RADIOLUCENT COMPOSITES PROVIDING HIGH RESISTANCE AGAINST STERILIZATION DECOMPOSITION

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We present a study of radiolucent composite materials for use in medicine, providing suitable mechanical properties and high resistance against sterilization decomposition. The composites are composed of carbon (C), aramid or glass (R-glass) fabrics embedded in polydimethylsiloxane (PDMS), polyetheretherketone (PEEK) or polyphenylene sulfide (PPS) matrix. The effect of multiple steam sterilization processes on degrading the mechanical properties, structural integrity and hydrolytic decomposition of the composites was verified. The radiolucency of the composites was also investigated. The mechanical performance of ARAMID/PDMS composite is strongly influenced by the sterilization technique that is applied. The mechanical behavior of R-glass/PDMS composite during steam sterilization is negatively influenced by its porosity. The relatively high porosity of C/PDMS composite may lead to lower ultimate bending strength values, but in general its mechanical behavior is influenced only at a low rate by steam sterilization. On the basis of our analyses, we can state that both C/PEEK and C/PPS composites are good candidates for application as radiolucent materials providing resistance against sterilization decomposition.

INTRODUCTION

Metallic materials such as stainless steel and titanium alloys have traditionally been used in the construction of medical devices. They exhibit suitable physical and chemical properties and are compatible with widely-used sterilization techniques. However, they are also, in general, radiopaque. For this reason, they provide poor radiographic quality of the inspection space due to imaging artifacts and scatter when using conventional imaging techniques such as X-ray, X-ray computed tomography (CT) and magnetic resonance imaging (MRI). Metals such as iron are also magnetic, which distorts the images obtained by MRI. For the surgeon and for other clinical personnel, difficulties in obtaining good images of implants within or after surgical placement may be as significant as the long-term problems of e.g. implant wear and bone resorption [1]. Accurate intra-operative imaging is vital in surgery in order to achieve precise reduction of fractures, precise placement of implants or screws and correct positioning of osteotomies [2, 3]. It has been suggested that the most common cause of revisions to total knee arthroplasty is error in surgical techniques [4], as small changes in component positioning can lead to significant changes in post-operative performance [5]. Several works on designing improved techniques have pointed out that there is a need to manufacture sections of the devices from radiolucent and mechanically stable materials, in order to specify the targeting process and to reduce radiation time [6-8].

The insufficient radiolucency of metal alloys can be resolved by the application of non-metallic materials. In general, plastics are inherently radiolucent, but their mechanical properties are generally inferior to those of metals. Unreinforced thermoplastics or thermosets generally have lower rigidity than metals, which can lead to poor results when using certain medical devices [1]. Composite materials can be turned toward radiolucent structural materials and materials providing mechanical

performance and mechanical properties competitive with the properties of some metals. From this point of view, high modulus carbon fabric reinforcements seem to be a good candidate for the construction of medical devices. Similarly, aramide, high molecular weight polyethylene (UHMWPE) and several kinds of glass fabrics can provide sufficient mechanical support [1]. They possess good stiffness, high strength, creep rupture resistance and sufficient fatigue properties.

Another important property of medical devices is their mechanical, shape and chemical stability after repeated sterilization without any sign of degradation. The specific application of sterilization methods depends mainly on the equipment and on the facilities of a hospital, taking into account different degrees of desired protection at varying costs. Ethylene oxide, steam, hydrogen peroxide plasma, and vapor-phase hydrogen peroxide sterilization processes are mostly in use for lower-level hospital disinfection processes [1, 9]. The effect of sterilization processes on the properties of the materials used in medical devices is often ignored [10]. As different sterilization processes have different characteristics, they will also have different effects on materials and devices. For example, steam is destructive to most engineering polymers, since the glass transition temperature of most polymers is lower than 120°C. Steam is not suitable for materials unable to tolerate high temperatures and high humidity, such as plastics and corrosion-susceptible metal alloys. Many polymers cannot be sterilized by all methods including gamma radiation, ethylene oxide and steam because of changes that occur within the polymer, often leading to embrittlement or hydrolytic decomposition [1, 9, 11]. The development of novel materials for use in medical devices necessarily encompasses an assessment of the effects of a range of commercially available sterilization processes.

The macroscopic behavior of composites, as sufficient candidates for medical device production, depends not only on the properties of their individual constituents but also on the elastic-plastic interaction between the different phases, such as fibers and matrix [12-16]. It has been demonstrated that commercially available sterilization can alter the physical and chemical properties of several polymers, e.g. polyurethanes [13-16]. However, in order to produce more oxidatively stable and environment-friendly stress-cracking resistant polyurethanes, polydimethylsiloxane has been incorporated into the soft segment of the polymer [17, 18]. Siloxane has good biocompatibility, high flexibility, low toxicity, good thermal and oxidative stability, and the properties of siloxane are not adversely affected by widely-used sterilization methods [19]. Similarly, polyphenylene sulfides demonstrate excellent chemical and temperature resistance, excellent chemical and oxidation resistance, very low water absorption and excellent creep resistance, even at elevated temperatures [20]. High-performance polymers can frequently offer properties unavailable even with metals or other types of materials. An example is polyetheretherketon (PEEK), which exhibits very high temperature and chemical resistance and the ability to be repeatedly sterilized without degradation of its mechanical properties, e.g., excellent toughness and strength.

