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Degradation of partially absorbable surgical mesh: a chemical and mechanical study

D. Pashkouleva[1*], M. Kirilova-Doneva[1,2], I. Borovanska[1], A. A. Apostolov[3]

[1]*Institute of Mechanics, Bulgarian Academy of Sciences, Bulgaria*
[2]*Faculty of Pharmacy, Medical University-Sofia, Bulgaria*
[3] *Faculty of Chemistry and Pharmacy, Sofia University St. Kliment Ohridski, Sofia, Bulgaria*

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Chemical and mechanical testing of partially absorbable surgical mesh after being kept *in vitro* under physiological conditions for four months was performed. Differential scanning calorimetry and X-ray diffraction were used to investigate the degradation behavior and the changes in structure and crystallinity of this surgical mesh. The degradation of the copolymer poliglecaprone 25, which is a constituent of the mesh, was confirmed. The mechanical characteristics of the mesh were compared in two different directions by performing uniaxial tensile tests. A progressive loss of the tensile strength and elongation was established. Failure tests showed that the mechanical properties of the mesh are anisotropic. The lower tensile strength is in transversal direction.

Keywords: Polypropylene, Poliglecaprone, Structure, Mechanical properties, Surgical meshes.

INTRODUCTION

Mesh hernioplasty is a common surgical procedure – approximately 20 million hernia repairs occur each year worldwide [1]. Currently, hernia meshes are made of non-absorbable polymers: polypropylene (PP), polyethylene terephthalate (PET), polytetrafluorethylene (PTFE), as well as from absorbable polymers such as polyglactin (PGA) or poliglecaprone 25 (PGC) [2].

Non-absorbable hernia meshes keep their mechanical stability, but induce high inflammatory reactions. Absorbable and partially absorbable hernia meshes are used in the clinical practice in cases of large defects or damaged tissues. Absorbable meshes are completely replaced by connective tissue, but are only recommended for a temporary closure of the abdominal wall or an infected wound and not for implantation because of their rapid degradation [3]. When it became clear that the tensile strength required is much less than originally presumed the material of meshes was reduced by adding partially absorbable components or by primary reduction of the material used. Today light-weight and partially resorbable meshes are recommended as a golden standard in surgical practice because of their advantage for abdominal wall function.

Most light-weight hernia meshes (16-35 g/m^2) with large pores (diameter of >1 mm) are a combination of PP fibers and PGA or PGC fibers [4]. One of the most popular partially absorbable hernia meshes is ULTRAPRO, distributed by Johnson-Johnson Inc. (Neuss, Germany) and consisting of approximately equal parts of absorbable PGC-25 and non-absorbable PP monofilament fiber.

The mechanical properties and shrinkage of ULTRAPRO are investigated and compared with other meshes [5-7]. To present we could not find information about long-term changes of chemical composition of ULTRAPRO. Chemical degradation that leads to a reduction of the physical and mechanical properties is the primary obstacle to long-term mesh stability. One of the most popular polymers used for hernia meshes is polypropylene (PP). PP is a linear aliphatic hydrocarbon, which has methyl groups attached to chain backbone. It is nonpolar, highly hydrophobic and resistant to many chemical solvents, bases and acids [8]. Chain entanglement and intermolecular secondary bond forces (van der Waals-London forces) from induced dipole hydrogen bonds between chains define the mechanical properties of PP. This polymer is considered to be an inert material that provides stable service life *in vivo* as a mesh material [8]. Actually, the chronic inflammatory cells secrete highly reactive radicals as superoxide anions, as well as strongly oxidative chemicals, for example, hypochlorous acid and hydrogen peroxide, which are potentially detrimental to the PP mesh [9]. The created free radicals along the broken bonds are possible to bind to oxygen to form carbonyl groups [10]. Oxidization of polypropylene results in chain cracking, flaking, strands fissuring and surface crazing [9]. Surface oxidative degradation of PP gives as a result bulk property changes such as loss of mass, lowering the glass transition and melt temperatures and diminished molecular mobility

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* To whom all correspondence should be sent:
E-mail: dessip@imbm.bas.bg

[11]. Both the polyester and ePTFE (i.e. expanded PTFE) have been shown to be much more inert to oxidation, which affects PP mesh at a greater severity [9].

