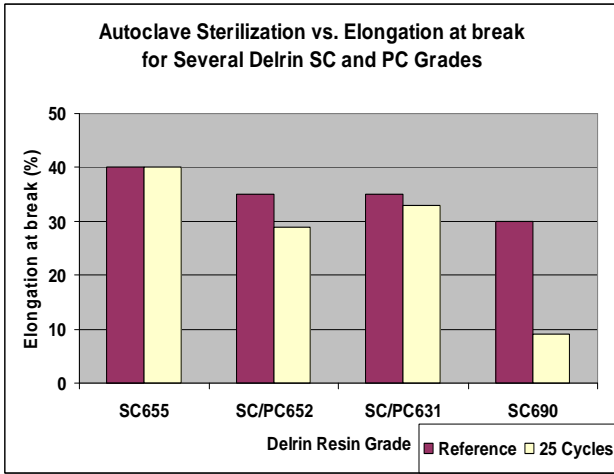


Zytel® SC315 (PA 612)

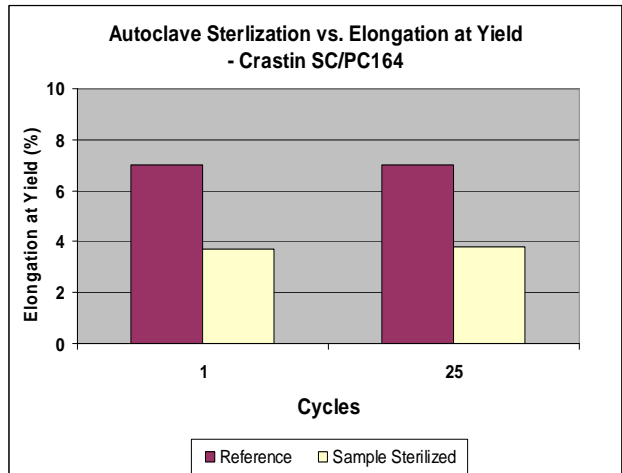
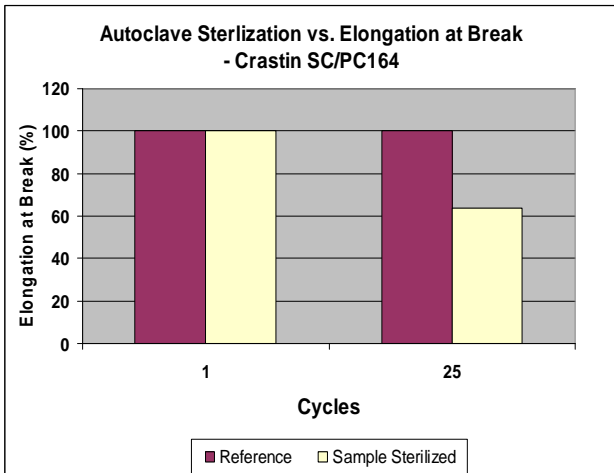
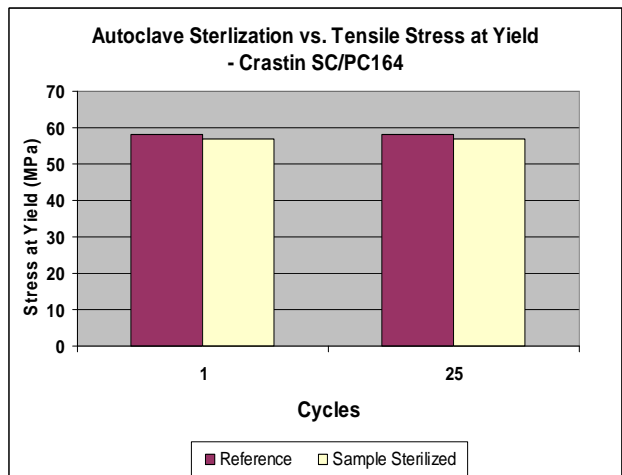
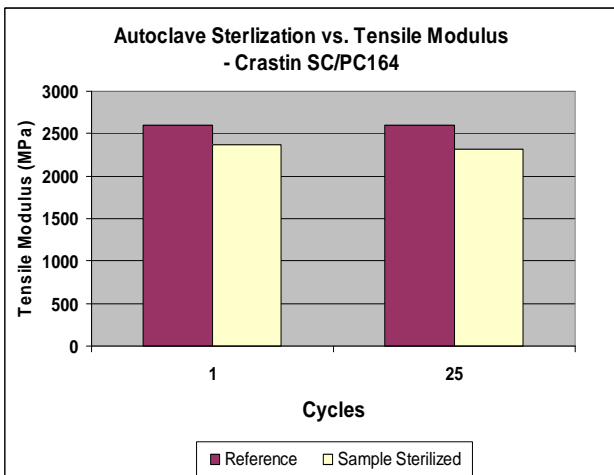


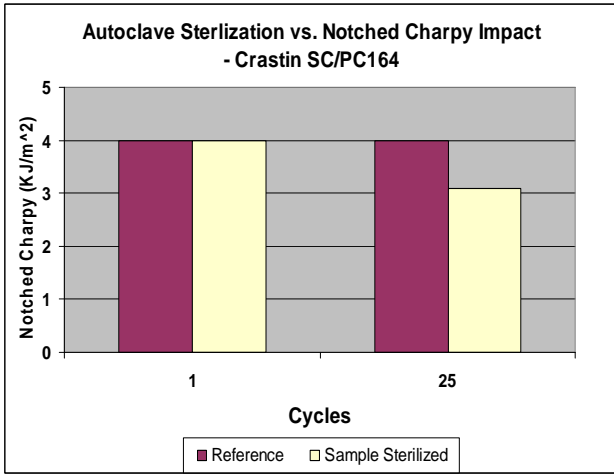
Delrin® SC/PC Grades (POM)





Crastin® SC/PC164 (PBT)