The aim of this study was to prepare radiolucent composite materials for use in medicine, providing suitable mechanical properties and resistance against sterilization decomposition. The composites are composed of three different fabrics and three different matrices. The effect of multiple sterilization processes on degradation of the mechanical properties, structural integrity and hydrolytic decomposition were studied, and also the radiolucency of the composites.

EXPERIMENTAL

Composites preparation

Composite materials were prepared as combinations of basic components (see Table 1 and 2), namely ARAMID/PDMS, R-glass/PDMS, C/PDMS, C/PEEK and C/PPS. Composites based on PDMS matrix were prepared by the following procedure. Each fabric was impregnated with the PDMS matrix precursor, after

Table 1. Basic composite components - fabrics.

Sample designation	Texture	Material of fibers	Producer
ARAMID	plain weave	polyamide (Aramid, HM215)	Hexcel, France
R-glass	sateen weave	R-glass (21055) [24]	Vetrotex, Saint Gobain, France
C	plain weave	carbon (T 300, Torayca)	Toray, Japan

Table 2. Basic composite components - fabrics.

Sample designation	Material	Producer
PDMS	Polydimethylsiloxane (Lukosil M130)	Lučební závody, Kolín, Czech Republic
PEEK	Poly-Ether-Ether-Ketone (3085-P17)	Porcher Industrie, France
PPS	Polyphenylene-Sulfide (CETEX-PPS)	TenCate, Holland

which it was cut into pieces of appropriate size for the curing mould (120 × 120 mm) after 24 hours (left in air an atmosphere at room temperature). The impregnated layers were placed into the curing mould, taking into account the axis of the fibers (each layer has the same orientation of the warp, with ply direction (0°) and the fill weft, with ply direction (90°)). The numbers of layers were as follows; ARAMID: 20, R-glass: 10 and C: 10. The green composite was cured under a pressure of 1.1 MPa at 225 °C in an air atmosphere for 4.5 hours and postcured under a pressure of 1.1 MPa at 250 °C for 4 hours in an air atmosphere. The preparation process was chosen on the basis of previous studies of composites based on PDMS matrix [21-23]. The numbers of fabric layers for each kind of composite were chosen to keep the volume fraction of the fibrous reinforcement equal to approx. 55vol.%. C/PEEK was consolidated under a pressure of 0.08 MPa at 395 °C for 15 min (rate of temperature increase and/or decrease: 10 °C/min). C/PPS was consolidated under a pressure of 1.0 MPa at 310 °C for 10 min (rate of temperature increase and/or decrease: 10 °C/min). The basic composite components were supplied by the producers in the form of prepregs, and the preparation technology was applied on the basis of the technical documentation that was supplied. The total content of the fibrous reinforcement in the matrix was kept at approx. 55 vol.%. After preparation, the homogeneity (volume fraction of each component, presence of pores, open porosity) was verified by image analysis and by open porosity measurement (as described below).

Mechanical properties

The mechanical properties were measured before sterilization (A), after 1 sterilization process period (B1), after 30 (B30) and after 100 (B100) sterilization process periods. An autoclave (Steridenť, Prodenta, CZ) for steam sterilization (134 °C, 304 kPa, 10 min) was used for this purpose. The mechanical properties in the direction of the fiber axis were determined. Namely the ultimate strength in bending with a three-point bending set-up and the modulus of elasticity in bending with a four-point bending set-up were determined using the Inspekt 100 HT material tester (Hagewald & Peschke, Germany), in accordance with ISO 14125.

Structural properties

In order to assess the homogeneity and the influence of multiple sterilization processes on the inner structure of the composites, an image analysis of the polished sections was performed using NIS-Elements AR software, ver. 2.30 (Laboratory Imaging, Inc., Czech Republic). Finally, the open porosity was determined (ASTM C20-00).

Radiolucency

The intensities of X-rays transmitted through the composites under study were measured when the following end conditions were applied; 80 kV, 2 mA, 1000 ms. The transmissivity was calculated for each sample on the basis of the Beer-Lambert law. The linear absorption coefficients (μ [mm^{-1}]) were calculated. Since the absorption coefficient is not influenced by sample thickness (it is influenced mainly by material properties), we were able to assess and compare the radiolucency of each studied material. For each sample, the absorption coefficients were measured from three areas 175 × 300 pixels in size. The mean values, medians, standard deviations and confidence intervals (at significance level 0.05) were determined. The transmissivity was measured by Shado-o-Box™ 4K (Rad-icon Imaging Corp., Dalsa Corp.,USA). X-ray Tubehousing ISOVOLT 420/5 (Agfa NDT Pantak Seifert GmbH & Co., Germany) was used as an X-ray source.

