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# Impact of a pulsed magnetic field on selected polymer implant materials

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*Purpose:* Physiotherapy with the use of pulsed magnetic fields is one of the methods of activating the processes of bone healing and regeneration. Exposing materials serving as membranes in guided bone regeneration (GBR) or guided tissue regeneration (GTR) to magnetic fields is an effective model that allows to monitor changes in the material under the influence of the magnetic field. *Methods:* Materials engineering methods were used to verify the extent of material degradation resulting from magnetic field exposure in an aqueous environment. Changes in surface morphology were observed under an optical microscope and a scanning electron microscope (SEM). Changes in surface wettability were analysed in relation to the direct contact angle. Chemical structural changes were verified with the use of infrared spectroscopy (FTIR-ATR). *Results:* The PCL-based membrane materials underwent relatively moderate surface degradation (altered contact angle, changes in surface morphology), but the absence of observable FTIR-ATR spectral shifts evidenced material stability under the influence of magnetic field. More extensive degradation processes were observed in the case of PLDLA-based materials, whose surface character changed from hydrophilic to hydrophobic. The spectra revealed enhanced intensity of the chain terminal groups, provided that modifiers (nanometric $SiO_2$ and TCP (water reservoir)) were present in the polymer matrix. *Conclusions:* The extent degradation in the polymer membrane was primarily dependent on the presence of aqueous environment, while the influence of the magnetic field on the analysed membrane materials was negligible. Therefore, GBR/GTR membrane implants can be considered to remain stable during rehabilitation with the use of alternating magnetic field.

*Key words*: *magnetic field, biomaterials, orthopaedic implants*

## 1. Introduction

There are numerous physiotherapeutic techniques that facilitate controlled and safe stimulation of musculoskeletal healing processes. One of such methods involves stimulation of the healing tissue using a magnetic field. Experimental and clinical studies have confirmed the beneficial effects of magnetic field stimulation on the processes of regeneration in the context of abnormal bone synostosis, arthritis, and degenerative changes as well as wound healing [3], [6], [15], [19].

Many bone-related diseases of the musculoskeletal system require the use of not only advanced surgical techniques, but also implantation. The grafted biomaterial aimed to induce the regenerative process of damaged tissues by providing the necessary osteoconductive or osteoinductive factors. Their presence facilitates the bone-forming processes, particularly in the first stage immediately after implantation. The literature describes numerous osteoinductive factors that have inorganic (e.g., hydroxyapatite – HAp; bioglass – BG), organic (e.g., PRP) or hybrid (biopolymer coated ceramic nanoparticles) origin, which effectively stimulate osteocytes to initiate osteosynthesis [1], [7], [14], [20]. This type of material, which is a combination of at least two different phases whose mutual interaction provides improved functional prop-

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erties, is known as a nanocomposite [2]. This trend in materials science is currently intensively developed due to their structural and microstructural similarity of newly created materials to natural tissues (biomimetics) [6]. However, materials of this type are very susceptible to environmental influence, particularly in highly hydrated conditions. The nanometric modifier is often the point where material degradation begins as water or ions are accumulated around it. Our previous studies demonstrated the influence of nanoparticles on the process of degradation of polymer nanocomposites and indicated changes which should be expected in a given material [13], [17]. When the matrix as such is either degradable or bioresorbable, and therefore sensitive to the aqueous/enzymatic environment, there are many evidences that indicate the impact of that factor on the biomaterial. The first one is the decrease in the molecular mass of the polymer matrix which increases molar mass dispersity. Other symptoms include changes in the length of the polymer chain and an increase in the number of chain terminal groups. Structural changes lead to physicochemical changes, such as a reduction of the contact angle, increase of the surface energy or changed surface morphology [12], [13], [17]. A good model reflecting the behaviour of material *in vitro* are polymer nanocomposites with membrane morphology. Due to their porous structure and the easier access of the medium (relatively small amount of polymer and easy infiltration of the medium into the nanocomposite matrix) materials of this type provide fast feedback regarding the phenomena occurring in the materials.

For the above reasons, two biodegradable polymers were selected for the model studies presented in this work: polylactide (PLA) and polycaprolactone (PCL). Their well-established position in the medical market as well as numerous studies demonstrating the benefits of modifications with nanoparticles of the said polymers further support their viability as the next group of materials usable in bone surgery. Especially that polymer and composite implants have become a permanent element of clinical practice. Both human medicine (particularly in the context of maxillofacial surgery and orthopaedics) and veterinary medicine (orthopaedics of small animal) currently takes advantage of the availability of resorbable implants, such as grafts and bone plates [9], [11].