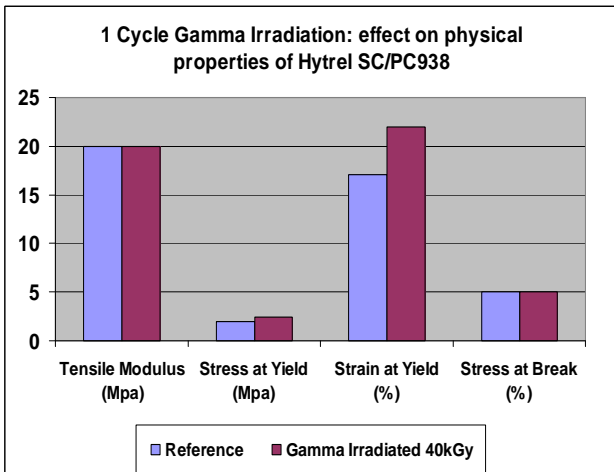


4.2. -Gamma Sterilization

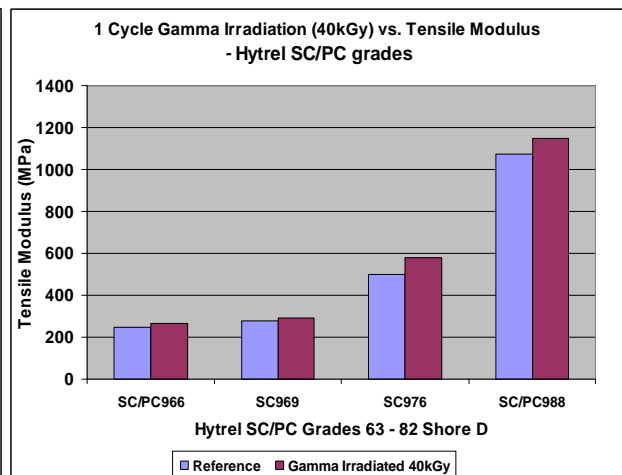
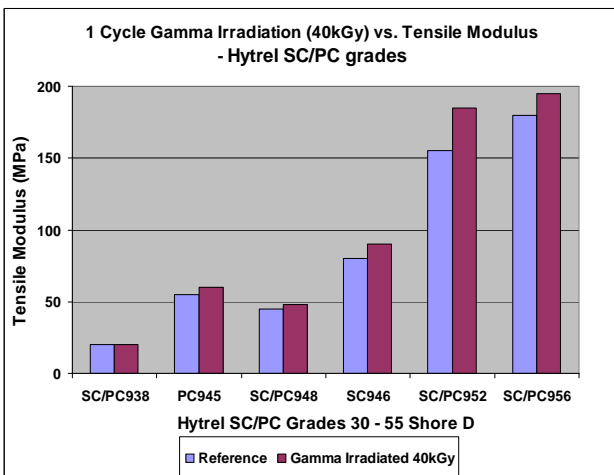
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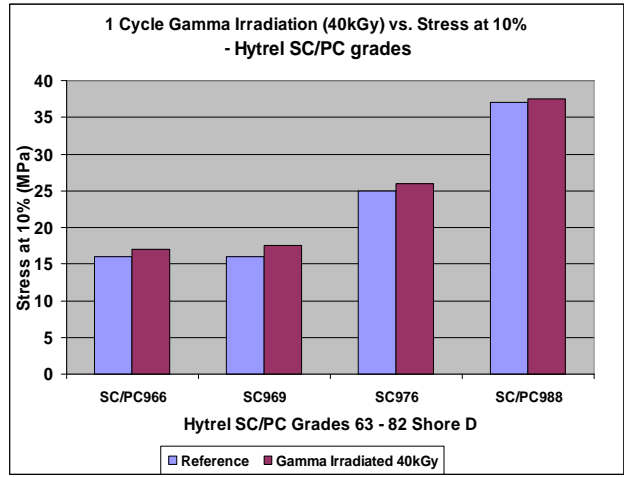
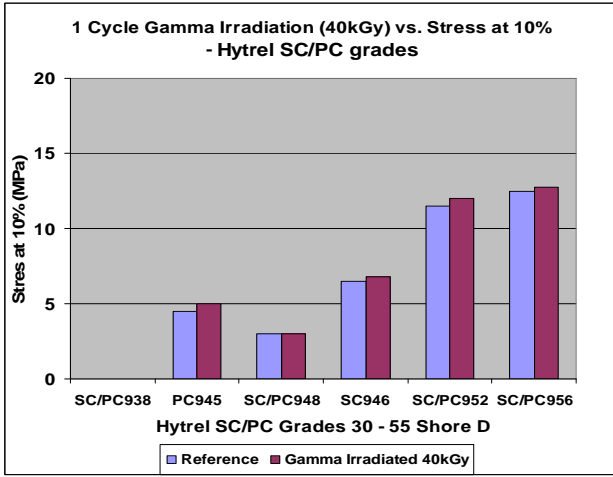
Hytrel® SC/PC Grades (TPC-ET)

Hytrel® SC/PC938

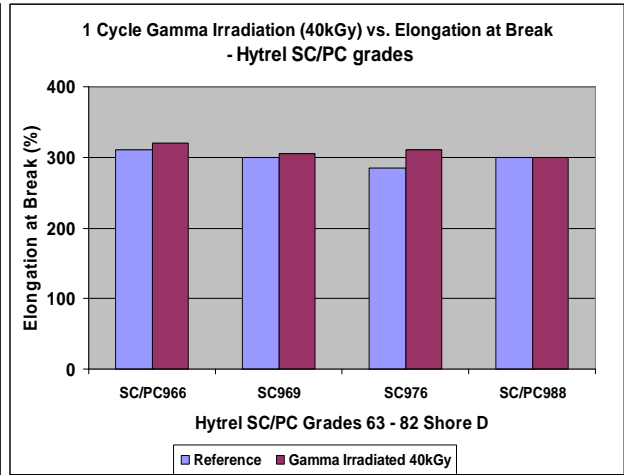
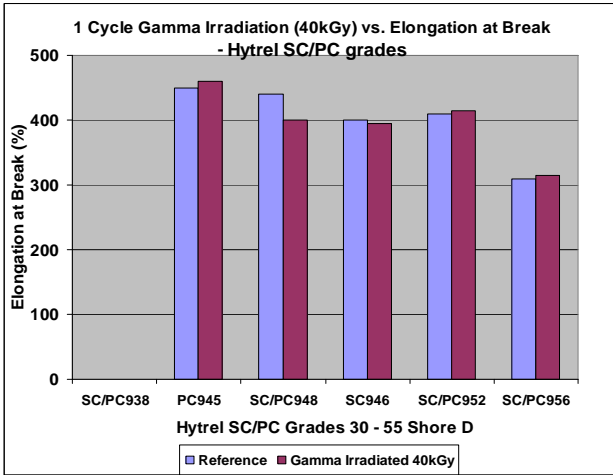
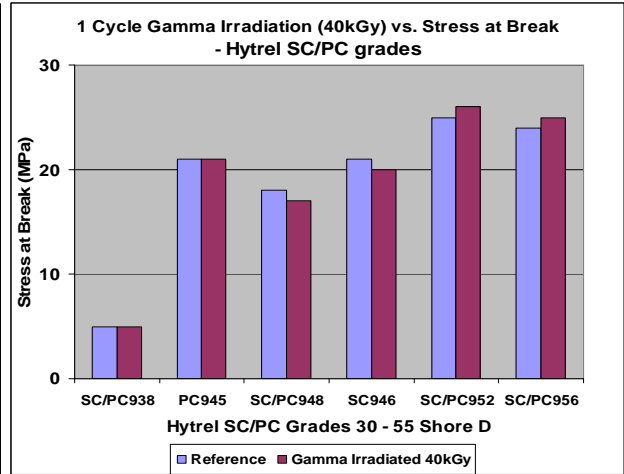
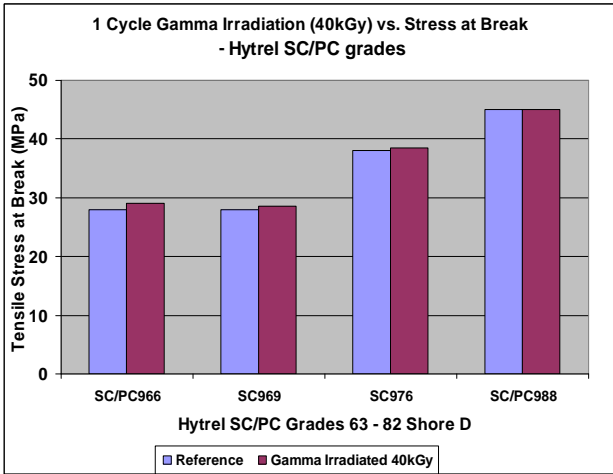


Hytrel® (TPC-ET)