With a view to making a comparison with the real environment (the radiolucency of human bone), the control material was added to the analyses that were performed. The control material consists of aluminum (Al) sample of various thicknesses (approx. 1, 2, 3, 4, 5, 6, 7 and 8 mm). An X-ray analysis of the Al sample was performed, and the transparency of its different thicknesses was compared with the transparency of the human humerus. This analysis was performed on equipment widely used in hospital facilities, and parameters widely used in X-ray examinations were applied (60 kV, 250 mA, 0.5 ms or 11.2 ms). The Stenoscop 2 X-ray device (GE Medical Systems, USA) was used for the analysis of the Al control sample. A densitometer for single point measurements of the optical densities of X-ray films was used for this purpose (Densoquick 2, PEHA med. Geräte GmbH, Germany).

Statistical analysis

A statistical analysis for all tests was carried out using the following methods (STATGRAPHICS Centurion XV, StatPoint, USA). Outlier identification was performed via the Grubbs and Dixon tests. Tests for normality were performed via the Chi-Squared, Shapiro-Wilk test. Homoscedasticity was checked for the application of ANOVA parametric tests (the Leven, Bartlett and Cochrans tests were used). The ANOVA parametric F-test was applied. The LSD, Tukey HSD, Scheffe, Bonferroni and Student-Newman-Keuls tests were used as post hoc tests. The statistically significant differences were in most cases checked by nonparametric methods. The Kruskal-Wallis test was used for this purpose. The Mann-Whitney test was used as a post hoc test. The confidence intervals for the mean values were calculated at a significance level of $\alpha = 0.05$. A parametric and nonparametric analysis of variance was performed at a significance level of $\alpha = 0.05$.

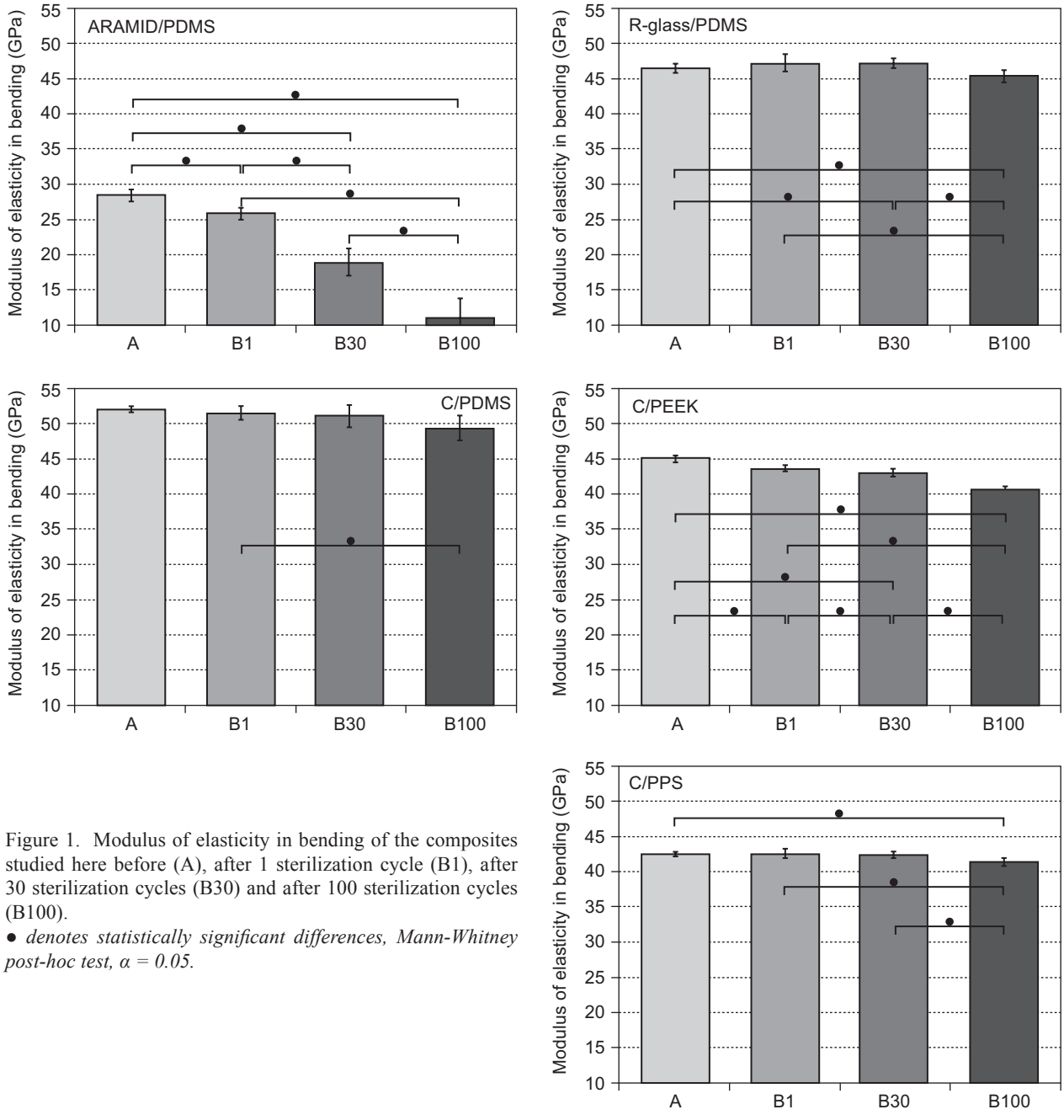


Figure 1. Modulus of elasticity in bending of the composites studied here before (A), after 1 sterilization cycle (B1), after 30 sterilization cycles (B30) and after 100 sterilization cycles (B100).
● *denotes statistically significant differences, Mann-Whitney post-hoc test, α = 0.05.*

