Preparation Possibilities and Examination of Calcium alginate UHMWPE blends

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***Abstract*—** *Previous researches were made on UHMWPE (Ultra-High-Molecular-Weight-Polyethylene) based implant material and its fusion with Ca-alginate. New methods were made for preparing UHMWPE-Ca-alginate blends. If the coating Ca-alginate salt can be achieved on the surface of UHMWPE, it might lead to an implant material which could promote the bone formation. Earlier results show that we can make the coating layer on the polymer powder surface. Our new approach is to modify the method we made earlier, and this way the alginate layer can withstand washing and sterilization as it's shown in the paper. We also realized that the layer slowly can give off Ca2+ ions which can be absorbed with specific cells. Since we modified the surface structure of the UHMWPE samples we carried out wear testing of the new prepared samples. All of these measurements and experiments have been done as preparative ones to make one time real prosthetic material.*

***Keywords*— UHMWPE, Na-alginate, Ca-alginate.**

I. INTRODUCTION

Previous research was carried out based on the work of Jian-Ping Wang, Xing-Xiang-Zhang, Xue-Chen Wang (1). As we had earlier experienced with UHMWPE implant materials, by modifying the surface properties of it using acrylate type monomersits wear resistance was enhanced, it was interesting to evaluate if further surface modifying would improve the biocompatibility of the prosthetic material (2).

We had a previous surface modification method experience with methyl-methacrylate monomer (MMA) (3,4) which didn't work with the hydrophillic alginate material. So after that we worked powder type of UHMWPE raw material. We made basic experiments with GUR 4210 UHMWE powder to form an alginate layer which could trap calcium from calcium solutions; we also have determined the optimal sequence of the treatments, and the necessity of etching the UHMWPE powder (5).

We used GUR 1020 UHMWPE powder for all of our experiments and we made two methods for making insoluble alginate layers. After preparation of the samples, morphological examinations, Ca2- ion extraction tests and wear tests were carried out (6,7,8)

II. APPLIED METHODS AND MATERIALS

Two methods were carried out to form the calcinated alginate layer on UHMWPE powder. The first method: First step was to make 1 wt% sodium alginate's (ISP Alginate) insoluble aquaneous solution and calcium chloride solution (2 wt% aquaneous solution). In this method the solutions were mixed and sprayed onto the polymer powder.

The second: The materials were the same but we used calcium sulphate despite of calcium chlorid. The methods were repeated in reverse order as well. First, the treatment with the Ca-salt solution then the alginate sprays coating. For all of the treatment we used HUR 1020 UHMWPE powder (average molecular weight: 4x10^6 g/mol (Mw).

The samples were dried at 50°C for 1 day. The treated and untreated UHMWPE powder was compressed into sheets at 175°C. After the forming, 35 kGy gamma irradiation followed, simulating sterilization of implant components and the irradiation might make bounds between the alginate and polymer chains.

III. MEASUREMENTS

We made different types of measurements to check the alginate content on the surface of the blends.

3.1 FTIR spectra

FTIR (Bruker Tensor 27) tests were made to answer whether the surface of the treated UHMWPE powder held the alginate and what forms we could find on it. We expected from the results that we would have been able to choose the most successful method to bind the Ca on the surface of the UHMWPE powder

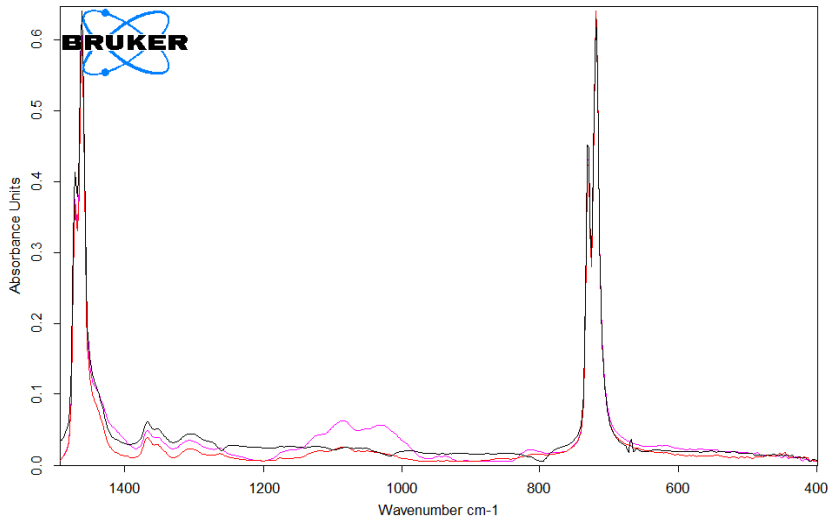

FIGURE.1. FTIR spectra on pressed UHMWPE alginate blend sheets (Black – GUR1020; Magenta – GUR1020-CaSO4-alginated blend, Red – GUR1020-CaCl2-alginated blend)

After the powders were treated (pressing and irradiation) we hoped that the FTIR curves will show us alginte absorption peaks. The sodium alginate is water soluble and the calcium alginate is not. If we can see any peaks about the alginate this would be the best for us, because it was our aim. After the alginated powders have been pressed into sheets, FTIR measurements were carried out to check the alginate's presence in the sample. The $CaSO_4$ treated samples gave higher peaks between 1080 and 1050 cm^{-1} wave numbers in the spectra than the $CaCl_2$ treated ones. (Fig.1.)

