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The Influence of Different Sterilization Techniques on the Time-Dependent Behavior of Polyamides

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ABSTRACT

For this investigation conventional polyamide 6 *with monomodal molecular mass distribution*, *and the newly developed bimodal one were used. Conventional polyamide* 6 *was used as a reference material in order to emphasize prospects of using bimodal material for medical applications from the point of view of sterilization resistance and improved creep behavior. Time-dependent mechanical properties of testing samples were characterized by torsional creep measurements in non-sterilized state and after sterilization with three different techniques*: *with autoclave, ethylene oxide*, *and hydrogen peroxide plasma. Results show that the two materials exhibit pronounced difference in morphology and consequently*, *mechanical properties. Both of them were not significantly affected by any of used sterilization techniques. However, bimodal material*, *originally being noticeably more time-stable in comparison to monomodal one*, *retains these preferences also post sterilization.*

***Keywords*:** *Sterilization*, *Polyamide*, *Creep*, *Time Stability*

1. Introduction

Polymers are often the materials of choice for medical devices, medical packaging, and food packaging, replacing traditional materials such as stainless steel and glass [1]. Polymers are beside non-dental applications extensively used in dentistry as composite (resin-ceramic) restorative materials, implants, dental cements, and denture based teeth.

Theoretically, they can be modified for maximum biocompatibility and acceptable mechanical properties. Although all three groups of polymers (thermoplasts, thermosets, elastomers) are used for medical applications, the thermoplastics are most widely used [2].

They offer manufacturing cost savings, lighter weight, and performance characteristics that meet and exceed the demand in many highend applications. However, the process of sterilization can strongly affect the properties of the polymers [1,3].

Sterilization is the complete elimination of microbial viability, including the vegetative forms of bacteria and spores. Sterilization of surgical equipment, implants, linens, and attire is one aspect of a series of highly regimented steps constituting aseptic technique. The methods of sterilization can be divided into two general groups: physi cal and chemical. Although sterility can be achieved with certain chemicals, physical methods are generally more reliable. Heat, filtration, and radiation are the most commonly used physical methods of sterilizing medical and surgical materials. Chemical sterilization is usually accomplished with ethylene oxide or hydrogen peroxide, although formaldehyde and β-propiolactone are also used occasionally. The most commonly used techniques in veterinary medicine are steam, ethylene oxide, and hydrogen peroxide gas plasma sterilization [4].

Sterilization has increasingly been a topic of discussion when comes to the implantology. There are several issues to be considered when sterilization methods are being selected for implantable medical devices [5].

The number of agents capable of sterilizing product or material without adversely or deleteriously affecting product quality or material integrity is few. There is no singular sterilization method that is compatible with all healthcare products including drugs, polymers, devices, and materials, because of the severity of a process to meet the sterilization criteria and definition [6].

In our investigation we applied the three most commonly used sterilization techniques: autoclave, Ethylene Oxide (EtO), and H_2O_2 plasma. In continuation, the brief overviews of the three sterilization methods effects on polymers' properties are presented.

Steam sterilization by autoclaving has traditionally been the most widely used method for medical instruments [7]. The steam method is convenient, fast, and widely available. It is inexpensive and can quickly sterilize porous materials and accessible surfaces and spaces [8]. However, this method has some disadvantages. It is well known that heat and steam can drastically alter the mechanical and chemical properties of many synthetic biomaterials. The main disadvantage of steam sterilization is the hydrophilicity of some polymers, which renders the implant mechanically weaker [9]. Lastly, the steam itself may carry contaminants to implant surfaces and directly lead to a lesser degree of *in vivo* biocompatibility [5].

Ethylene oxide-EtO (CH_2-O-CH_2) and gamma sterilization are the most common sterilization methods for thermoplastics used in the disposable medical device industry [10]. The gas vapor sterilant most commonly used is ethylene oxide; it is capable of killing very efficiently all the species and forms of micro-organisms in a short time, but in pure form is extremely toxic, irritating, water and common organic solvents soluble, and explosive. EtO is bactericidal, virucidal, and sporicidal. Its germicidal activity results from its action on the proteins, DNA and RNA.

The flammability hazard of EtO has been reduced by mixing it with an inert gas, usually Freon chlorofluorocarbon, and after year 1995, an alternate gas, hydrochlorofluorocarbon is being used as a carrier for EtO sterilization [10]. A non-flammable preparation is also obtained when EtO is mixed with carbon dioxide in a ratio 1:9.