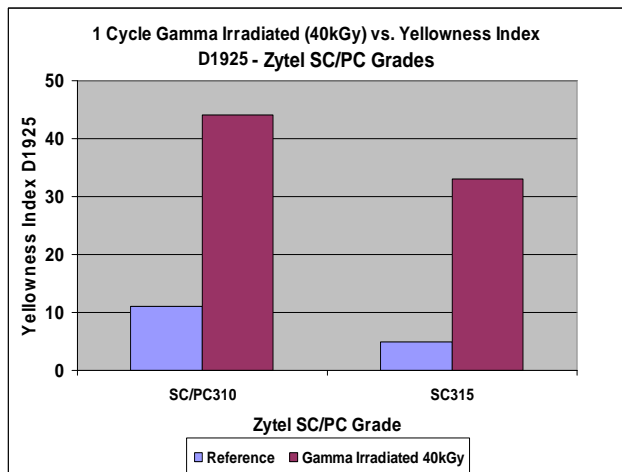
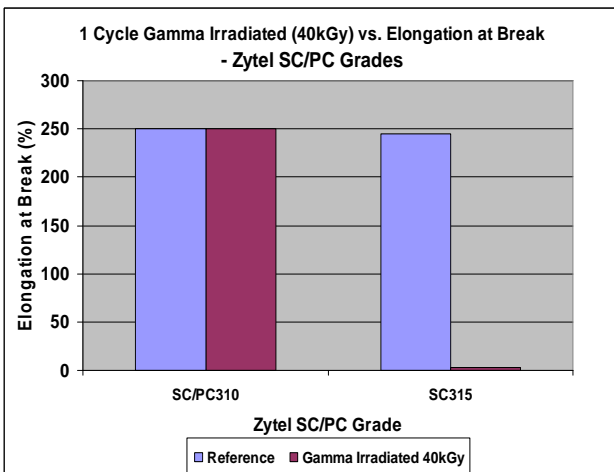
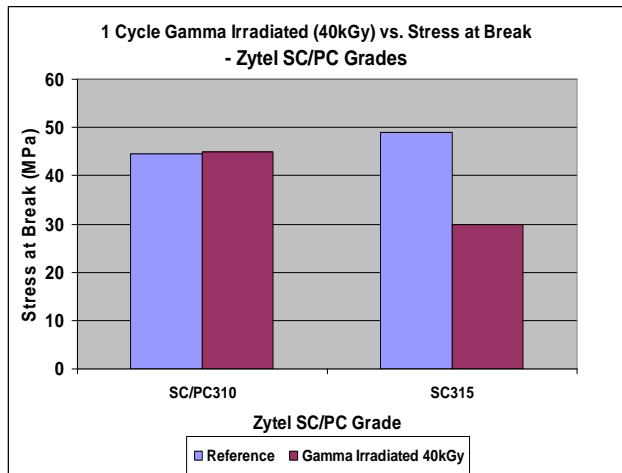
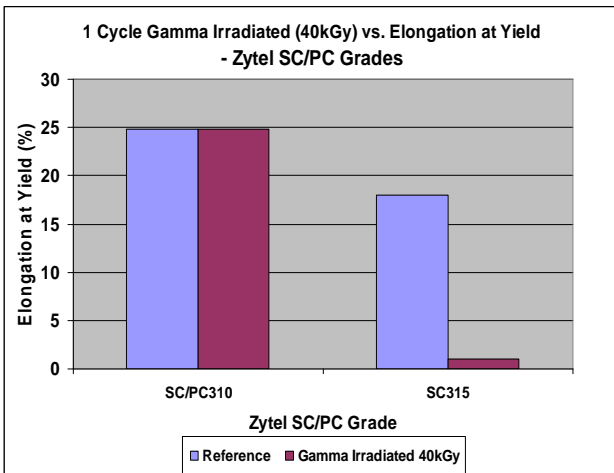
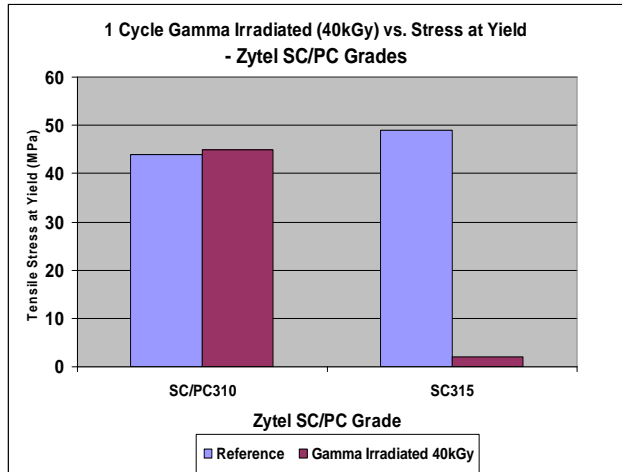
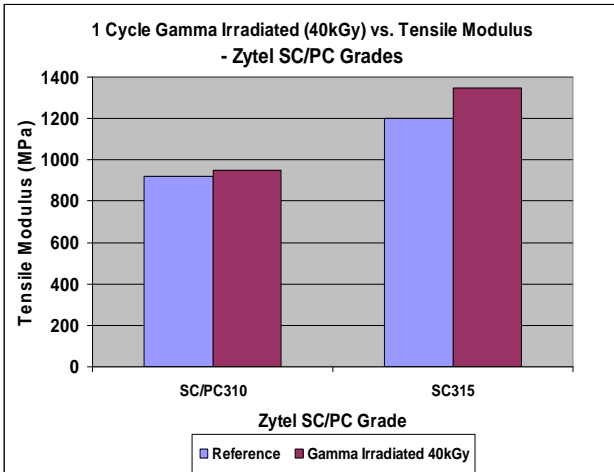


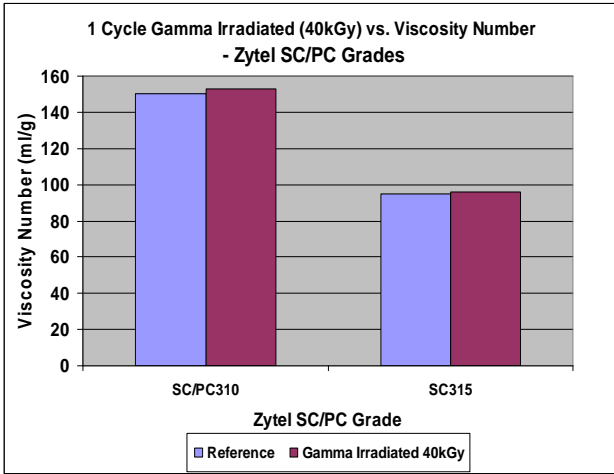
Note: no data for Hytrel® SC/PC938



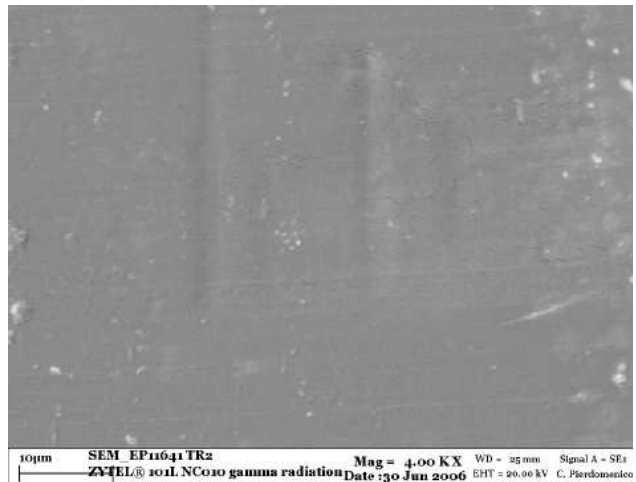
Note: no data for Hytrel® SC/PC938

Zytel® SC/PC Grades (PA)
 DAM tensile bars tested.

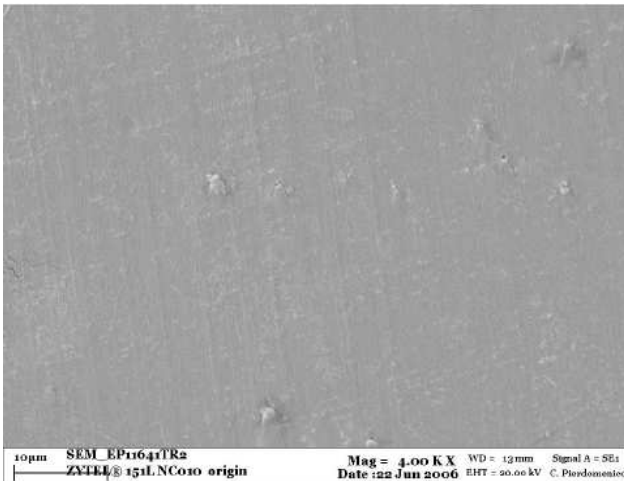




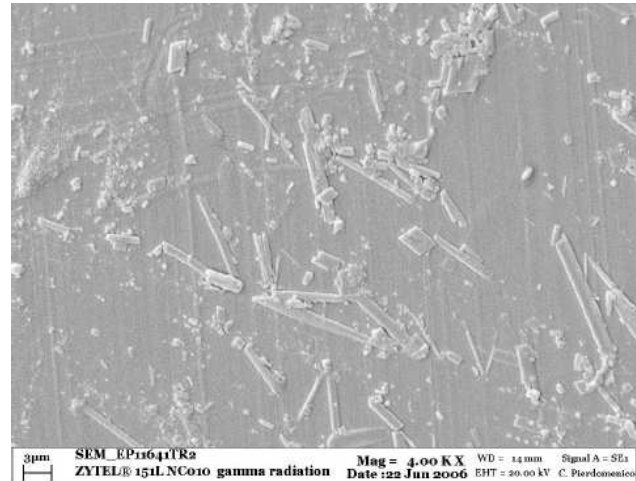
Zytel® SC310 (PA66): SEM before Gamma radiation