At the same time, there are a number of studies confirming the beneficial effect of magnetic field stimulation on the process of implant osteointegration with the bone tissue [4], [18]. Therefore, it is commonly employed in both human and veterinary medicine as a supportive treatment facilitating healing process. Considering the overall prevalence of this method of rehabilitation, it seems natural to investigate to what extent it influences the degradation processes of the implant material. However, literature does not currently provide such data and no studies have been published that would take into account the direct effect of magnetic field stimulation on materials used to reconstruct bone defects and regenerate injuries having the size of a critical defect. Therefore, the aim of this paper was to evaluate the impact of magnetic field on selected biomaterials used in bone implantation.

# 2. Material and methods

The study was conducted on two selected biomaterial groups, whose production and full characteristics were discussed in previous papers [16], [17]. These biomaterials are based on biodegradable matrices of polylactide (PLDLA 8035, PURAC) or polycaprolactone (PCL, Sigma-Aldrich, 80 kDa). As a solvent used into pretparation of membrane were: tetrahydrofuran (THF, chemical pure, POCh SA), dimethyl sulfoxide (DMSO, chemical pure, POChSA) and water (ultra hihg quality, UHQ). All membranes were prepared by casting method, then evaporated in the air (24 h). Dry membranes were washed by alcohol. Polymeric membranes are characterised by similar thickness ~280 μm and similar density ~1,02 d/cm$^3$. The pores size was smaller in PLDLA membrane (5–25 μm) than in membrane based on PCL (50–60 μm). The total porosity of membranes was about 50%. Commercially available nanometric fillers (silica (Sigma-Aldrich, 5–10 nm particles) and TCP (Sigma-Aldrich, 30–60 nm) were used as modifiers. The fillers were added in the amount of 2% by weight, since it was discovered in earlier studies that materials with this percentage composition were characterised by better mechanical properties and a more controllable degradation time. Membranes were obtained by casting and phase inversion and the membrane without nano-additives was the reference. The materials were divided into two groups:

**Group I** – polycaprolactone membranes: PCL membrane (reference), PCL/$SiO_2$ (polycaprolactone modified with 2% by weight of silica), PCL/TCP (polycaprolactone modified with 2% by weight of tricalcium phosphate).

**Group II** – poly-L/DL-lactide membranes: PLDLA (reference), PLDLA/$SiO_2$ (poly-L/DL-lactide modified with 2% by weight of silica), PLDLA/TCP (poly-L/DL-lactide modified with 2% by weight of tricalcium phosphate).

The tested biomaterials were placed in containers with physiological fluid (0.9% NaCl) and then placed inside the applicator spool of a Magner Plus magnetotherapy device by Astar (Fig. 1A). The samples were subjected to a pulsed magnetic field at the frequency of 20 Hz and a magnetic induction of 10 mT for a period of 30 minutes. The values were intended to reflect the settings used in the rehabilitation of small animal during the treatment of musculoskeletal system. Samples were placed on the inner edge of the ring applicator in the location where the generated magnetic field is known to reach the highest values. After drying, the samples were analysed to determine the effect of magnetic field stimulation on the morphology, physiochemistry and structure of the material.

The surface morphology of implants before and after stimulation with a magnetic field was analysed using the VHX-900 optical microscope. A more detailed microstructure analysis was conducted with using the NOVA NanoSEM scanning electron microscope (FEI, USA). Prior to the examination, the surface of the analysed specimens was coated with carbon (carbon layer thickness 500 μm). Physiochemical changes of membrane materials were determined by contact angle measurement with the sessile drop test (DSA 10 Mk2 Kruss goniometer). Five measurements the angle were performed, on the basis of which the mean value and the standard deviation were calculated. Furthermore, nanocomposite membrane materials were analysed by FTIR-ATR spectroscopy using an Excalibur FTS 3000 spectrometer, on a PIKE MIRacle diamond crystal. The samples from the control group were not subjected to any stimulation with a magnetic field.

# 3. Results

The measurement system proposed in the experiment was aimed at possibly accurate approximation of the environment in which the real implants are subjected to a pulsed magnetic field. In order to achieve this, samples submerged in an aqueous solution (physiological fluid) were exposed to magnetic stimulation in sequences corresponding to those typically recommended during rehabilitation. The exposure time was the longest single-procedure time applicable in the treatment of patients with injuries and the magnetic field parameters were in accordance with the manufacturer's recommendations for such procedures. Material subjected to two synergistic environmental factors: physiological fluid solution and pulsed morphology changes.