In order to present all aspects of the degradation process of absorbable meshes we decided to characterize a pristine mesh ULTRAPRO before and after exposure to conditions similar to human physiology using Differential Scanning Calorimetry and X-ray Diffraction. The changes in the structure and crystallinity of this brand will be described. The information about long-term chemical, physical and mechanical changes of ULTRAPRO will be useful to determine the brand of explanted meshes.

MATERIALS AND METHODS

Materials

Partially absorbable light-weight mesh with brand name ULTRAPRO (Ethicon, a Johnson&Johnson Company, Germany) for surgical applications was used in this study. This monofilament mesh with large pores (3-4 mm) is made of two-component PROLENE^{TM} (polypropylene – PP) and absorbable MONOCRYL^{TM} (poliglecaprone 25 – PGC-25). PGC-25 is a copolymer of glycolide and ε-caprolactone [11], i.e., poly(glycolide-*co*-caprolatone). ULTRAPRO mesh has a different coloration (white and blue stripes) (Fig. 1). This design facilitates the orientation for positioning of the mesh. The pristine mesh was 150×150 mm^2, with thickness of 0.5 mm, fiber diameter of 90 μm and 55 g/m^2 average weight.

Fig. 1. Photo of ULTRAPRO mesh

Ageing of the mesh

In order to age the samples they were placed in the chamber of the digital thermostatic bath DIGIBATH-2 (Raypa, Spain) full of 0.9% saline solution. The chamber conditions were strictly controlled – 120 days at 37 ± 1°C temperature in saline solution exposure.

Various methods for chemical, physical and mechanical characterization of the mesh properties were used.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used as a test for identification of the changes in the structure of the surgical polymer mesh. DSC tests were performed on the Q200 DSC apparatus (TA, USA). The samples were investigated in a heating/cooling/second heating mode from -80 to 250^{o}C with a heating/cooling rate of 10^{o}C/min in nitrogen atmosphere. The crystallization (T_c) and melting temperature (T_m) were determined from the cooling and heating curves, respectively. In order to check if there is detectable glass transition in the two samples, separate experiments with a high heating rate of 50^{o}C/min from -80 to 250^{o}C were performed. In all cases the sample weight was between 1.5 and 3 mg.

X-ray diffraction (XRD)

This is another measurement tool, which assesses the physical structure of the materials. In our case the goal was to show which of the polymers present in the ULTARO mesh before and after the ageing was in crystalline form. A Siemens D500 diffractometer (Germany), with secondary monochromator and Cu-Kα radiation was used to obtain the diffractograms over the 2θ range of 10-40^o with a step of 0.05^o and count time of 5 s.

Mechanical characterization

In addition to the physical and chemical characterization, the mechanical properties of the mesh were determined. Uniaxial tensile test was conducted using a universal testing machine (Fu1000e, Germany) at room temperature and with the traverse velocity of 0.13 mm/s. All tests were performed in two perpendicular directions – longitudinal (along the loop columns) and transverse (across the loop columns) in order to determine the influence of anisotropy on the mechanical properties. Uniaxial testing in both directions may be not the perfect solution to describe the mechanical properties but is an established method. The orientation of ULTRAPRO mesh is easy to control, because the blue strips of the material are along the loop columns. For each direction, five specimens of 10 × 70 mm^2 were cut. The specimen's thickness was determined with a caliper. The force and the displacement were recorded. The relative breaking strain in % was computed as $\Delta L/L_o \times 100$, where L_o is the initial length before any load is applied and ΔL is the elongation of the sample. The tensile strength was obtained using the expression *Force*/*Width*, where *Force* (N) is the load applied during the test and *Width* is the specimen width (mm). The stress cannot be computed, because the value of the thickness of the meshes is not measurable due to its discontinuous cross sectional area, where filaments and empty areas exist and are interspersed. The results are reported as mean ± standard error of the mean.