RESULTS AND DISCUSSION

Mechanical and structural properties

The flexural properties after multiple sterilizations were tested and compared with those of the corresponding unsterilized samples (Figures 1 and 2). The modulus of elasticity in bending is influenced by multiple sterilizations, mainly in the case of ARAMID/PDMS composite. The expressive decrease in the modulus is equal to approx. 60 % after 100 sterilization cycles. In the case of C/PEEK composite, the modulus decreases slightly after 100 cycles, the decrease being equal to approx. 10 %. The modulus values of composites C/PDMS (approx. 5 % decrease), R-glass/PDMS and C/PPS (both approx. 5 % decrease) show only an unexpressive decrease, which is not statistically significant for R-glass/PDMS composite. The ultimate strength in bending values of all composites studied here show statistically significant decreases after 100 sterilization cycles. The highest decrease in ultimate strength in bending can be observed in the case of ARAMID/PDMS composite. The expressive decrease in the strength is equal to approx. 60% after 100 sterilization cycles. The further decrease in the strength of the composites is as follows: R-glass/PDMS (approx. 45 %), C/PDMS (approx. 28 %), C/PEEK (approx. 13 %) and C/PPS (approx. 5 %).

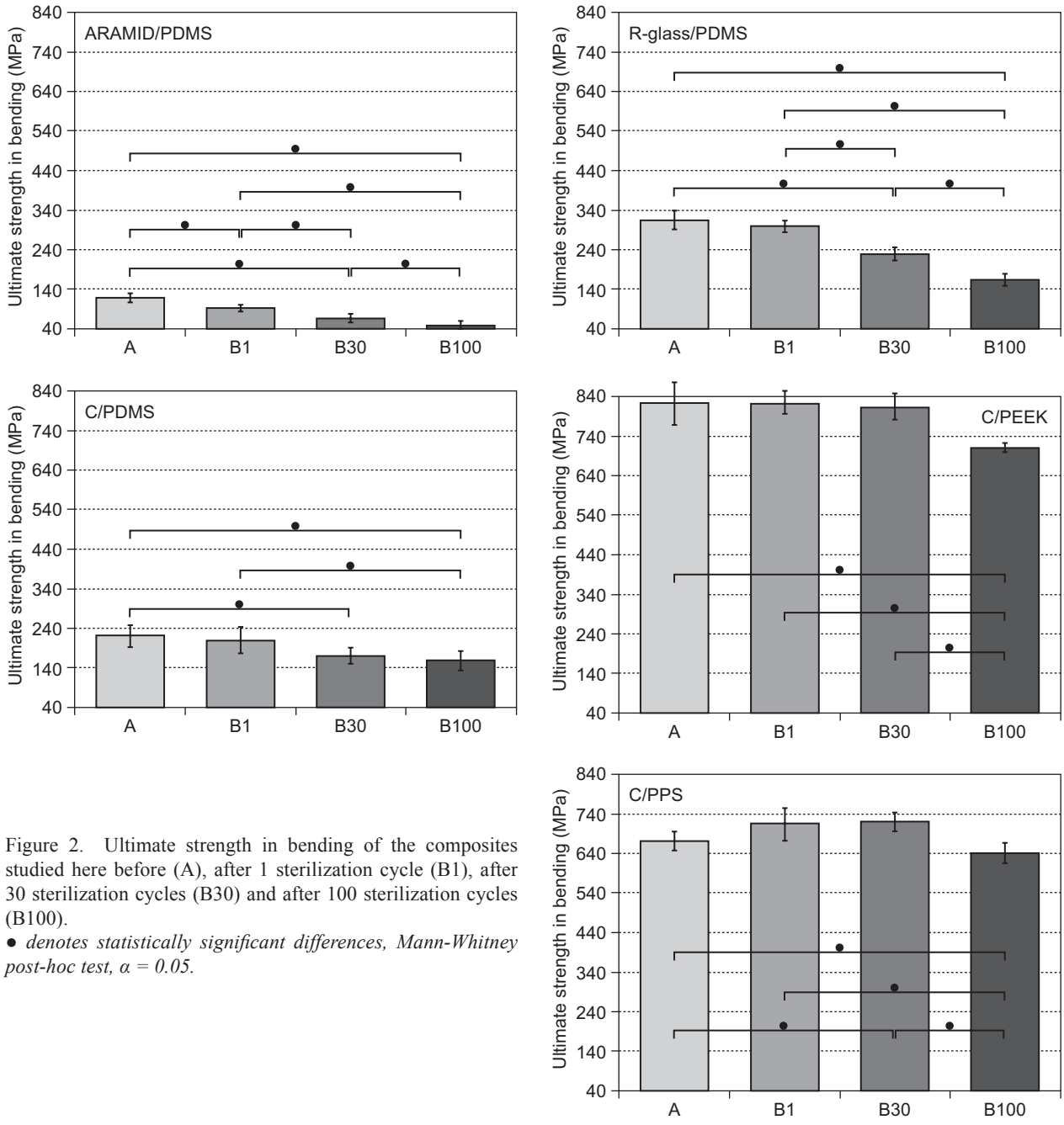
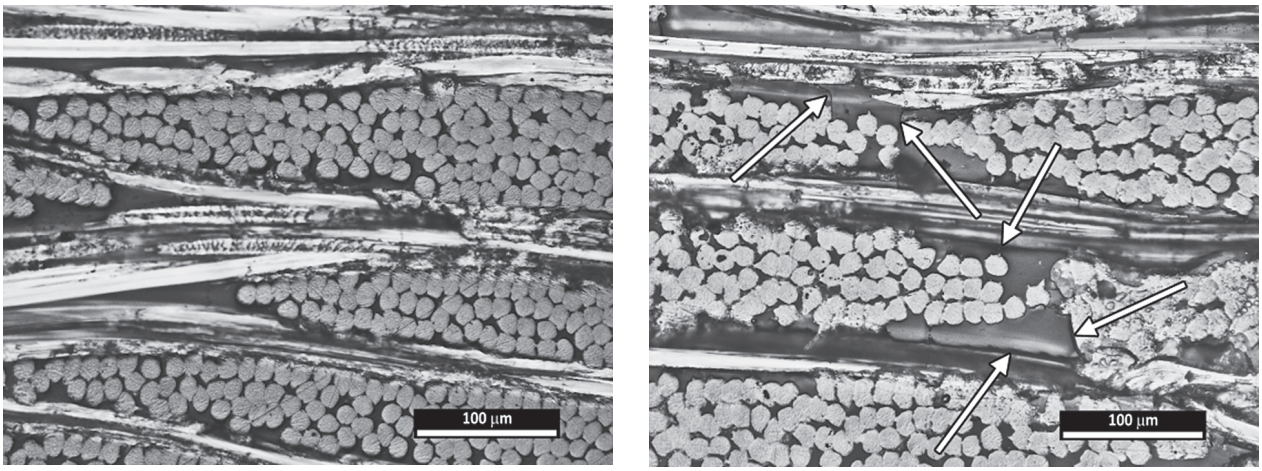