The microscopic observations of materials subjected to magnetic field stimulation compared to the starting material carried out using optical microscope revealed no significant changes in the morphology changes (Fig. 1B, D, F). Visible cracks were caused due by manipulation of the material when placing it inside the chamber of the apparatus (Fig. 1C, E, G). The same can be observed in case of the membrane modified with nanometric TCP, which is not a surprise, taking the results of previous studies into account. Mechanical tests revealed that this material is the most rigid and the least durable [17].

A more detailed microscopic analysis with the use of a scanning microscope (Fig. 2A–F) indicated the highest extent of degradation in PCL/TCP membranes; the membrane pores were significantly deformed compared to the surface of the starting material (Fig. 2E–F). The reference membrane also showed signs of degradation, with significant surface changes observed: increased number of pores and impaired material continuity. The modification of PCL matrix with nanometric silica seemed to increase the material's resistance to environmental impact: not surface changes were observed (Fig. 2 C–D).

Subsequent analyses concerned physiochemical changes of the tested materials. After exposure to pulsed magnetic field stimulation, the membranes became more hydrophobic, compared to the starting biomaterial (Table 1). Exposure to the magnetic field caused not only changes in the surface morphology (SEM) but also affected wettability as a result of degradation of the membrane material. The highest degree of degradation was again confirmed in the case of PCL (angle changed by 25%) and PCL/TCP (angle changed by 43%) compared to the starting materials.

Changes in the analysed materials were also analysed at the molecular level. The spectra obtained from FTIR-ATR examinations were identical for both modified and reference membranes, furthermore no significant spectral differences were observed for materials subjected to magnetic field stimulation.

Materials based on PLDLA matrix, constituting the second group of materials tested, were also exposed to stimulation with the magnetic field in the aqueous environment and the influence of this exposure was evaluated using the same methods as mentioned above. Microscopic analysis with an optical microscope revealed no significant difference between membranes before and after exposure. Pores of similar sizes and shapes, and overall similar membrane morphology was observed regardless of the modifier used as well as its absence (Fig. 3A–F).