Marois *et al*. reported on investigation of sterilization effect on poly beta-hydroxy octanoate (PHO). The physical and structural properties of PHO were shown to be well preserved following EtO (ethylene oxide) sterilization, whereas gamma radiation caused random chain scission and physical cross-linking, a frequent phenomenon observed with organic polymers [11].

Lucas *et al*. reports that EtO residues in medical devices and polymers depend on the type and size of the material. Some materials retain little EtO residues, such as polyurethane PU 80A and hollow catheters, whether others retain much larger amounts, such as polyurethane PU 75D and nylon 66. Presented work illustrates that EtO levels and effects are highly dependent on the type of material used. Residual EtO, the amount of EtO that is bioavailable, and the effect of EtO *in vitro* must be considered for each type of material or device [12].

Buben *et al*. report on rough generalizing conclusions: acrylate polymers and copolymers frequently used as hard components of medical devices release absorbed EtO very slowly. This applies to the following materials: ABS, MBS, MMABS, SAN/ABS. In addition to acrylate polymers EtO is released also by other hard polymers e.g. parts of polycarbonate medical devices, hardened PVC or cross-linked polypropylene [13].

The study of Brown *et al*. investigated the effects of a range of methods on the tensile strength of latex rubber, silicone elastomer, 2 different formulations of polyurethane, nylon, and high-density polyethylene (HDPE) specimens. The methods of disinfection and sterilization used were hypochlorite bleach, peracetic acid + hydrogen peroxide, formaldehyde gas, low-temperature peracetic acid and gas plasma, and low-temperature hydrogen peroxide gas plasma. The results showed that silicone elastomer was minimally affected, whereas the strengths of nylon, polyethylene, and latex were reduced by some of the methods [14].

Plasma-based methods *a priori* offer the required efficacy near ambient temperature to sterilize polymeric devices, but they inevitably also modify the exposed polymer surfaces. The hydrogen peroxide plasma sterilization causes surface oxidation of many types of polymers [15]. The study has shown that two commercial plasma-based sterilizers, Sterrad® and Plazlyte™, can substantially alter the surface characteristics of all the polymers investigated in this paper, namely their surface composition and morphology, and their wettability, even after a single sterilization cycle [15].

Regarding sterilization with EtO, they have generally found a lesser extent of surface modification than following plasma-based techniques, but this advantage must be weighted against the possible hazards of retained EtO or its toxic by-products in treated polymers [15].

It has already been noted that nominally identical polymer materials, for example the PVC film and tubing, or the two polyurethane catheter materials, could reveal quite different surface compositions, oxidation behaviours, wettabilities, and surface topographies. This underlines the important fact that the generic composition of a polymer is insufficient for judging whether a particular device can be safely resterilized; clearly, the nature and concentration of additives in the polymer formulation, the manufacturing process, and numerous other variables must also be taken into account [15].

Polymer degradation caused by sterilization is more often associated with oxidative processes rather than with hydrolysis. As known, there are some sterilization technologies, such hydrogen peroxide plasma sterilization systems, which use hydrogen peroxide (H_2O_2)-pla-

sma and peracetic acid, respectively, as an oxidative sterilizing agent [16].

In our study we compared the effects of steam under pressure as physical sterilant and of ethylene oxide and plasma gas as gas vapour method of sterilization on the time-dependent mechanical properties of two types of polyamide PA6 (Nylon).

Nylon is biostable polymer [10]. Polyamide and copolymers utilized for healthcare products such as catheters used in cardiovascular procedures, sutures, epidural catheters, laparoscopy devices, blood sets, joints, kidney dialysis, composite materials and films, and special packages might be submitted to the following sterilisation processes: steam, limited dry heat depending on sterilization temperature up to 130˚C [6], EtO, limited radiation, limited H_2O_2. Polyamides are sensitive to crosslinking from radiation, but are suitable for a single dose of radiation. PA6 may be at least radiation resistant [6].

The sterilization stability of nylon and filled nylon with EtO is very good but there exist some susceptibility of material to oxidizing agents. The stability of nylon to autoclave sterilization is very good but components may swell slightly due to water absorption [17].

Sicard *et al*. have shown that sterilization by steam or EtO had no significant effect on the strength of the nylon fishing material. Ethylene oxide was the preferred method of sterilization to preserve strength and minimize elongation of the fishing material [18].