Zytel® SC310 (PA66): SEM after Gamma radiation



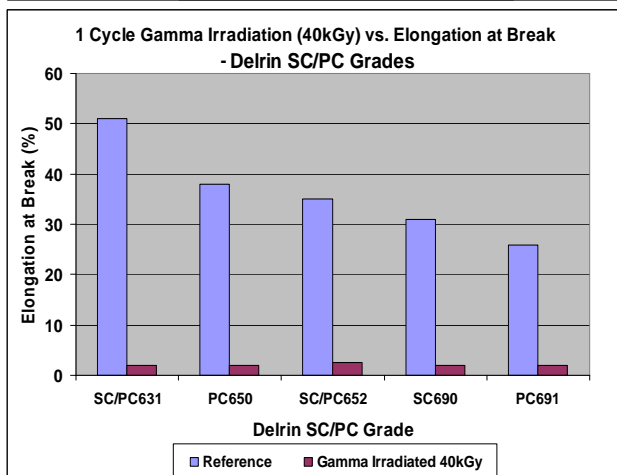
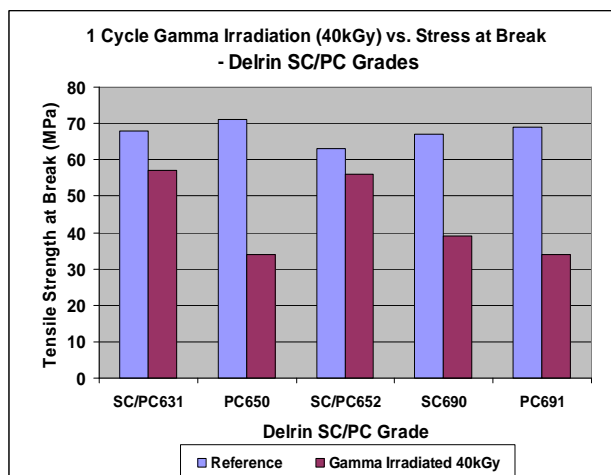
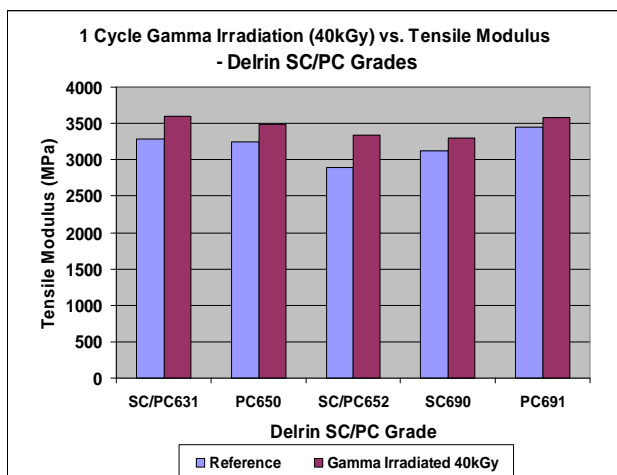
Zytel® SC315 (PA612): SEM before Gamma radiation



Zytel® SC315 (PA612): SEM after Gamma radiation

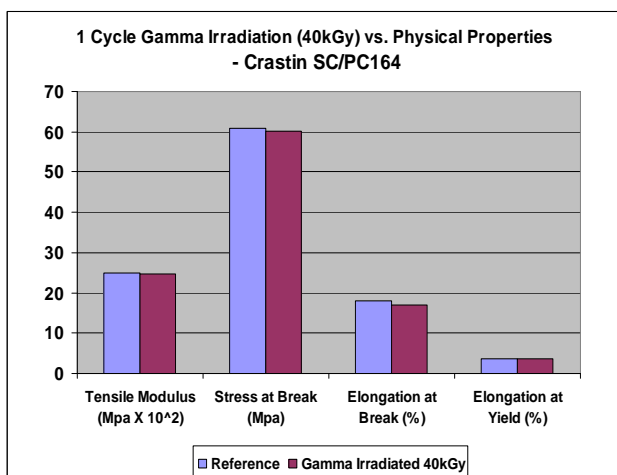
PA 612 becomes more brittle after gamma sterilization, whereas PA 66 maintains its properties. Since the viscosity measurements do not show any difference between the radiated and the reference samples it must be concluded that only the surface of PA 612 is being attacked. The SEM pictures clearly show the surface deterioration of the PA 612, whereas the surface of PA 66 is not affected. It can be concluded that the loss of properties of PA 612 parts is due to crack propagation from the surface inwards. Therefore, the use of PA 612 should be avoided when sterilizing by gamma radiation.

Delrin® SC/PC Grades (POM)

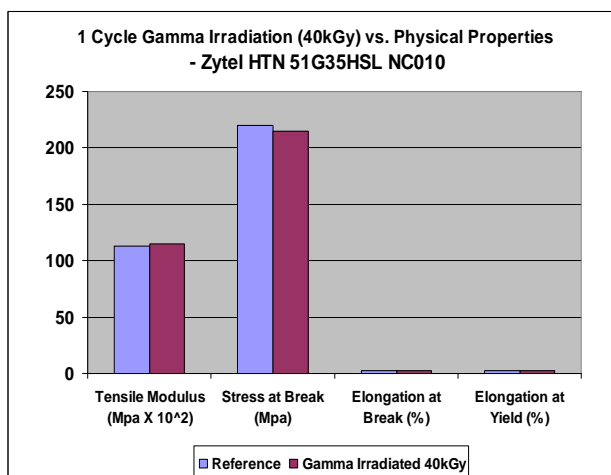


Gamma radiation severely damages the backbone of the polyacetal molecules. This is reflected in the loss of elongation as well as toughness and an increase in the melt flow rate. Therefore, POM should not be used when components are gamma radiated.

Crastin® SC/PC164

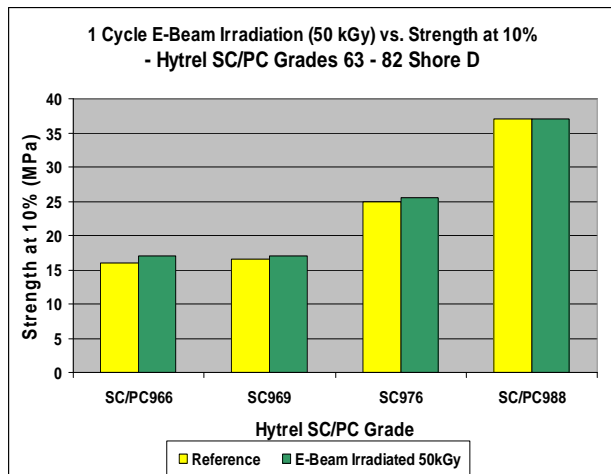
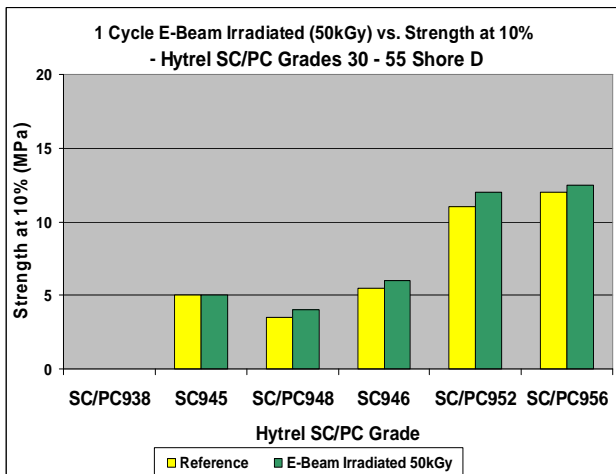
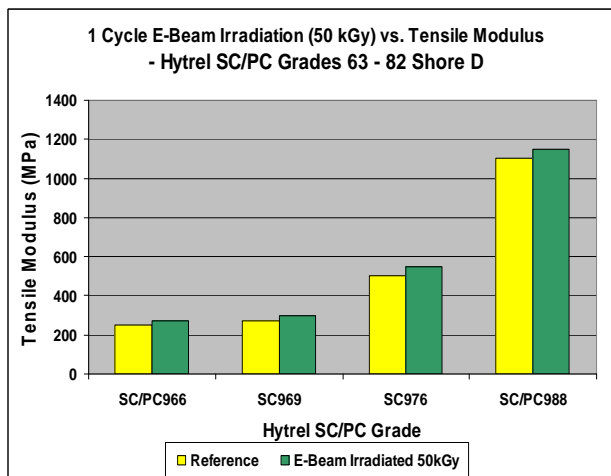
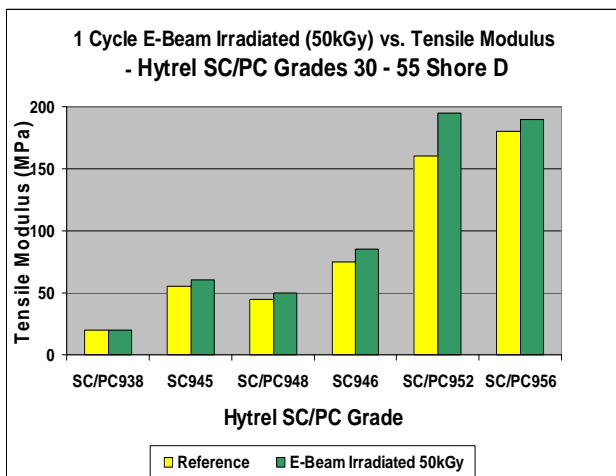