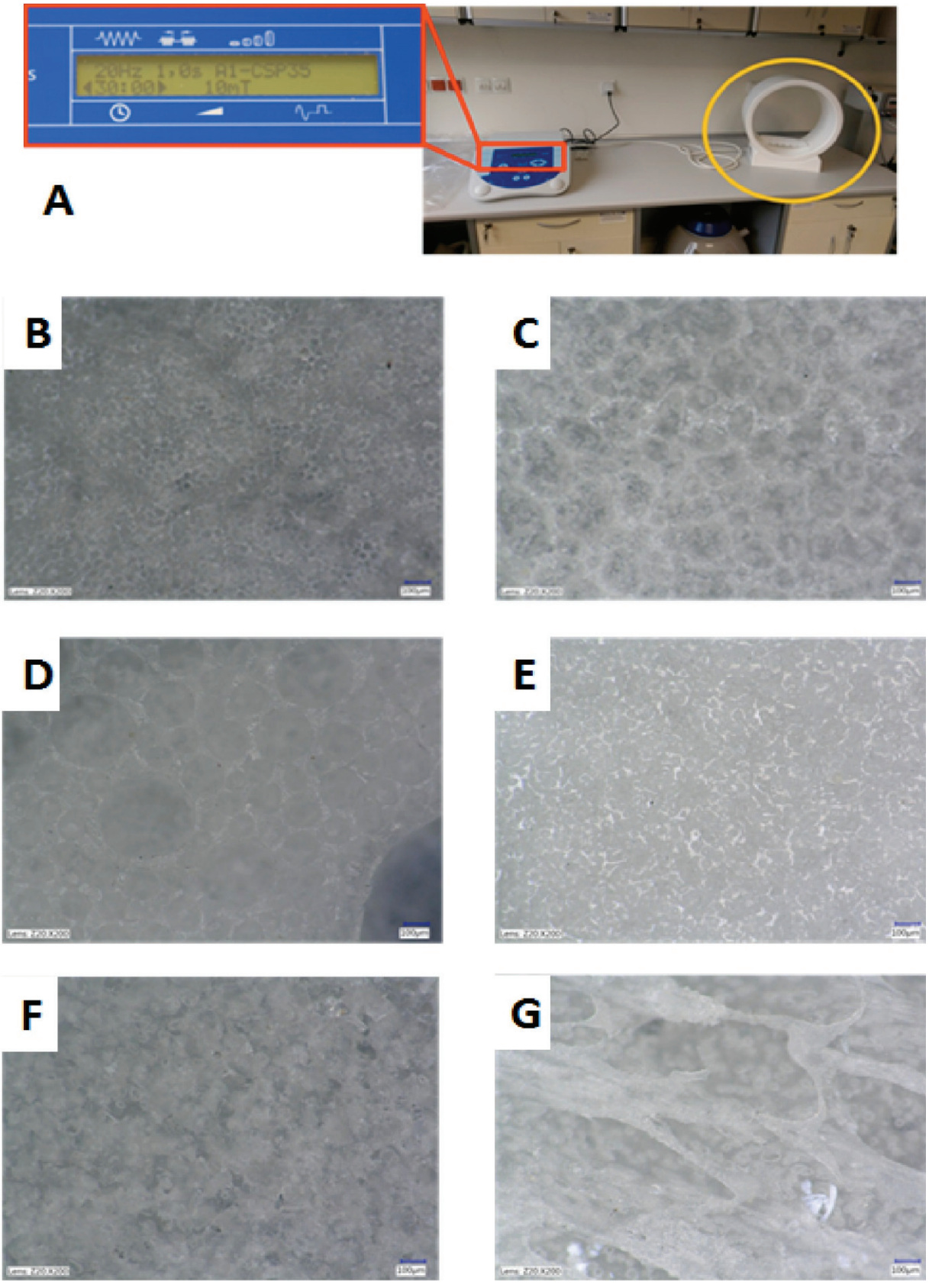


Fig. 1. The apparatus for magnetotherapy and its chamber in which the analysed samples were placed (A). Surfaces of the analysed implant materials: starting PCL membrane (B), after magnetic stimulation (C), starting PCL/$SiO_2$ membrane (D), PCL/$SiO_2$ membrane after magnetic stimulation (E), starting PCL/TCP membrane (F), after magnetic stimulation (G)