Kirby *et al*. reported that there was no difference between untreated and EtO sterilized bands with respect to testing to failure using a splint circular jaw mounted on a tensile testing machine, whereas bands subjected to autoclaving failed at less force [19].

Bochkova *et al*. investigated the uniaxial stretching of microfiltration membranes made of polyamides. Changes were found in the mechanical properties of the membranes after autoclaving, which had been induced by spon-taneous polymer arrangement on heating; the arrangement was expressed as either a great self-elongation of the membrane or its shrinkage [20].

As analyzed by Navarrete & Hermanson (1998), after exposure to HCFC 124, HCFC 124/22 and pure EtO, the tensile and Izod properties of Nylon appear relatively unaffected. The physical properties of Nylon, and Acrylic were not significantly affected by any of the three sterilant gases [10].

Gatineau *et al*. compared the effects of hydrogen peroxide gas plasma (HPGP) and ethylene oxide (EtO) sterilizations on the mechanical properties of nylon lines used for stabilization of the canine stifle. Sterilization with HPGP seems a good alternative to EtO for nylon lines [21].

For the purpose of our investigation two different types of polyamide material PA6 were used, conventional one with monomodal molecular distribution, and novel material with bimodal one. The objective of this paper was to analyze how three of the commonly used sterilization methods will affect novel bimodal material in comparison to monomodal one with respect to their time-dependent (long-term) mechanical properties. Characterization of the investigated materials was performed by means of torsional creep tests.

2. Experimental Part

2.1. Materials

We have tested the effect of sterilization on the newly developed I-PA6 (intelligent polyamide) described by Emri *et al.* [22], which was compared to commercially available PA6 material. Conventional PA6 has monomodal molecular mass distribution, whereas the new I-PA6 has bimodal one. Multimodality of the material was achieved by proper modification of its molecular mass distribution to put it more precisely, by varying the average chain length of the PA6 polymer chains during polymerization process starting from the same PA6 monomer units. The average molecular weight of both materials is roughly the same.

Structure of both materials, observed by means of optical microscopy, is shown in the **Figure 1**. By comparison one may infer significant difference in morphology of non-sterilized standard material and modified one, prepared by the same technology. In the case of monomodal PA6 obtained image indicates formation of coarse spherulites that can be observed as Maltese cross patterns (**Figure 1(a)**), while bimodal I-PA6 forms homogeneous fine grain structure when exposed to the same processing conditions (**Figure 1(b)**).

From both types of polyamide materials samples were prepared to test their time-dependent mechanical properties after exposure to three different sterilization techniques: autoclave sterilization, EtO sterilization, and H_2O_2 plasma sterilization. Standard monomodal PA6 was used as a control material in this study.

2.2. Sample Preparation

In order to perform creep measurements PA cylindrical

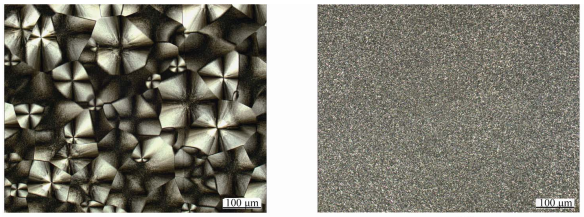

Figure 1. (a) Morphology of non-sterilized monomodal PA6, and (b) bimodal I-PA6; Axioskop 2 MAT (Carl Zeiss), polarized transmitted light, 200×.

specimens with diameter D = 3.0 mm and length L = 60.0 mm were made from both materials by gravimetric casting procedure, which is briefly described below. This method was developed to avoid orientation of molecules caused by melt flow when using injection molding or extrusion in sample preparation. After casting all samples are annealed to minimize the effect of physical ageing to the level that is negligible. The annealing procedure was thoroughly studied in our laboratory in the past. Based on these studies we determined the temperature profile which brings sample sufficiently close to thermodynamic equilibrium.

The specimen preparation equipment is illustrated in **Figures 2(a)** and **2(b)**. The casting procedure starts with filling up a glass tube with an inner diameter of 3 mm with PA pellets (**Figure 2(a)**). Following this, the heater is placed on the bottom of the tube to start the melting process, and a pressure of about 1MPa is applied from above to overcome friction forces between the material and the tube inner surface. The heater temperature is maintained at 270˚C and it is moved upwards the glass tube at slow rate (2.25 mm/min), giving the pellets enough time to melt (**Figure 2(b)**). The applied pressure pushes upper non-molten pellets into the melt, thus removing any possible trapped air. This procedure is followed until the spiral heater slides over the whole surface of the tube. Then the heater is removed from the glass tube and the specimen is left to cool down slowly to the room temperature. Finally, received cylindrical rod is extracted from the glass tube, cut down to the length of 60mm, and then polished and glued to the special grips as shown in **Figure 3**.