Zytel® HTN51G35HSL (PPA)

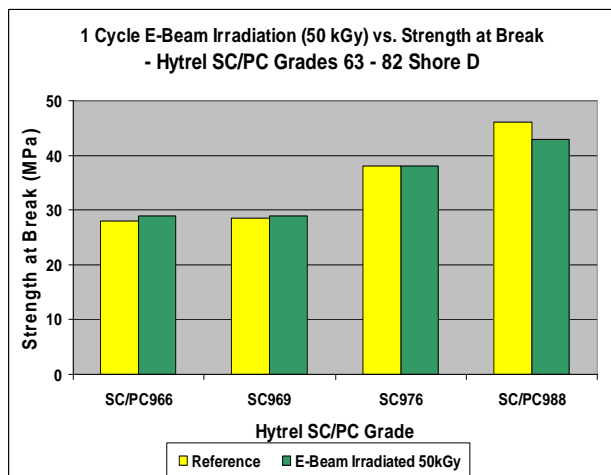
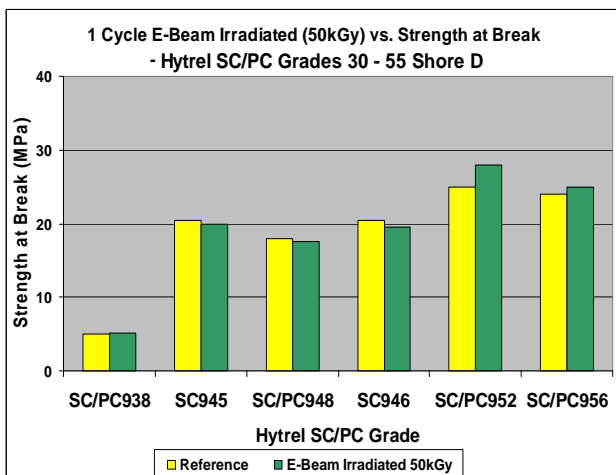


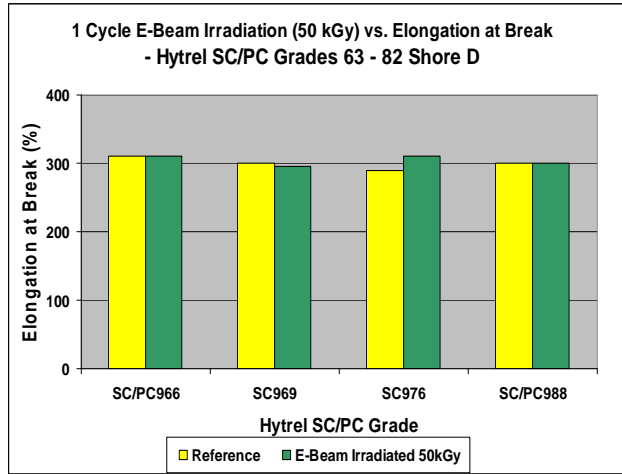
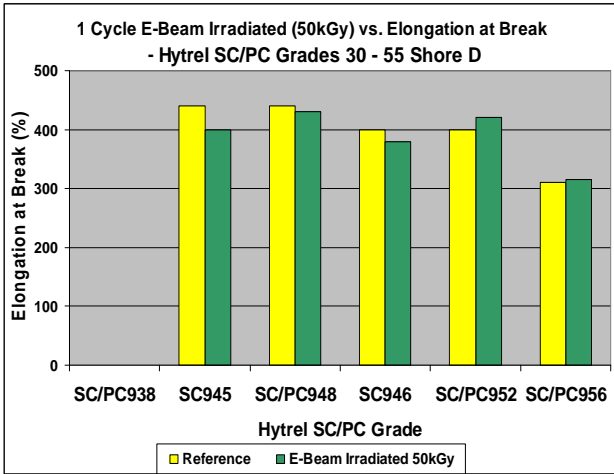
4.3. - Electron Beam (E-beam) Test Conditions: 50kGy radiation

Hytrell® SC/PC Grades (TPC-ET)



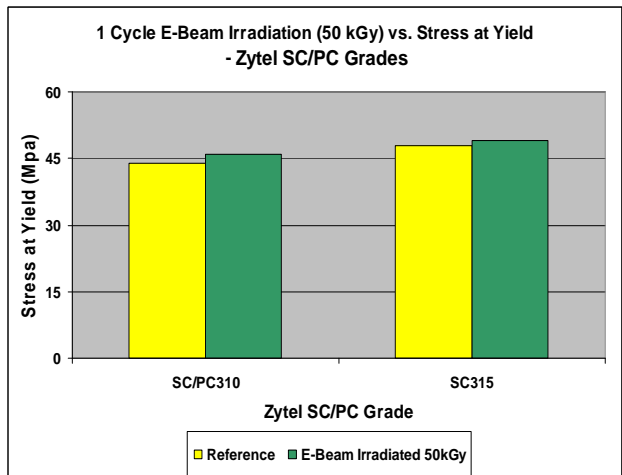
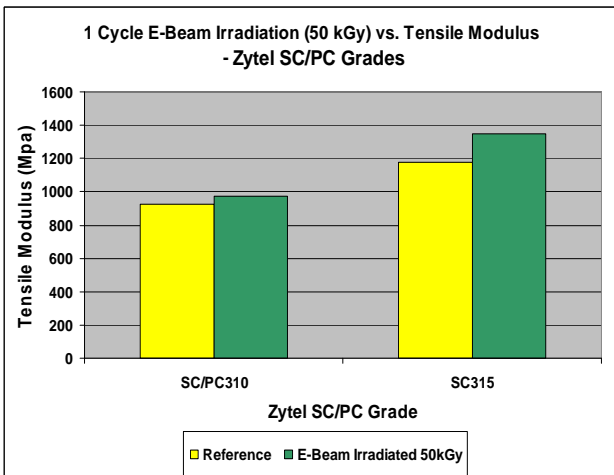
Note: no data for Hytrell® SC/PC938



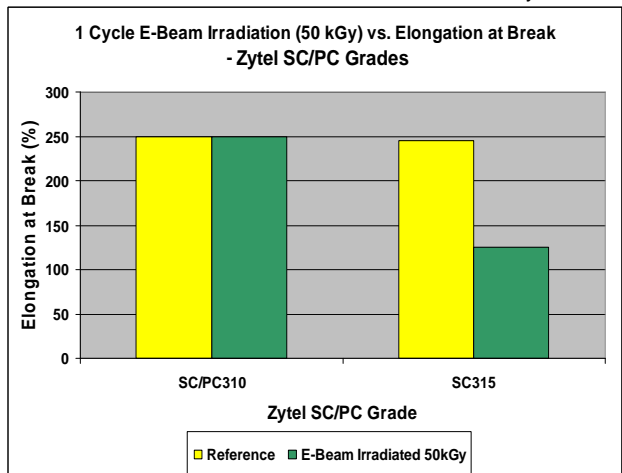
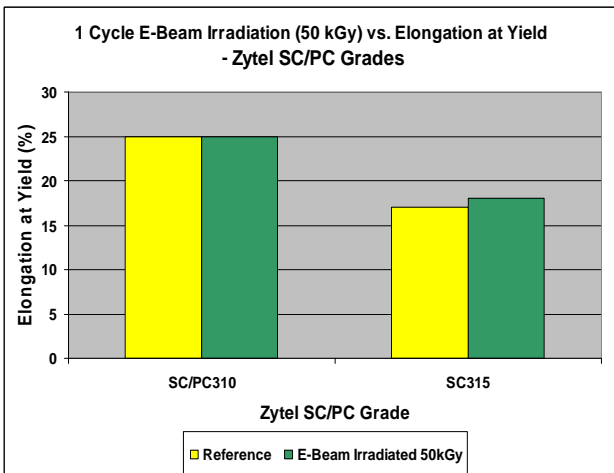