Figure 2. Ultimate strength in bending of the composites studied here before (A), after 1 sterilization cycle (B1), after 30 sterilization cycles (B30) and after 100 sterilization cycles (B100).
● *denotes statistically significant differences, Mann-Whitney post-hoc test, α = 0.05.*

The following conclusions can be drawn from the image analysis and from the open porosity measurements of the composites under study. A greater number of cracks can be observed on polished sections of ARAMID/PDMS composite, mainly after 100 sterilization cycles (see Figure 3). These cracks are observed in close proximity to the bundles of fibers. A factor that may influence this crack formation is the volume changes of the fibers during and after sterilization, due to moisture absorption of the aramid fibers. In the case of C/PDMS, a greater number of cracks can also be observed (see Figure 4). Unlike in ARAMID/PDMS, these cracks can be observed in the inner structure both before and after sterilization. From this fact we can assume that the inner morphology of C/PDMS is influenced more by the curing cycle that is applied than by sterilization (possibly due to the different thermal expansivity of the fibers and matrix). This statement can also be supported by porosity measurements. Porosity yields statistically significant differences only after 100 sterilization cycles, where the increase in porosity is equal to approx. 10%. In the case of R-glass/PDMS, C/PEEK and C/PPS, the inner structure appears to be without any signs of damage (see Figure 5), both before and after sterilization. The open porosity of R-glass/PDMS composite is possibly influenced by sterilization. In this case, porosity yields

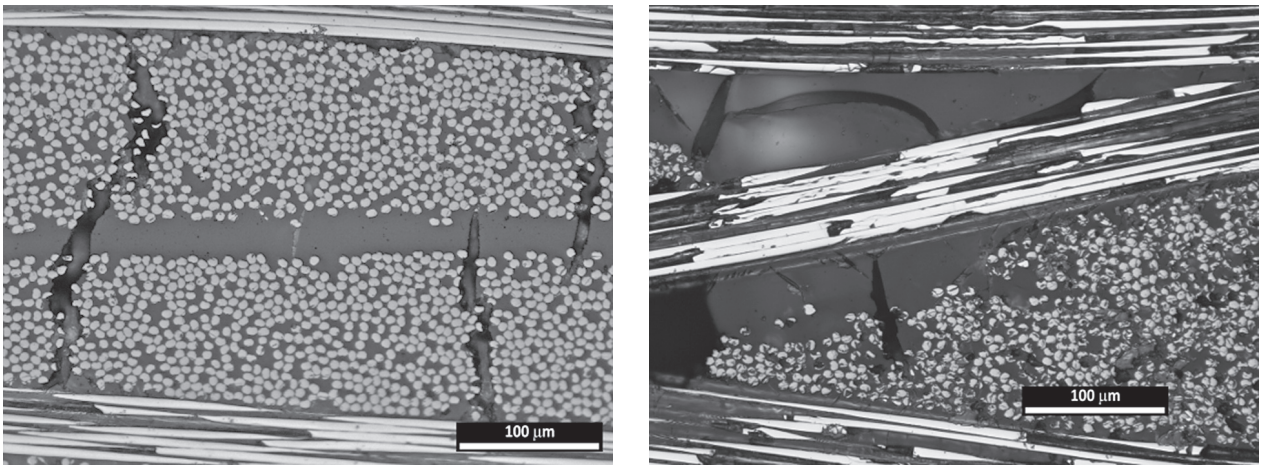
a statistically significant increase (approx. 40%) after 100 cycles. The lowest porosity values (with the lowest increasing tendency) were attained when analyzing both C/PEEK and C/PPS composites (Figure 6).