2.3. Methods of Sterilization

In this investigation we have applied three commonly

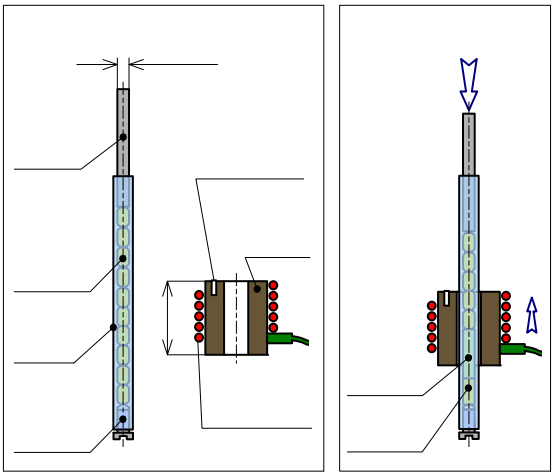

Figure 2. Schematic representation of cylindrical rods preparation for creep measurements.

Figure 3. Cylindrical rod sample glued to the special grips.

used sterilization techniques: a) autoclave sterilization, b) EtO sterilization, and c) H_2O_2 plasma sterilization. Conditions of each method are briefly explained below:

2.3.1. Autoclave or Steam Sterilization

Investigated samples were sterilized by the autoclave type Euroklav 23 V-S, manufactured by Melag, Germany. Before sterilization was applied, thin slices were placed inside the sterilization bags and sealed. The cylindrical rod specimens were put and sealed directly into sterilization bags. Steam sterilization was applied for 75 min at 121˚C and 0.2 MPa. After the procedure the specimens were allowed to dry for 2 hours.

2.3.2. Ethylene Oxide

In our study sterilizer De Lama S. Martino Sicc. (Pavia It.) of Blood Transfusion Centre of Slovenia has been utilized. The characteristics of the gas sterilizer are: EtO pressure 0.2 MPa, EtO/CO_2 mixing ratio of 10%/90%, sterilization temperature 50˚C, relative humidity 60%, exposure time 8 hours. After the sterilization cycle 10 repeated air flushing cycles per hour are applied to remove the EtO retained gas. The aeration procedure is validated with regard to sterilization cycle and nature of the material designed to be fumigated. For sterilization of our polyamide samples the chamber DLOG, manufactured by De-Lama was used. The samples were sterilized for 1 hour, and then they were aerated for 2 hours inside the chamber. Then, the sterilized samples in the sealed bags were taken out of the chamber and allowed to aerate for 10 days before tests were performed.

2.3.3. Hydrogen Peroxide Plasma

Sterilization of our samples was done by using the Sterrad® 100S system manufactured by Johnson & Johnson, USA. Both materials were sterilized at 50˚C for 1 hour.

2.4. Methods of Characterization

Since properties of polymers may considerably change with time, which means that functionality and stability of polymeric products may be affected over time of their exploitation [23,24], we investigated how the sterilization affects mono- and bi-modal polyamide time-dependent (long-term) mechanical properties. In order to characterize the effect of different sterilization techniques on materials' long-term behavior, shear creep compliance measurements were performed according to the procedure described below.

Shear creep measurements of investigated PA materials were performed with the Apparatus for Torsional Creep Measurements that has been designed and manufactured at the Centre for Experimental Mechanics at the University of Ljubljana, Slovenia [25,26].

Initial part of the creep measuring procedure started with the annealing phase at higher temperature (110˚C) that should erase mechanical stress-strain history of the material. The thermal history to which specimens were exposed during the creep experiment is schematically shown in **Figure 4**.