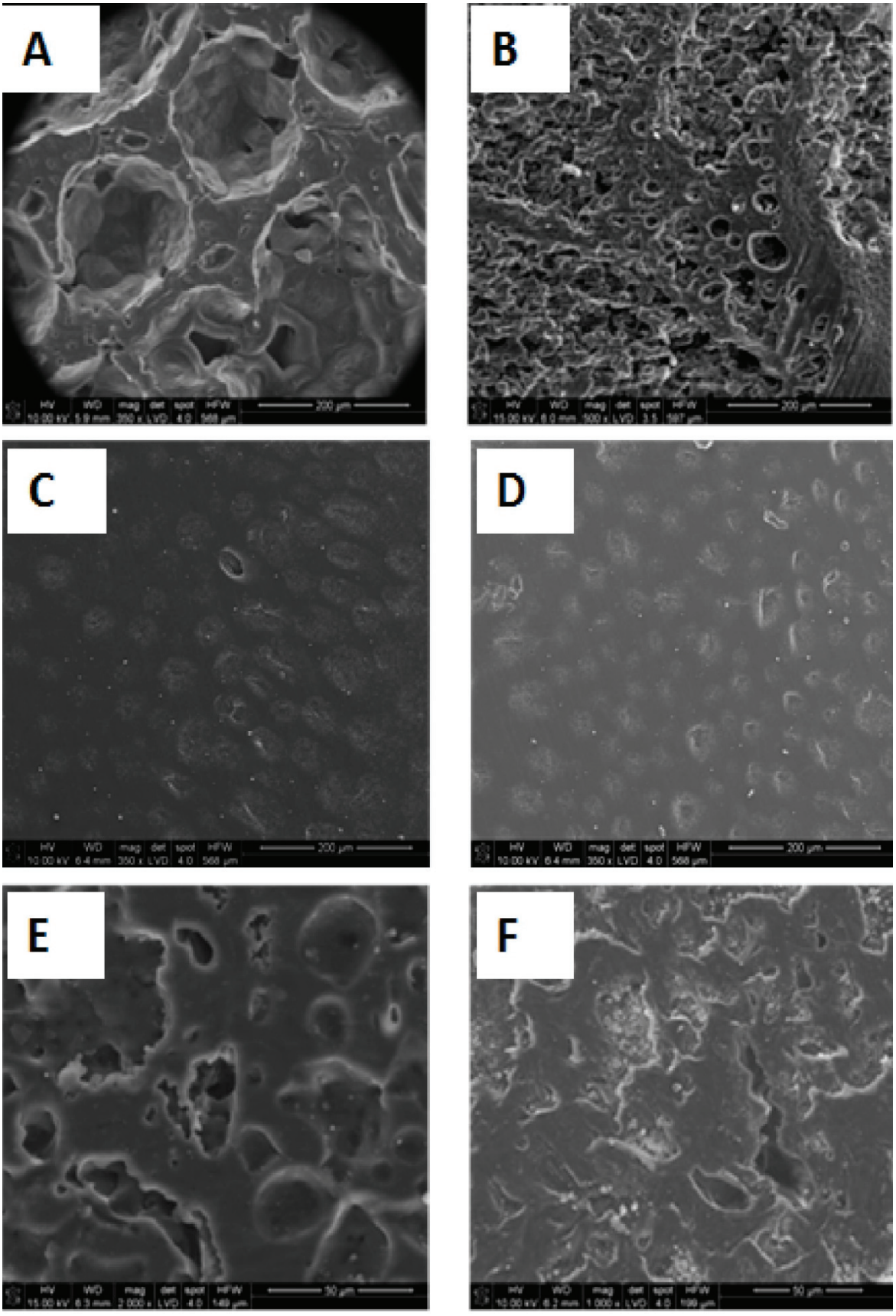


Fig. 2. Electron microscopy images of membranes before and after magnetotherapy: PCL membrane before (A) and after magnetotherapy (B), PCL/$SiO_2$ membrane before (C) and after magnetotherapy (D), PCL/TCP membrane before (E) and after magnetotherapy (F)

Table 1. Changes in the contact angle in the analysed PCL-based material before and after exposure to the pulsed magnetic field

| Material | Initial contact angle [°] | Contact angle after exposure to magnetic field [°] |
|---|---|---|
| PCL | 78 ± 2.7 | 98.1 ± 5 |
| PCL/$SiO_2$ | 49.8 ± 4.6 | 73.5 ± 4.81 |
| PCL/TCP | 81.5 ± 3.1 | 116.4 ± 5.2 |

Only the analysis of images obtained from the observations in the scanning electron microscope allowed to distinguish the differences in the morphology of the membranes subjected to the magnetic field stimulation (Fig. 4A–F). Visible changes in pore shape were observed only in materials modified with $SiO_2$ (Fig. 4C–D) and TCP (Fig. 4E–F) nanoparticles. Enlargement of pores (by approx. 15% for TCP and 8% for $SiO_2$), deformation of their shapes, and, above all,