The mechanical performance of fiber-reinforced composites depends primarily on the mechanical properties of their basic constituents, the chemical stability of the matrix, and the effectiveness of the bond between



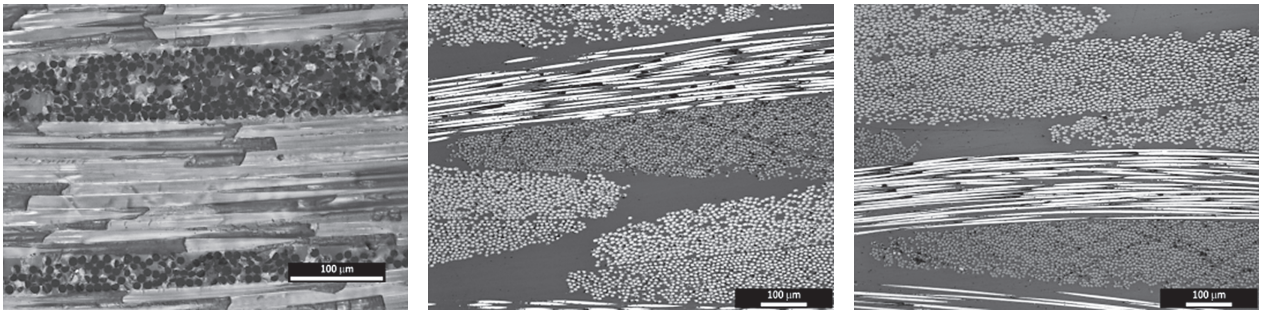
a) b)

Figure 3. Micrographs of polished cross sections of ARAMID/PDMS composite before (a) and after (b) 100 sterilization cycles.



a) b)

Figure 4. Micrographs of polished cross sections of C/PDMS composite before (a) and after (b) 100 sterilization cycles.



a) b) c)

Figure 5. Micrographs of polished cross sections of composites: R-glass/PDMS (a), C/PEEK (b) and C/PPS (b) after 100 sterilization cycles.