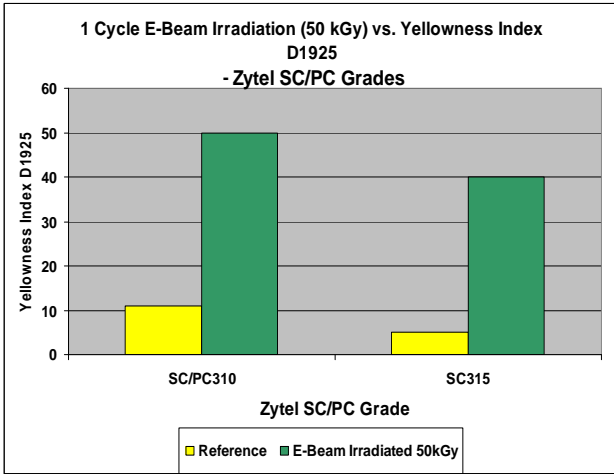
Note: no data for Hytrel® SC/PC938

Zytel® SC/PC Grades (PA) Testing on DAM Tensile bars

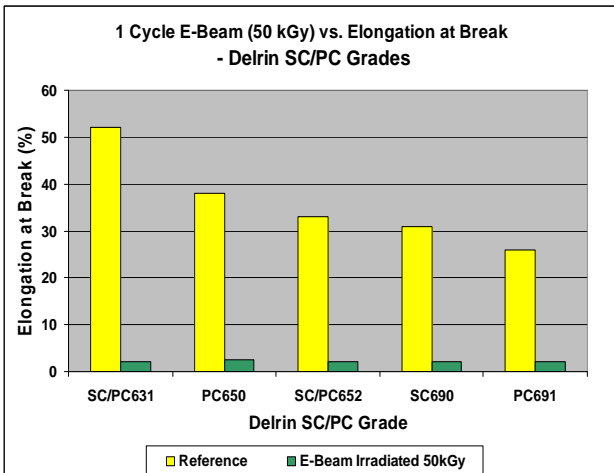
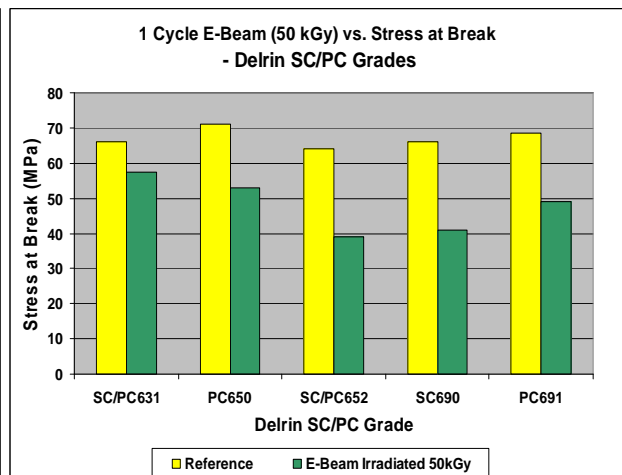
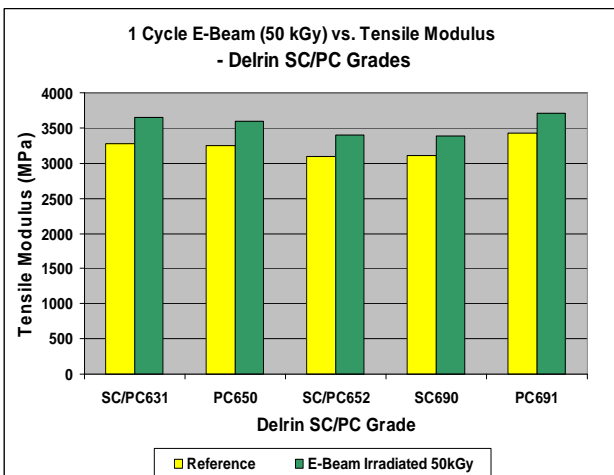


Note: the stress at break is similar to the stress at yield





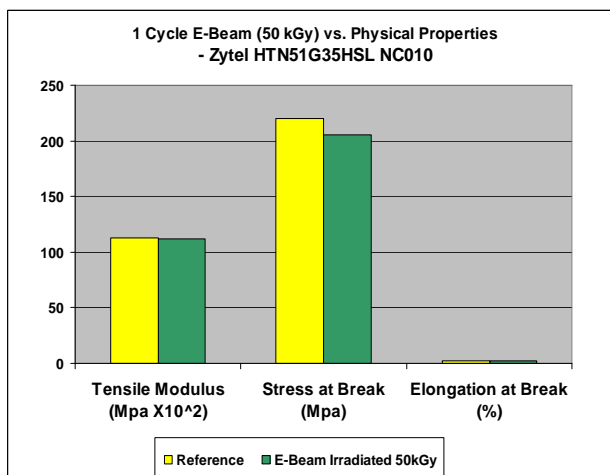
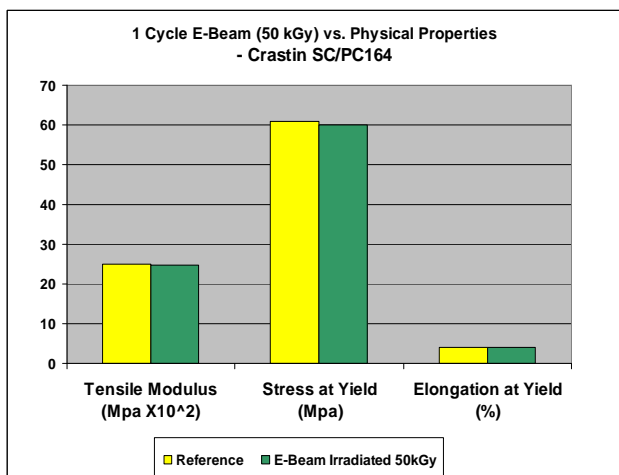
Delrin® SC/PC Grades (POM)



The use of polyacetals is to be avoided in components that are sterilized with electron beam radiation.

Crastin® SC/PC164 (PBT)

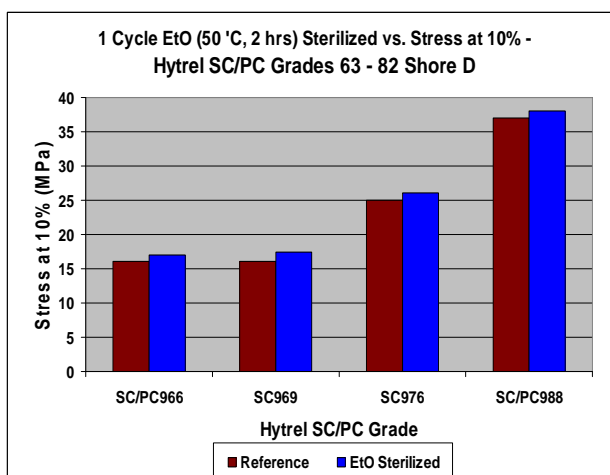
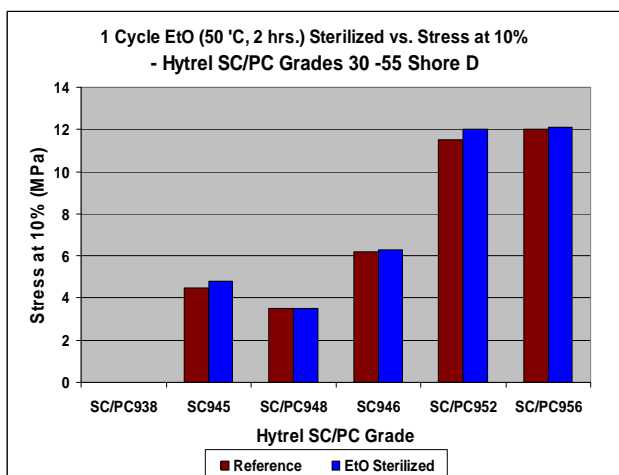
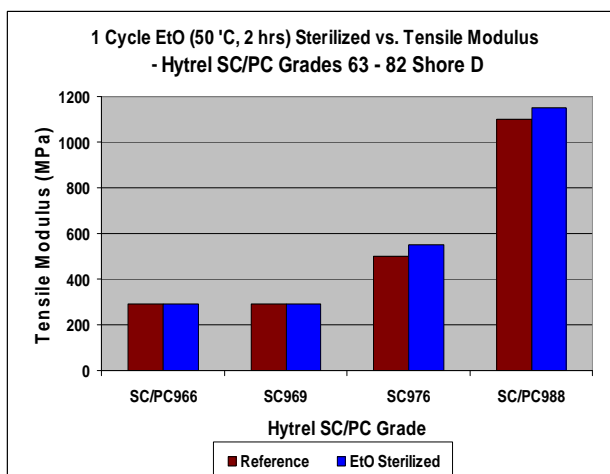
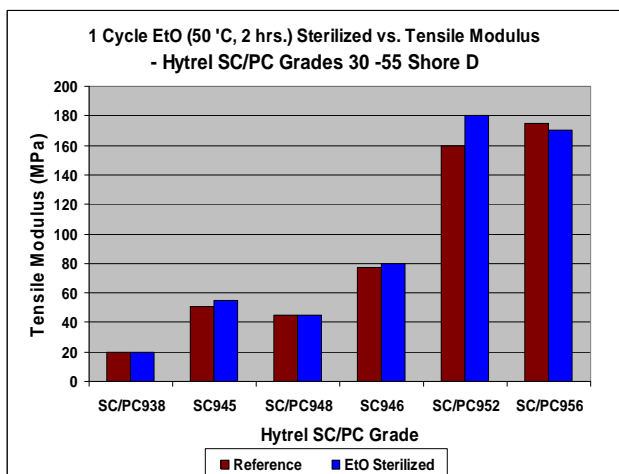
Zytel® HTN51G35HSL (PPA)