After the annealing phase the torsional creep measurements were performed in segmental form at 8 different elevated temperatures, nominally at 30˚C, 40˚C, 50˚C, 60˚C, 70˚C, 80˚C, 90˚C, and 100˚C in the time interval of 3 hours, under loading in shear by torque, M_t, of the constant magnitude ranging from 0.007 - 0.07 MPa, depending on the temperature at which the measurements were performed. In all cases the applied torque resulted in shear strain, not exceeding 0.05%. The response of the material was measured in terms of rotational angle of the specimen, $\varphi(t)$ as a function of time and then recalculated to the material creep compliance:

$$J(t) = \varphi(t) r / l \tau_0 \quad (1)$$

where r denotes radius of the circular cross section of the sample and l -length of the sample. τ_0 is the magnitude of constant shear stress loading, calculated as:

$$\tau_0 = M_t r / I_p \quad (2)$$

with polar momentum I_p for circular cross section geometry of cylindrical samples. The magnitudes of applied shear stress loading were sufficiently low to ensure that the entire measurement procedure remained within the scope of the theory of linear viscoelasticity.

Following the time-temperature superposition principle, measured segments were shifted along the time-scale in relation to the segment, measured at the nominal reference temperature, T_{ref} = 50˚C. Shifting was executed by using the recently developed closed-form shifting (CFS) procedure [27]. CFS shifting methodology brings in error that is more than 10-times smaller as the underlying experimental error of data being shifted.

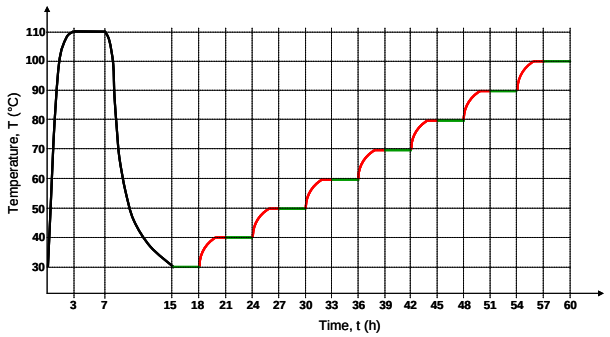

Figure 4. Schematic representation of the temperature-loading profile of the shear creep measurements on PA samples.

Obtained shift factors were then modeled by the WLF equation in order to obtain material constants, C_1 and C_2, which are presented in **Table 1**. By knowing these constants we calculated shift factors that corresponded to the shifting of master curves in order to represent the creep behavior at the reference temperature of 37˚C, which is a relevant temperature for medical applications.

3. Results and Discussion

3.1. Non-Sterilized Monomodal and Bimodal Materials Comparison

Performing creep tests according to the procedure described above we firstly investigated the difference in time-dependent mechanical behavior of non-sterilized monomodal and bimodal PA6. In the concerned case it is appropriate to present the long-term creep behavior at the reference temperature close to the temperature of a human body with respect to the proposed conditions of use. **Figure 5** shows comparison of time-dependent creep compliances for both non-sterilized PA6 materials for the reference temperature 37˚C.

Comparison of creep compliances may be interpreted in terms of long-time stability for the products made of such materials. In the diagram it is clearly seen that creep compliance of both materials increase with time, but, nevertheless, creep compliance of bimodal material is lower than such of monomodal along the complete examined time scale. From the point of view of desired life-span of dental implants, which is more than 20 years [28], it seems to be reasonable to analyze mechanical properties and their change during this period of time. In our research the time period of 30 years was considered. In 30 years $\approx 10^9$ s, it can be observed that creep compliance of bimodal material is approximately 25% lower

Table 1. Constants C_1 and C_2, calculated from WLF modeling of shift factors for non-sterilized and sterilized mono- and bimodal PA6.

Type of material	Type of sterilization	C_1 (/)	C_2 (˚C)
Monomodal PA6	Non-sterilized	17.88	69.25
	Ethylene Oxide (EtO)	10.41	31.40
	Steam (autoclave)	13.84	58.92
	H_2O_2 plasma	10.96	36.52
Bimodal PA6	Non-sterilized	17.50	81.72
	Ethylene Oxide (EtO)	7.86	26.48
	Steam (autoclave)	13.95	63.97
	H_2O_2 plasma	17.98	84.44

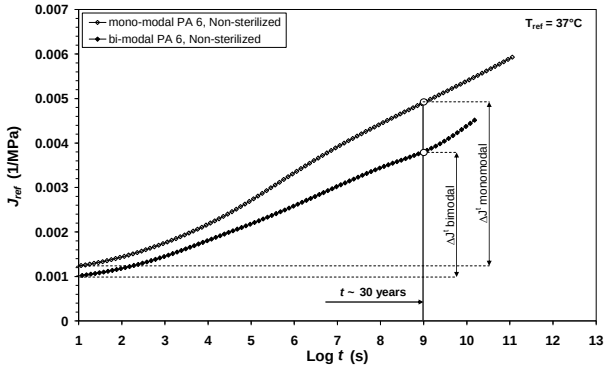

Figure 5. Comparison of creep compliances of non-sterilized monomodal PA6 and bimodal PA6 at reference temperature T_{ref} = 37˚C.