RESULTS AND DISCUSSION

Thermal characterization

The DSC curves of the pristine samples (white and blue stripes) and the sample soaked in solution are presented in Fig. 2 for the first heating (a), cooling (b) and second heating (c), respectively. The curves of the pristine white and blue samples are similar**.** Hence, these two parts of ULTRAPRO mesh are identical and the colouring does not influence its chemical characteristics. For this reason we will designate both as a pristine sample in contrary to the aged one.

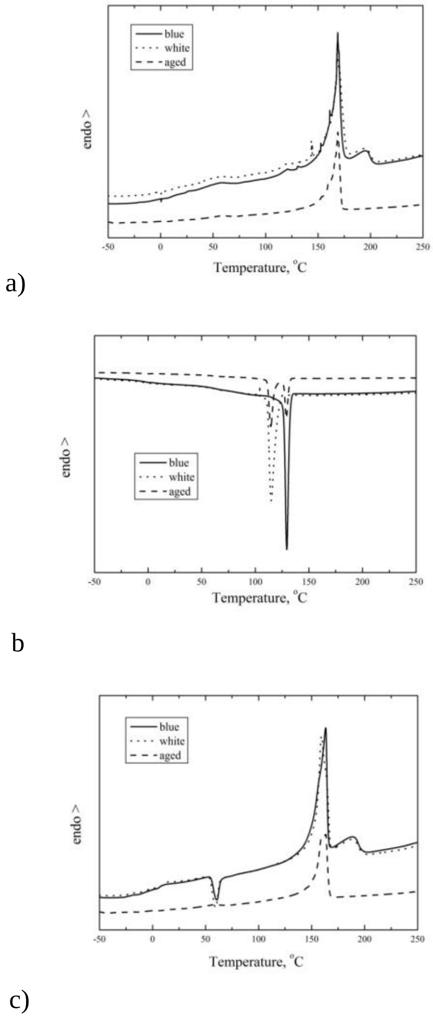
There is a very weak low-temperature melting peak at ca. 55^{o}C, a very strong peak at ca. 169^{o}C of both pristine and aged sample in the thermograms of the first heating. An additional broad peak at around 183^{o}C is present in the thermogram of the first heating of the pristine sample (Fig. 2a).

The thermograms of cooling (Fig. 2b) are characterized by a single maximum at 114.3^{o}C for the pristine sample and a doublet at 114.3/129.0^{o}C after the stay in the physiologic solution. It is interesting to note the coincidence of the single peak at 129.0^{o}C for the aged sample with the high-temperature peak of the doublet for the aged one.

There is a peak of crystallization at 55.0^{o}C, a very strong peak of melting at 159.7^{o}C and a moderate peak of melting around 183^{o}C for the pristine sample in the thermogram of the second heating (Fig. 2c). A weak peak of melting at 55.0^{o}C and a strong one at 163.4^{o}C are also indicated in the thermogram of the aged sample (Fig. 2c).

A clear glass transition is indicated in the thermogram of fast heating of the pristine sample at 8.0^{o}C (Fig. 3). The registered melting T_m, glass transition T_g, and crystallization T_c temperatures together with the enthalpy of melting ΔH_m and DSC degree of crystallinity w_c are summarized in Table 1.

Generally, the changes in the shape of the first melting endotherms give some qualitative information about the content of different phases, as well as on the perfection of the crystal structure which depends on the prehistory of the material. The existence of multiple peaks in the DSC thermograms can appear in (a) a sample that consists of more than one plastic; (b) a sample that consists of only one plastic but with different molecular weights; (c) a sample that consists of crystals of different size and/or type; (d) a degraded sample [12].



a)

b

c)

Fig. 2. DSC curves of pristine and aged samples of (a) first heating, (b) cooling and (c) second heating. (The curves are shifted vertically for the sake of clarity.)