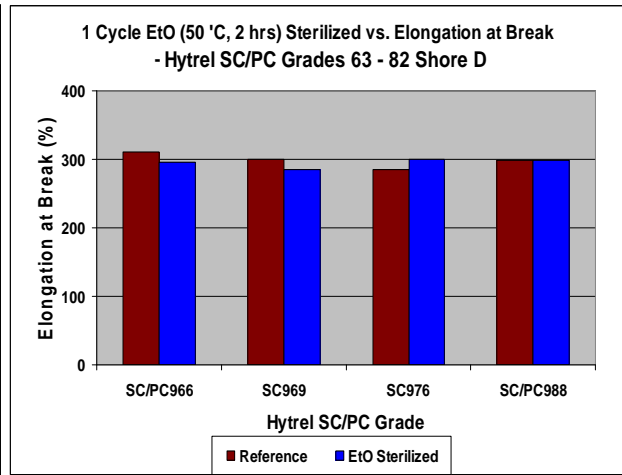
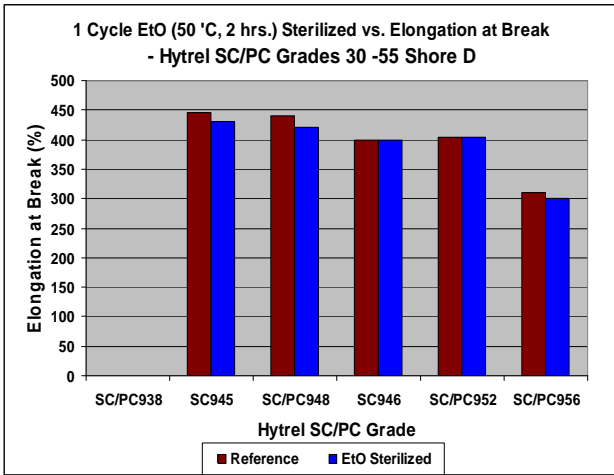
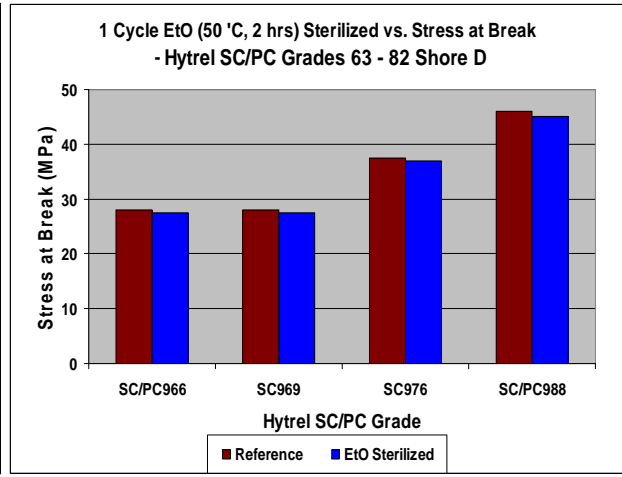
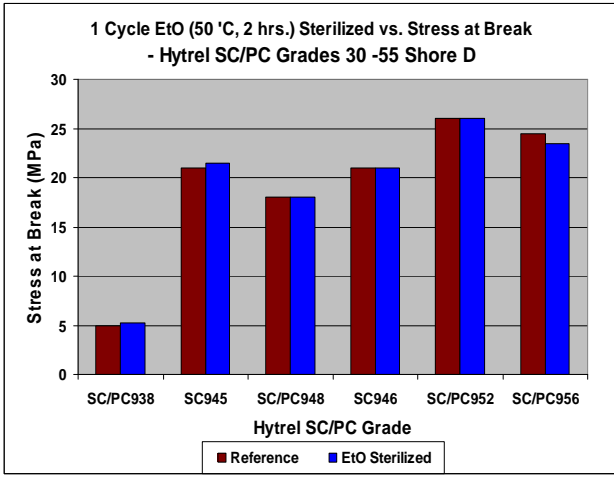
4.4. - EtO Sterilization

Test Conditions: at 50°C, shallow vacuum, 2 hours exposure

Hytrell® SC/PC Grades (TPC-ET)

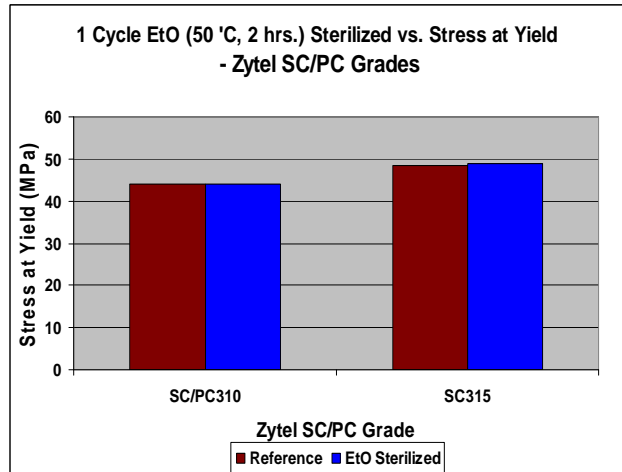
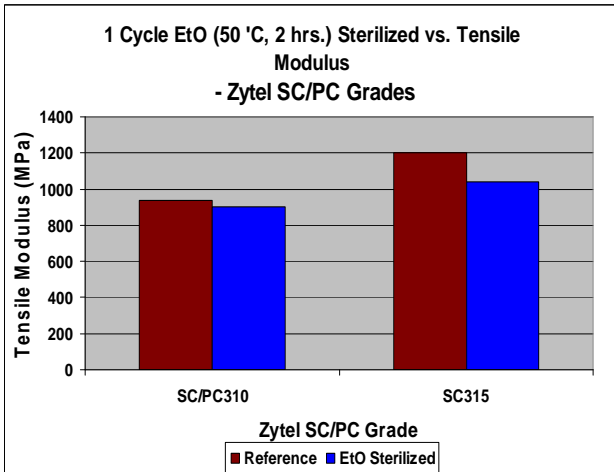


Note: no data for Hytrell® SC/PC938

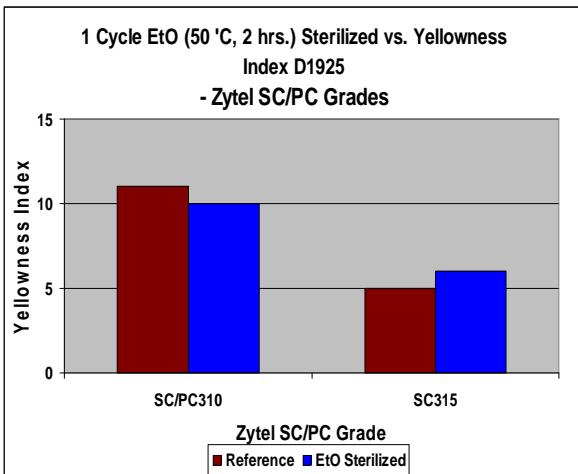
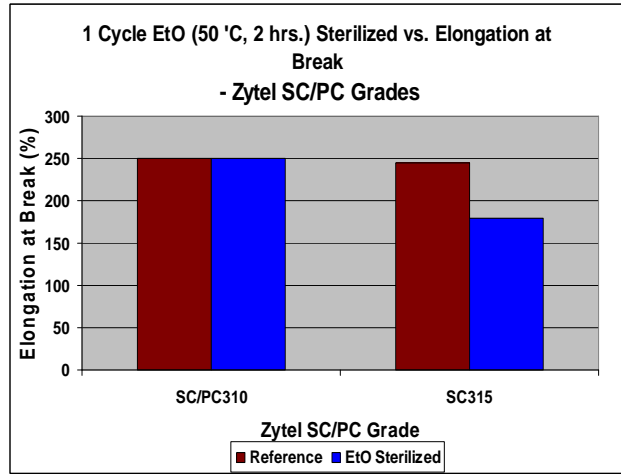
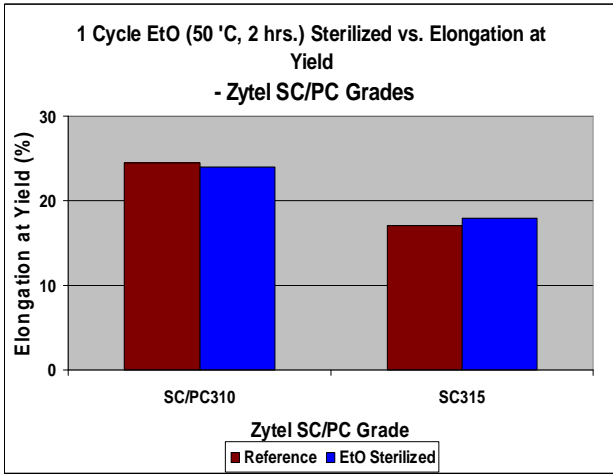