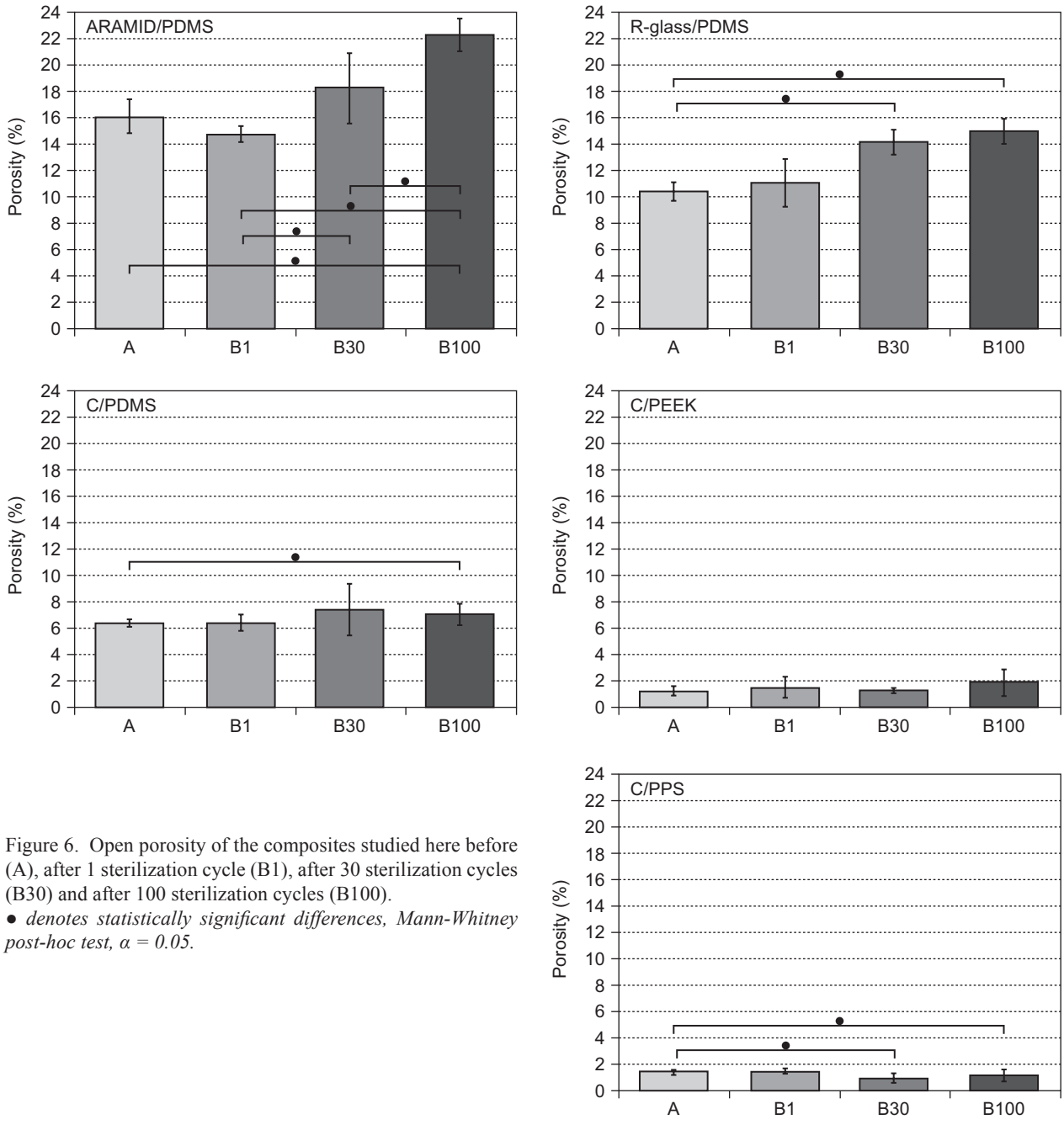


Figure 6. Open porosity of the composites studied here before (A), after 1 sterilization cycle (B1), after 30 sterilization cycles (B30) and after 100 sterilization cycles (B100).
● *denotes statistically significant differences, Mann-Whitney post-hoc test, α = 0.05.*

matrix and fibers in transferring the stress across the interface [25]. The decrease in both the modulus and the strength of the ARAMID/PDMS composite may show that the bond between matrix and reinforcement is not tight and is hydrolytically unstable. This supposition can be supported by the image analysis findings and by the increasing porosity after sterilization. The moisture absorption of aramid fibers is probably another factor that influences the process [22]. In addition, degradation in mechanical performance was shown in the case of the R-glass/PDMS composite. The extensive increase in open porosity after 30 and 100 sterilization cycles is accompanied by an extensive decrease in ultimate strength in bending. The higher porosity of the R-glass/PDMS composite may enable an increase in the rate of water diffusion. It may enable the formation of swelling effects, the development of additional inner tension leading to further violation of the interfaces and their ability to transfer the stress into the fibers. The relatively higher porosity of the C/PDMS composite may influence its lower ultimate bending strength values. Unlike the R-glass/PDMS composite, the porosity of the C/PDMS composite is influenced by sterilization only at a low rate. In the case of composites with PDMS matrix, we can deduce from the different tendency in changes in mechanical properties during sterilization

that no chemical changes occurred in the polymeric matrix itself. The different bond between the PDMS matrix and various kinds of fibers probably influences the mechanical behavior of the resulting composites.

Radiolucency

The radiographic analyses of composite materials were aimed at verifying the rate of radiolucency. First, it was necessary to prepare a control sample to enable a comparison of radiolucent properties (when searching for composite materials with radiolucency higher than the radiolucency of human body parts). An X-ray analysis of the Al sample was performed, and the transparency of its different thicknesses was compared with the transparency of the human humerus (see Figure 7). Suitable radiolucency was found in the case of Al control sample thicknesses up to 3 mm. The part 1 mm in thickness shows the highest rate. It was concluded that the Al control sample can be used as a reference sample for comparing the studied composites with the real environment. The linear absorption coefficients of the studied composites are listed in Figure 8. All studied composites showed statistically significant lower absorption coefficients than the Al control sample. From this fact we were able to assume that all the composites are sufficiently radiolucent.

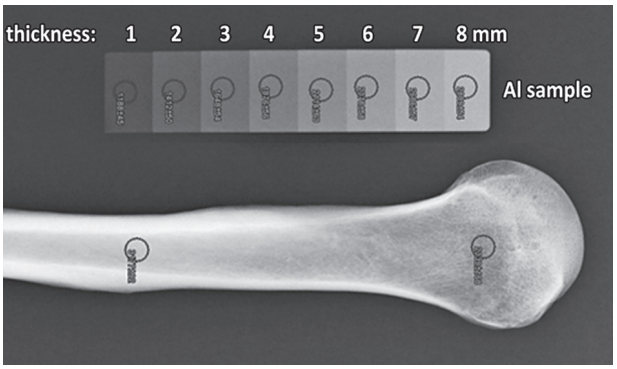


Figure 7. An example of the optical densities of X-ray film measurements - a comparison of the radiolucency of the humerus and the radiolucency of an Al control sample for simulating the X-ray absorption of the human body.

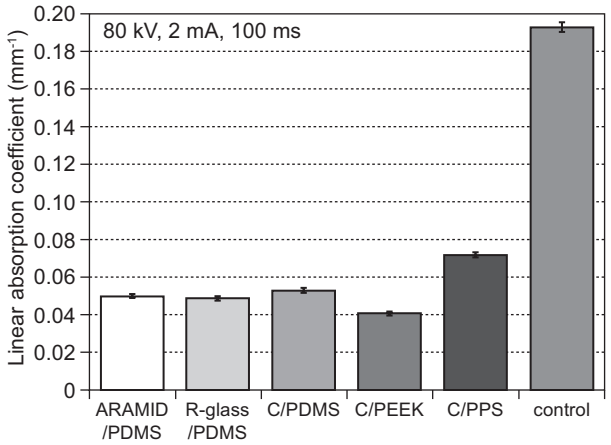


Figure 8. Linear absorption coefficients of the studied composites and the Al control sample (all values display statistically significant differences).