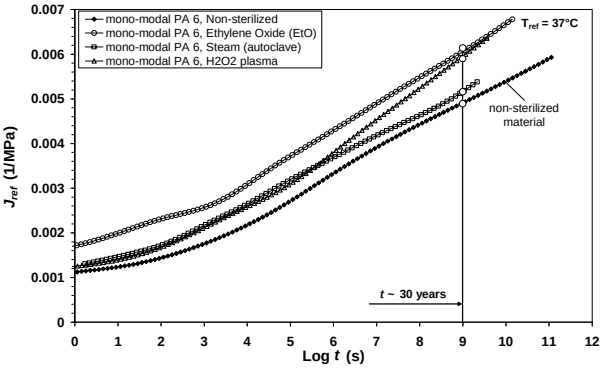

Figure 6. Creep behavior of sterilized and non-sterilized monomodal PA6 at T_{ref} = 37˚C.

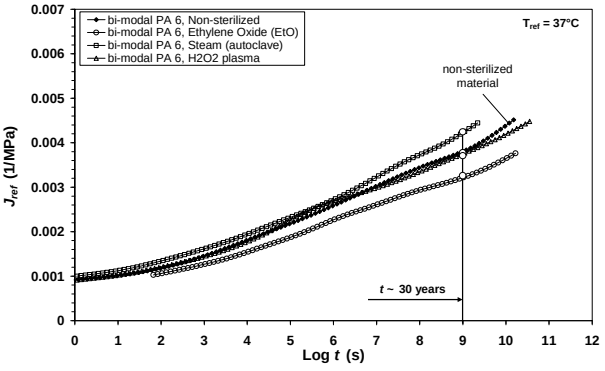

Figure 7. Creep behavior of sterilized and non-sterilized bimodal PA6 at T_{ref} = 37˚C.

relative to the creep compliance of monomodal PA6 (**Figure 5**) which indicates better creep resistance (long-term stability) properties of bimodal PA6. As it was observed from the optical microscopy pictures above (**Figure 1**), bimodal PA6 has finer structure in comparison to monomodal PA6, which can consequently lead to better creep resistance properties of bimodal material. It is evident that both materials become less stiff with time, but for monomodal material this process is much faster than that of bimodal one.

The absolute change in creep compliance, $\Delta J\left(t_{ref}, T_{ref}\right)$, which represents the magnitude of total deformation when the implant is exposed to constant load over certain period of time, for both materials may be estimated from the same diagram as well. For the monomodal material this change is bigger than for the bimodal one. Thus, one may summarize that bimodal PA6 creeps much less in the same time period in comparison with monomodal PA6 both in absolute and relative numbers.

3.2. Sterilization Techniques Influence on Materials Long-Term Mechanical Properties

After exposure of both materials to three different sterilization techniques it was investigated how much the process of sterilization affected their mechanical properties. **Figure 6** presents the comparison of creep compliances of non-sterilized and sterilized monomodal PA6 materials at reference temperature 37˚C, whereas **Figure 7** shows the same comparison for bimodal PA6.

From **Figure 6** one may observe all sterilization techniques have noticeable effect on long-term stability of monomodal material and all exhibit a tendency to deteriorate it at that. From the diagram it is clearly seen that EtO has the most severe effect on monomodal material time stability within whole time scale.

The diagram in **Figure 7** shows that in case of bimodal PA6 sterilization effect is not as significant: the creep compliance curves of sterilized material stand much less apart from the one of non-sterilized than in case of monomodal material. At the same time it is also observed that EtO has the strongest effect on both materials.

In **Table 2** the magnitudes of creep compliance, $J\left(t_{ref}, T_{ref}\right)$, are presented at the reference time $t_{ref} = 10^9 s \approx 30 years$, and reference temperature, T_{ref} = 37˚C. Besides this, the information in the columns named $\delta J_{rel}^{non-ster}\left(t_{ref}, T_{ref}\right)$ in **Table 2** shows the relative difference in the magnitude of creep compliance at the reference time, $t_{ref} = 10^9 s \approx 30 years$, and reference temperature, T_{ref} = 37˚C for sterilized samples in relation to the creep compliance magnitude of non-sterilized sample.