Note: no data for Hytrel® SC/PC938

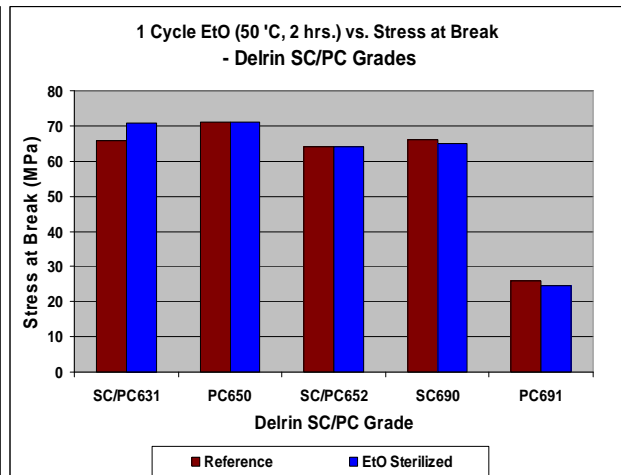
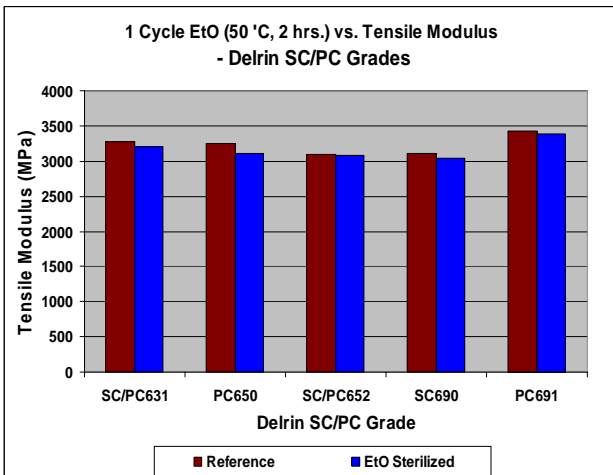
Zytel® SC/PC Grades (PA)

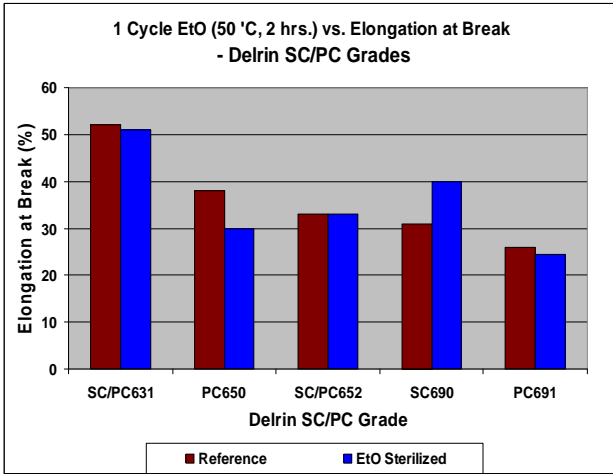


Note: the stress at break is similar to the stress at yield

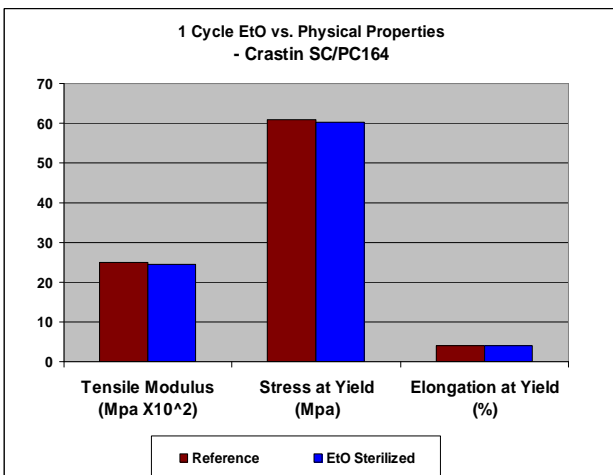


Delrin® SC/PC Grades (POM)

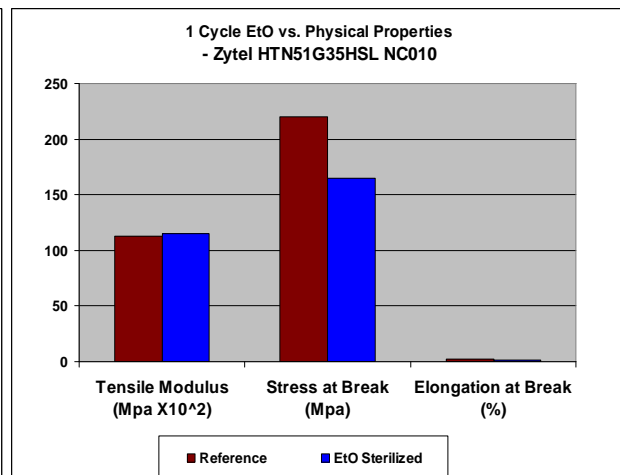




Crastin® SC/PC164 (PBT)



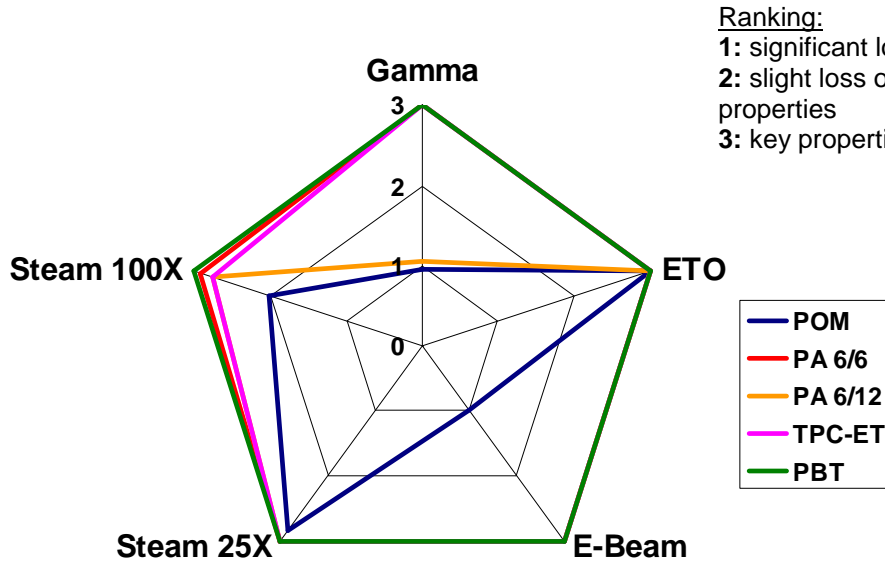
Zytel® HTN51G35HSL (PPA)



5. – Conclusions

The following conclusions can be drawn from this study:

- Zytel® PA is subject to yellowing in most sterilisation techniques, except EtO.
- Zytel® PA66 can be sterilized by any of the methods investigated.
- Zytel® PA612 should not be used in components that are Gamma radiated.
- Delrin® POM should not be used in components that are Gamma or E-Beam radiated.
- Delrin® POM shows good steam sterilisation behaviour up to 25 cycles
- Hytrel® can be sterilized by any of the methods investigated. Only soft grades need to be watched in terms of E-modulus with autoclaving.
- Crastin® can be sterilized by any of the methods investigated. High cycle (100+) autoclaving must be validated.
- Zytel® HTN can be sterilized by any of the methods investigated.



6. - Disclaimer

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