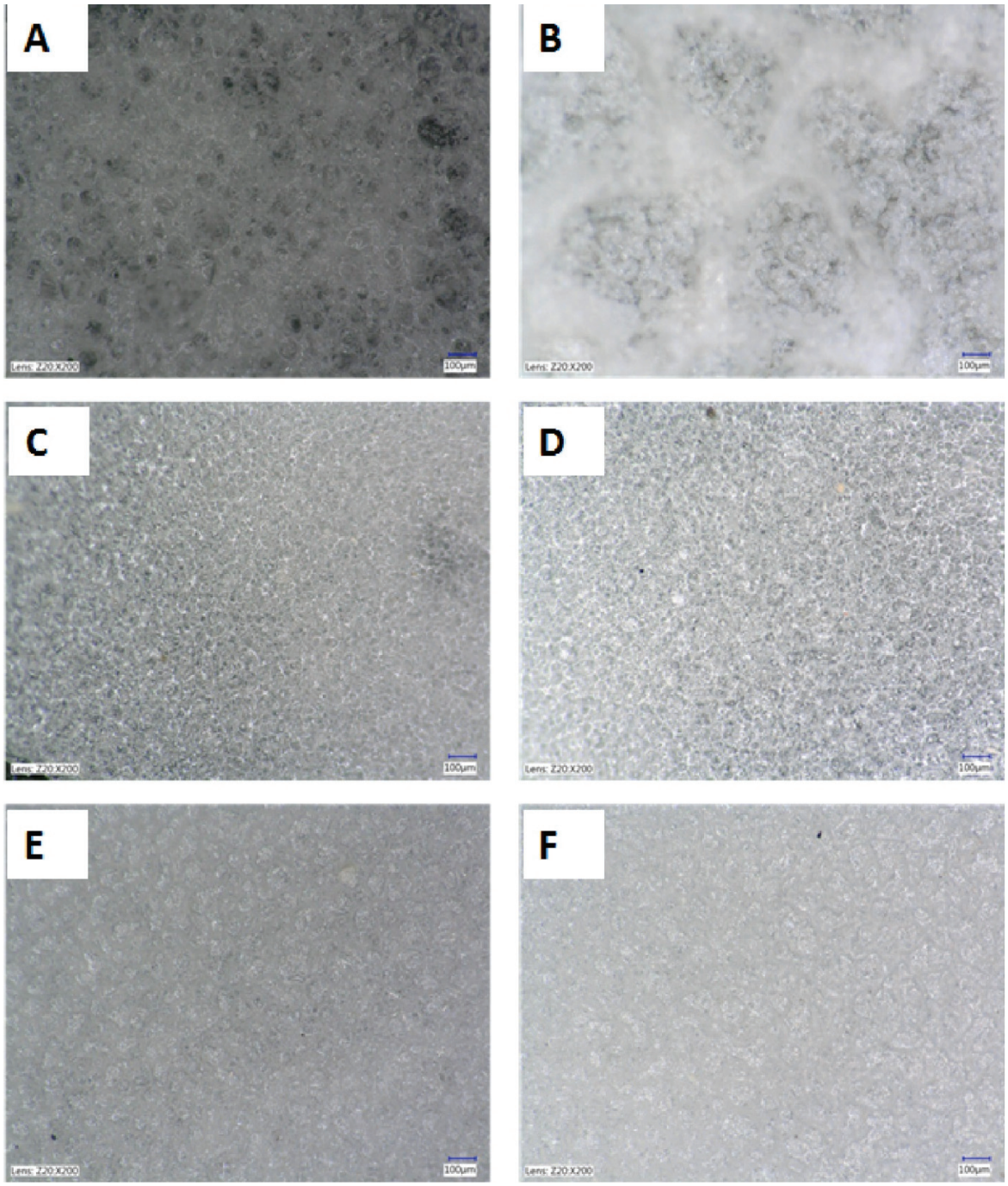


Fig. 3. Surfaces of the analysed PLDLA-based implant materials: starting membrane (A), after magnetotherapy (B), starting PLDLA/$SiO_2$ membrane (C), PLDLA/$SiO_2$ membrane after exposure to magnetic field (D), starting PLDLA/TCP membrane (E) after exposure to magnetic field (F)