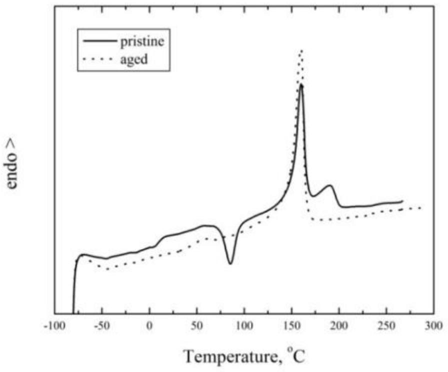


Fig. 3. DSC curves of heating of samples with a high heating rate of 50 ^{o}C/min. (The curves are shifted vertically for the sake of clarity.)

Table 1. DSC characteristics of the pristine and aged sample.

Sample	First heating, 10°C/min			Cooling, 10°C/min	Second heating, 10°C/min				Heating, 50°C/min
	T_m (°C)	ΔH_m (J/g)	w_c (%)	T_c (°C)	T_m, (°C)	ΔH_m (J/g)	w_c (%)	T_c (°C)	T_g (°C)
Pristine	55, 169.8 and 183	94.4	45.2	114.3	159.7, 183	82.5	41.2	55.0	8.0
Aged	168.8	89.5	42.8	114.3 /129.0	163.4	85.9	43.0	-	-

The melting at 169-170°C is obviously due to melting of PP crystals (Fig. 2). According to Wunderlicht [13] the melting temperature of 100% isotactic PP is 174 °C and that of 60% isotactic PP is 171-172°C. This is also supported by Keith and Padden [14] who state that 100% isotactic PP melts at 171°C, 60% at 165°C and 40% at 162°C. Other authors claim that perfectly isotactic PP has a melting point of 171°C, whereas commercial isotactic PP has a melting point that ranges from 160°C to 166°C, depending on atactic material and crystallinity. The observed melting temperature (Fig. 2a) of around 169-170°C in the first heating of both pristine and aged samples, respectively, matches that of homo-PP containing isotactic fraction of about 60-80%. The lower T_m of 163.4°C in the second heating may be attributed to worse crystallization conditions during the fast cooling, i.e., the created crystallites are imperfect and the crystallization has not taken fully place in both samples. This is indirectly proved by the additional crystallization at 55.0°C during the second heating of the pristine sample and also witnessed by the decrease in enthalpy of melting of the pristine sample from the first to the second heating by about 14 % (Table 1).

The observed peak at about 183°C for the pristine sample is probably due to melting of short polyglycolide blocks in the copolymer since polyglycolide melts at 225-230°C and the monomer glycolide melts at about 83°C [15], hence the glycolide oligomers melt in a very broad temperature interval depending on the length of the blocks. By the same token the observed melting peak at about 55°C is due to melting of short ε-caprolactone blocks in the copolymer since polycaprolactone melts at 60°C and caprolactone melts at -1,5°C. If we assume a mole ratio of the two components of poly(glycolide-*co*-caprolactone) of 1:1 (see e.g. [16]), then formation of both short glycolide and caprolactone blocks is possible. In fact we do not know the mole ratio of the PGC since it is a proprietary information and lacks in the producers‘s datasheets. Nary *et al.* [11] concluded that the best response from PGC 25, as well as its monofilament characteristic is related to its chemical composition, 25% ε-caprolactone and 75% glycolide. As can be easily calculated on the basis of the monomer molecular weights that this ratio corresponds to approximately 1:6 monomers capralactone: glycolide, i.e. oligoglycolide blocks will be formed thus explaining the melting around 183°C. Based on the above ratio, the caprolactone will form very short blocks, hence the corresponding very weak peak (Fig. 2a,c).