CONCLUSIONS

This paper has investigated the effect of 1, 30 and 100 steam sterilization cycles in an autoclave that is widely used in medical practice. The aim was to verify the possible influence on the mechanical performance and on the laminate morphology of radiolucent composite materials. It has been shown that the mechanical and structural properties are strongly influenced by steam sterilization, mainly in the case of ARAMID/PDMS composite. The decrease in the modulus of elasticity in bending and in the ultimate strength in bending was shown to be equal to approx. 60%. On the basis of our analysis, we can state that C/PEEK and C/PPS composites seem to be appropriate candidates that provide high resistance against sterilization decomposition. This statement is supported by stable mechanical performance and inner structure without significant signs of degradation. The sufficient radiolucency of all studied composites was verified by X-ray analysis and by comparison with an aluminum sample.

As a further step, it will be necessary to increase the number of applied sterilization processes and to perform further physical properties analyses before the materials can be recommended for application. Finally, a biological evaluation of some medical devices or parts based on a categorization of the nature and duration of their contact with the human body is another important factor that must be taken into account. Medical devices in contact with human body surfaces are defined as surface-contacting [26], and are included in the scope of ISO 10993 (e.g. instruments and non-implanted devices whose single or multiple use or contact is likely to be up to 24 h). Their biological performance must therefore be taken into account when designing a successful medical device product.

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References

1. Ramakrishna S., Huang Z.M., Kumar G.V., Batchelor A.W., Mayer J.: *An Introduction to Biocomposites*, 1st ed., p. 1-17, Imperial College Press, London 2004.
2. Norris B.L., Hahn D.H., Bosse M.J. Kellam J.F., Sims S.H.: J.Orthop.Trauma. *13*, 414 (1999).
3. Routt Jr. M.L., Nork S.E., Mills W.J.: Clin.Orthop.Relat. Res. *375*, 15 (2000).
4. Stulberg S.D., Loan P., Sarin V.: J.Bone Joint Surg. AM. *84-A*, 90 (2002).
5. Siston R.A., Giori N.J., Goodman S.B., Delp S.L.: J.Biomech. *40*, 728 (2007).
6. Whatling G.M., Nokes L.D.M.: Injury *37*, 109 (2006).
7. Tyropoulos S., Garnavos C.: Injury *32*, 732 (2001).
8. Rahman M.M., Taha W.S., Shaheen M.M.: Injury *29*, 789 (1998).
9. Halfmann H., Bibinov H.N., Wunderlich J., Awakowicz P.: J.Phys.D.Appl.Phys. *40*, 4145 (2007).
10. Block S.S.: *Disinfection, Sterilization, and Preservation*, 4th ed., p. 172-180, Lea and Febiger, Philadelphia 1991.
11. Simmons A., Hyvarinen J., Poole-Warren L.: Biomaterials *27*, 4484 (2006).
12. Godara A., Raabe D., Green S.: Acta Biomater. *3*, 209 (2007).
13. Lerouge S., Guignot C., Tabrizian M., Ferrier D., Yagoubi N., Yahia L.: J.Biomed.Mater.Res. *52*, 774 (2000).
14. Nair P.D.: J.Biomater.Appl. *10*, 121 (1995).
15. Gogolewski S., Mainil-Varlet P., Dillon J.G.: J.Biomed. Mater.Res. *32*, 227 (1996).
16. Premnath V., Harris W.H., Jasty M., Merrill E.W.: Biomaterials *17*, 1741 (1996).
17. Shibayama M., Suetsugu M., Sakurai S., Yamamoto T., Nomura S.: Macromolecules *24*, 6254 (1991).
18. Hergenrother R.W., Yu X.H., Cooper S.L.: Biomaterials *15*, 635 (1994).
19. Simmons A., Hyvarinen J., Poole-Warren L.: Biomaterials *27*, 4484 (2006).
20. Ishigaki I., Yoshii F.: Radiat.Phys.Chem. *39*, 527 (1992).
21. Suchý T., Balík K., Černý M., Sochor M., Hulejová M., Pešáková V., Fenclová M.: Ceramics-Silikaty *52*, 29 (2008).
22. Suchý T., Balík K., Sucharda Z., Sochor M., Lapčíková M., Sedláček R.: Wein. Med. Wochenschr. *161*, 493 (2011).
23. Rýglová Š., Sucharda Z., Černý M., Suchý T., Šupová M., Žaloudková M.: Ceramics-Silikaty *54*, 386 (2010).
24. Balík K., Sochor M., Hulejová H., Suchý T., Černý M.: Ceramics-Silikaty *51*, 198 (2007).
25. Broutman L.J., Krock R.H.: *Composite Materials*, 1st ed., p. 51-97, Academic Press, New York 1974.
26. ISO 10993-1. Biological evaluation of medical devices. Part 1: Evaluation and testing.