Taking into account spread of experimental data, we may say that sterilization affects both materials. It should be taken into account that due to the accuracy of the measuring technique (which is within 10%) the calculated relative difference, $\delta J_{rel}^{non-ster}\left(t_{ref}, T_{ref}\right)$, below 10% could not be recognized as the difference.

There were found rather discrepant data on polyamide sterilization resistance in the literature. Most likely it can be explained with variety of properties that are taken into

Table 2. Creep compliance, $J(t_{ref}, T_{ref})$, and relative difference in creep compliance, $\delta J_{rel}^{non-ster}(t_{ref}, T_{ref})$, at the reference time $t_{ref} = 10^9\ s \approx 30\ years$, and reference temperature $T_{ref} = 37$°C for monomodal and bimodal PA6.

	Monomodal PA6		Bimodal PA6	
Type of sterilization	$J(t_{ref}, T_{ref})$, (1/MPa)	$\delta J_{rel}^{non-ster}(t_{ref}, T_{ref})$, (%)	$J(t_{ref}, T_{ref})$, (1/MPa)	$\delta J_{rel}^{non-ster}(t_{ref}, T_{ref})$, (%)
Non-sterilized	0.0049	/	0.0038	/
Ethylene Oxide (EtO)	0.0061	23.4	0.0032	15.5
Steam (autoclave)	0.0052	5.2	0.0042	10.8
H_2O_2 plasma	0.0060	21.4	0.0038	1.6

account when sterilization effect is analyzed as how different sterilization techniques affect different properties. Generally, it is stated that PA materials are affected by high humidity, temperature and oxidants. This makes sense, since polyamides are very sensitive on moisture, which has analogous effect as increase of temperature [29], and susceptible oxidative and thermal degradation.

Regarding steam sterilization, in a number of sources it is recommended not to sterilize polyamides in autoclave since they are susceptible to water vapor and heat sensitive [8]. From another hand, some publications [1,6, 18] claim that nylon exhibits very good resistance to steam sterilization. According to the experimental results we observed, time stability of both mono- and bi-modal materials sterilized with autoclave was not significantly affected, which is in agreement with the second statement.

As reported by Sicard *et al*. [18] sterilization stability of nylon and filled nylon with EtO is very good but there exist some susceptibility of material to oxidizing agents. Generally in literature it is stated that PA appear relatively unaffected after exposure to EtO [1,19]. In practice, PA sutures are mostly EtO sterilized. But, regarding observations in our study, results of performed experiments go in contradiction with information that PA exhibits very good resistance to EtO, since it was observed that sterilization with ethylene oxide had the most significant effect on time-dependent mechanical properties of both investigated materials. Deteriorated time stability of monomodal PA6, but improved both characteristics of bimodal PA6. This observation merits further attention.

As to H_2O_2 plasma sterilization it is mentioned in literature that it causes oxidation in several types of polymers [15,16]. Thus, the use of this technique is limited. In the performed measurements there was observed no significant effect on monomodal PA and modified I-PA time-dependent behavior after H_2O_2 plasma sterilization.

4. Conclusions

From the performed analysis of mechanical properties for both, monomodal and bimodal PA6 materials in non-sterilized state and after exposure to three different sterilization techniques, the following observations may be summarized:

1) Non-sterilized bimodal material yields more complex structure (finer and more homogeneous) than non-sterilized standard PA6 material, when exposed to the same processing conditions during solidification (**Figure 1**).

2) Characterization of time-dependent behavior in terms of the creep compliance has shown that in non-sterilized state bimodal PA6 has better time stability than monomodal, since it creeps less (**Figure 5**).

3) Applied sterilization techniques had more significant influence on the monomodal PA6 than on bimodal one (**Figures 6** and **7**). Time stability of monomodal material was deteriorated with all used sterilization techniques, while in the case of bimodal material time-dependent mechanical properties remain nearly the same before and after sterilization. Thus, bimodal material, originally being noticeably more time stable, retains these preferences post sterilization.

From the stand point of view of the time stability at 37˚C within the whole investigated time scale the most significant effect on creep behavior of monomodal PA6 as well as bimodal PA6 was observed after EtO sterilization.

5. Acknowledgements

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