Both peaks around 55 and 190°C are not present in the thermograms of the aged sample (Fig. 2a,c) thus confirming the degradation of the copolymer during the ageing of the composite ULTRAPRO mesh.

The crystallization temperature of 129.0°C, registered at cooling (Fig. 2b) clearly indicates that the thermal history of the pristine sample has been cleared during the first heating. The presence of the low temperature crystallization peak at 114.3°C together with a peak at 129.0°C on the thermogram of the aged sample is probably due to inhomogeneous crystallization where the nuclei are the low molecular products formed after the degradation of the copolymer during the ageing.

The observed glass transition temperature of 8.0°C on the thermogram of the pristine sample (Fig. 3) may be attributed to the copolymer PGC since the glass transition temperature of its constituents is 35-40°C for polyglicolide and -60°C for the polycaprolactone. It is worth noticing that Lee *et al.* [16] reported T_g of PGC with glycolide/caprolactone feed ratio of 5.1/4.9 as -19.3°C, i.e. the slightly lower temperature may be explained by a slightly different feed ratio. The lack of T_g in the thermogram of the aged sample (Fig. 3) again indicates that degradation of the copolymer has taken place after the ageing. According to the literature [17], T_g of PP is -10°C. Nevertheless, it cannot be seen in the thermograms due to the relatively small quantity of amorphous PP; this is based on the fact that the composite ULTRAPRO mesh consists of equal parts of semicrystalline PP and PGC [15].

X-ray characterization

In Fig. 4 the normalized diffractograms of the two samples – the pristine and the aged one are shown. The two diffractograms match those of isotactic alpha-form of PP [18] and differ only slightly due to some change in the orientation in the aged sample, expressed by the decrease of the 111+131+041 complex maximum situated at 22.0 °2θ as well as to the 200+220 complex maximum situated at 28.5 °2θ. An attempt to estimate the half-width of the three main maxima was made, but these half-widths of the corresponding maxima of the two samples turn out to be equal within the experimental error. Thus, no conclusions about an eventual process of worsening of the perfection of the PP crystallites due to the ageing can be made based on the diffraction line half-width. Since the well distinguished strong maximum of the β-phase at 21.31°2θ is not seen, the latter is not present [18]. The presence of isotactic α-form of PP only is in agreement with the reported melting temperatures, see above. Since neither peaks of the copolymer PGC nor of its constituents (that are both crystalline as polymers) are seen, the copolymer PGC is random or blocky with short blocks. This is in agreement with the DSC data.

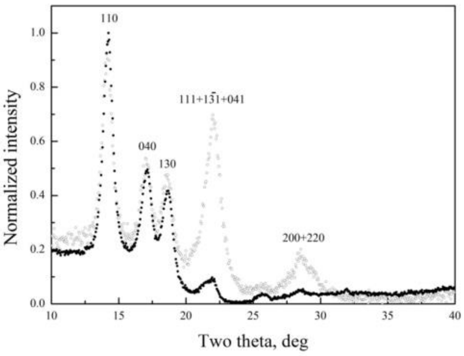


Fig 4. Normalized diffractograms of the two samples: ○-pristine sample and ●-aged sample. The Miller indices of the main maxima are shown.