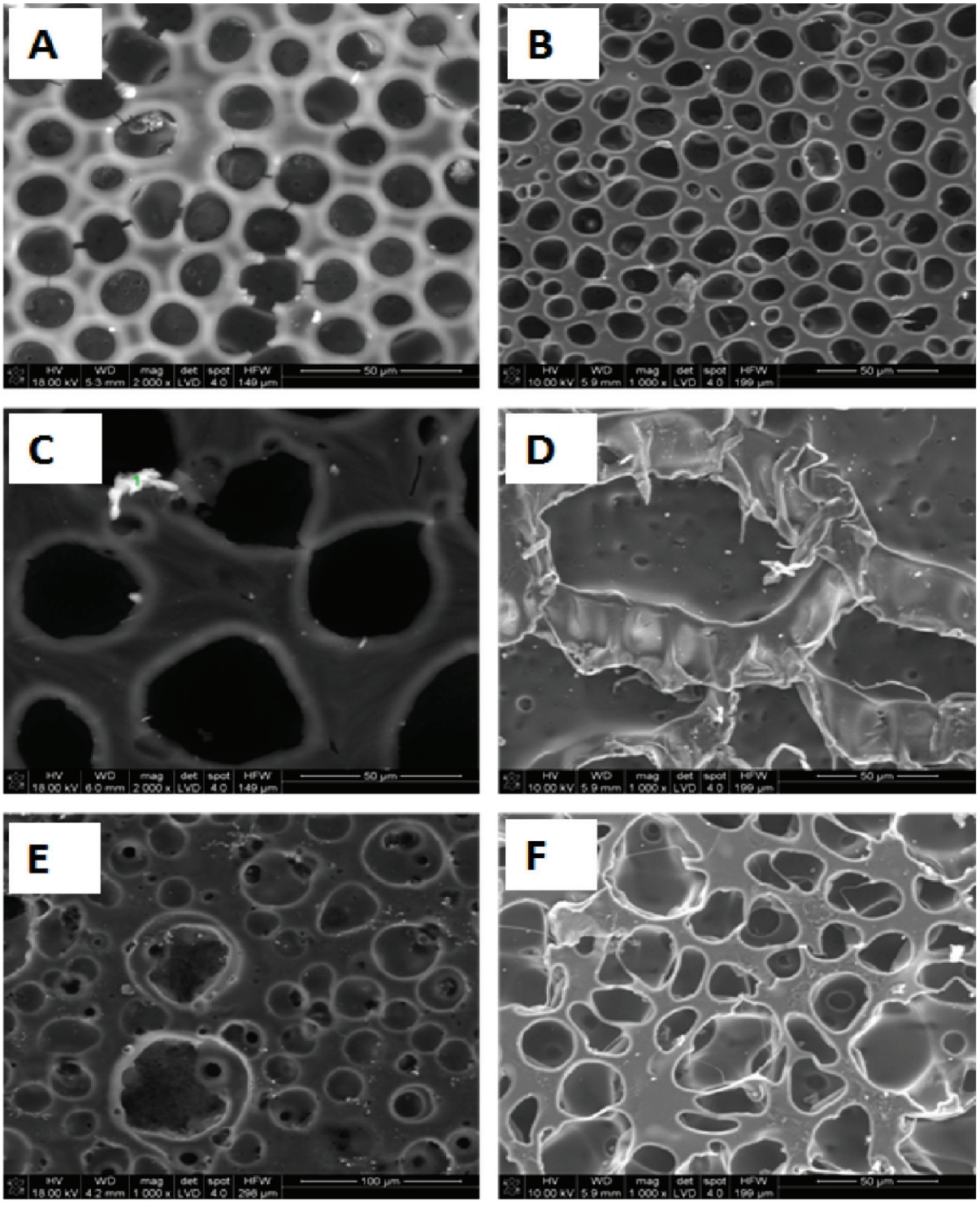


Fig. 4. Electron microscopy images of membranes before and after magnetotherapy: PLDLA membrane before (A) and after magnetotherapy (B), PLDLA/$SiO_2$ membrane before (C) and after magnetotherapy (D), PLDLA/TCP membrane before (E) and after magnetotherapy (F)

irregular (torn-like) pore boundaries prove that the PLDLA/$SiO^2$ and PLDLA/TCP materials degradation process has been started. This is most likely caused by the presence of nanoparticles, as the unmodified PLDLA membranes did not show such changes (Fig. 4A–B).

In the case of PLDLA-based membranes, environmental factors inducing degradation changes influenced a change in the surface wettability of at least 40% (Table 2). The above effect was stronger in the case of materials with PLDLA matrices containing nanoparticles of modifiers: $SiO_2$ or TCP, and eventually

all materials became hydrophobic (contact angle approx. 100°). This means that the polymer chains were shortened and gained some degree of mobility (possible changes with respect to conformation and exposition of functional groups with a more hydrophobic character).

Table 2. Changes in the contact angle in the analysed PLDLA-based materials before and after exposure to the pulsed magnetic field

| Material | Initial contact angle [°] | Contact angle after exposure to magnetic field [°] |
|---|---|---|
| PLDLA | 67.3 ± 3.15 | 101.1 ± 7.1 |
| PLDLA/$SiO_2$ | 62.8 ± 2.87 | 102.9 ± 5.4 |
| PLDLA/TCP | 57.5 ± 1.75 | 100.5 ± 4.2 |

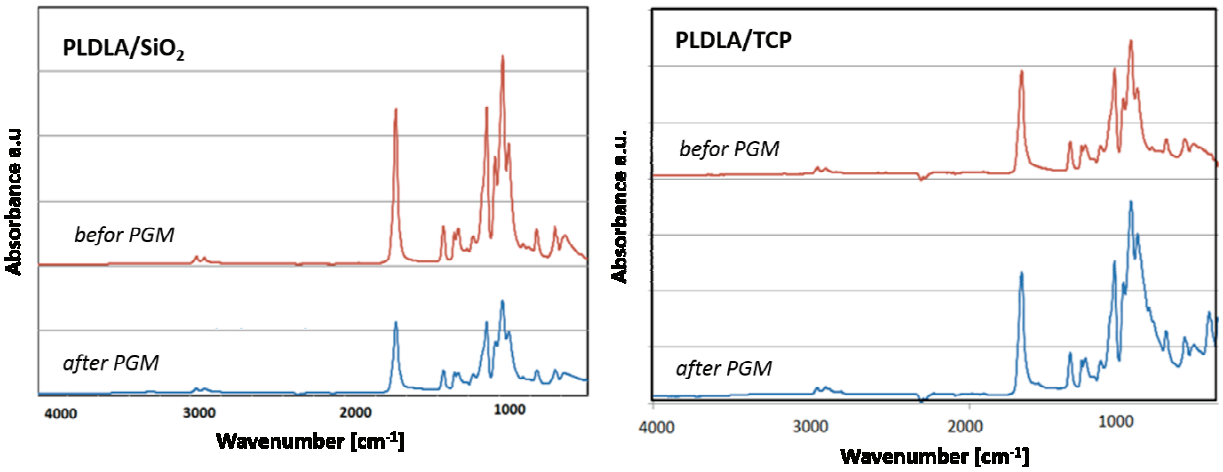


Fig. 5. FTIR-ATR spectra for PLDLA/$SiO_2$ and PLDLA/TCP membranes, before and after exposure to magnetic field