Mechanical characterization

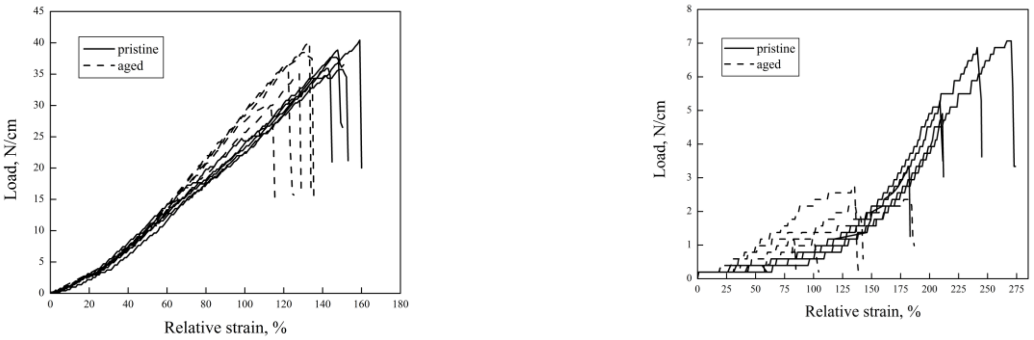
The characteristics of the mechanical properties are shown in Fig. 5. The results of the tensile test of the mesh are presented in a “longitudinal” (Fig. 5a) and a “transverse” (Fig. 5b) direction, as the anisotropic behavior was in agreement with the reported ones [6, 7].

The maximum equivalent stress for the pristine mesh in longitudinal and transverse direction is 37.7±0.9 N/cm and 5.5±0.7 N/cm, respectively. The equivalent stress is approximately 7 times higher in longitudinal than in transverse direction. The elongation at break is 151.8±2.5% in longitudinal and 191.2±23.8% in transverse direction. The obtained anisotropy of the ULTRAPRO mesh is also reported in [6, 7]. Unfortunately, the researchers use many different non-comparable settings for defining the mechanical characteristics of hernia meshes and the degree of anisotropy cannot be compared.

The degradation of PGC leads to a change in the mechanical properties of the mesh (see Fig. 5). The maximum equivalent stress in both directions slightly decreases (from 37.7±0.9 N/cm to 35.9±1.8 N/cm in longitudinal direction and from 5.5±0.7 N/cm to 2.0±0.3 N/cm transverse direction). The elongation at break also decreases (from 151.8±2.5% to 127.8±3.6% in longitudinal and from 191.2±23.8% to 131.5±17.5% in transverse direction).

CONCLUSIONS

It was shown that the poly(glycolide-lactone) copolymer in the ULTRAPRO mesh is a block copolymer, consisting of very short caprolactone blocks and much longer glycolide blocks. Degradation of the above copolymer during the ageing of the composite ULTRAPRO mesh was proven by DSC. Presence of only iso-PP in crystalline (α-) form in the mesh was proven by XRD both before and after the ageing. Degradation of PGC in the ULTRAPRO mesh was indicated by a change in the mechanical properties of the mesh after the ageing. Strong anisotropy of the mechanical properties in longitudinal and transverse direction was observed.



a) b)

Fig. 5. Strength-strain diagrams for ULTRAPRO mesh samples before and after saline solution exposure in (a) longitudinal and (b) transverse direction.

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РАЗГРАЖДАНЕ НА ЧАСТИЧНО РЕЗОРБИРУЕМА ХИРУРГИЧНА МРЕЖА: ХИМИЧНО И МЕХАНИЧНО ИЗСЛЕДВАНЕ

Д. Пашкулева[1*], М. Кирилова-Донева[2], И. Борованска[1], А. А. Апостолов[3]

[1] *Институт по механика, Българска академия на науките, София, България*
[2] *Факултет по фармация, Медицински университет-София, България*
[3] *Факултет по химия и фармация, Софийски университет „Св. Климент Охридски”, София, България*

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(Резюме)

Химично и механично тестване на частично резорбируема хирургична мрежа е проведено след чегиримесечно престояване *in vitro* при физиологични условия. Диференциална сканираща калориметрия и рентгенова дифракция са използвани за изследване на разлагането и промените в структурата и кристалността на хирургичната мрежа. Потвърдено е разлагането на съполимера полиглекапрон 25, който е съставна част на мрежата. Механичните характеристики на мрежата са сравнени в две различни направления чрез провеждане на едноосови тестове на опън. Установена е прогресивна загуба на якост на опън и удължаване. Механичните изпитвания показват, че механичните свойства на мрежата са анизотропни. По-малка якост на опън е установена в напречно направление.