Changes in chemical structure PLDLA/TCP can be observed based on the bands in the range from 2800 to 2900 $cm^{-1}$ which correspond to the vibrations of the $CH_3/CH_2$ groups while the band at 1150 $cm^{-1}$ is associated with the vibrations of the COC group. Both of these bands are visible in the spectra of PLDLA after exposure to magnetic field stimulation (Fig. 5). Furthermore, the post-degradation spectrum of PLDLA/TCP includes visible bands originating from phosphate groups, which indicates a better visibility of the marker in the matrix and evidences the mobility of the polymer chain (band at 890 $cm^{-1}$).

# 4. Discussion

Surgical techniques employed in orthopaedics and traumatology increasingly rely on the use of implant materials, and, because magnetic fields are able to penetrate all body tissues, it is also important to determine the mechanism by which magnetic field affect the implant materials used in surgery.

During the post-operative period, it was observed that magnetic field therapy reduces the swelling of soft tissues, facilitates circulation at the site of injury as well as has analgesic and relaxation properties. The mechanism of the magnetic field effect on soft tissue is complex and entails increasing the secretion of intracellular calcium ions $Ca^{2+}$, increasing the production of NO, increasing the productioPTEn of bone morphogenetic protein BMP as well as increasing the amount of ATP. The above effects help to accelerate tissue healing processes, reduce susceptibility to inflammation and improve microcirculation in tissues [6], [15].

To date, studies on the influence of magnetic fields on healing processes in the presence of biomaterials have focussed primarily on the response of living tissues to the therapy applied. Mohammandi et al. [10] described the beneficial impact of magnetic stimulation on sciatic nerve regeneration in a rat with the presence of a chitosan implant. Veronesi [18] demonstrated the beneficial effect of magnetic fields on the integration of titan implants in bone tissue. However, so far, there have been no reports regarding the effect of exposure to magnetic field on the durability of the implants themselves, which can be especially crucial in the cases when they are an integral element of the surgical intervention.

The described attempt to determine the effect of magnetic field exposure on the durability of polymeric biomaterials in the form of model implants (membranes) revealed that the analysed materials are not sensitive to the influence of a pulsed magnetic field.

The observed changes were similar to those described in the literature where the actual factor inducing the degeneration was the aqueous environment [12], [13], [16]. Easier migration of water into the polymer matrix leads to a decrease in molecular mass, which is reflected in the mechanical parameters of the material that becomes more brittle [17]. Another symptom of the hydrolysis is the change in surface parameters: deformations, cracks and surface erosion observed in the scanning microscope appear hear. However, the degree of hydrolysis is negligible compared to data known from the literature [13], [16], in which, as shown by earlier studies on the analysed materials, hydrolytic degradation could quickly lead to material decomposition [12], [17]. In the studies described in this work, despite the combined effects of the aqueous environment and the magnetic field, visible changes did not result in destruction of the material. In the case of PCL no chemical changes were observed while in the case of PLDLA the changes occurred only in a very limited extent (FTIR data). The obtained results also indicate that a very important factor determining the durability of the implant the presence of a second phase (nanofiller) in the polymer matrix. As it is known form other works, it accelerates the degradation polyhydroxy acids in the PLDAL/$SiO_2$ materials [8]. The same effect is also evident in the present study, and the presence of TCP and $SiO_2$ clearly affects (though to a lesser extent) the initiation of material degradation. This phenomenon should be linked to the influence of nanoparticles, which form a water reservoir and initiate the process of bulk degradation. As a consequence, the increased area under the bands referred to the vibrations of $CH_3/CH_2$ groups and COC bonds is clearly visible the spectra. The number of these groups in turn influences the state of the surface causing an increase in its hydrophobicity (methylene and methyl groups are hydrophobic, as well as COC bond). Thus, observed phenomena occur far more likely as a result of contact and interaction with the aqueous environment than in the effect of exposure to alternating pulsed magnetic field.

# 5. Conclusions

The magnetic fields generated by standard devices used in rehabilitation does not significantly influence the structure and selected physiochemical properties of biomaterials produced on the basis of PCL and PLDLA polymeric matrices. The observed changes result from the synergistic effect of the aqueous environment, which triggers hydrolytic degradation processes in polymer materials. This model study suggests that the use of magnetotherapy to stimulate healing processes is indeed safe. Nevertheless, further studies are necessary to determine the stability of implants and their degradation under real *in vivo* conditions.

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