We also tested the presence of the alginate components after irradiation. The result is that the samples show less alginate content but it is still present on the surface of the blends. (Fig.2.)

After both treatments ($CaCl_2$ and $CaSO_4$) the FTIR spectra showed alginate peaks between 1750 and 750 cm^{-1} wave numbers.(Fig.3.)

In case of the samples prepared by the "direct order", the spectra showed higher alginate content.

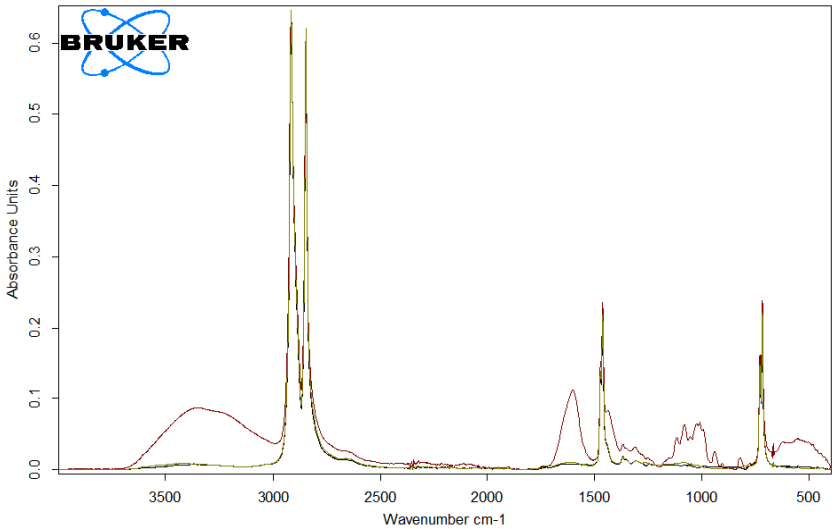

FIGURE 2. FTIR spectra on pressed and irradiated UHMWPE CaCl2-alginated blend sheets (Black – GUR1020; Red – GUR1020-CaCl2-alginated blend, Gold – GUR1020-CaCl2-alginated blend after irradiation treatment)

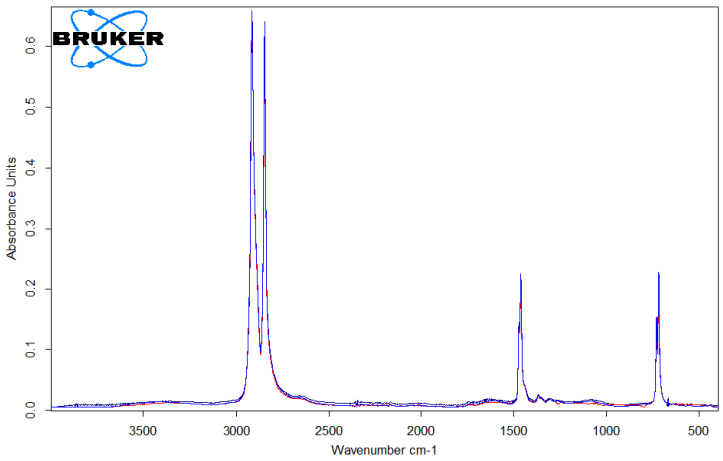

FIGURE 3. FTIR spectra on irradiated UHMWPE alginated blend sheets after irradiation treatment (Red – GUR1020; Blue – GUR1020-CaCl2-alginated blend, Dark blue – GUR1020-CaSO4-alginated blend)

3.2 Tribological tests

For the wear tests we also used the samples which had been prepared by using the "direct" order, first alginate and than Calcium treatment.

We made wear tests on our specimens CMS pin-on-disc tribometer with the pin material of 6Cr100 chromium bearing steel 6 mm diameter polished spherical surface roughness of Ra~0,01 μm. The loading normal force was 10 N and the rotation speed 10 cm/sec and we set the wearind distance to 1000 m. The tribological tests were performed along a circle with a radius of 8 mm at room temperatures.

The resulting traces of wear on the samples were measured using 3+Surtronic wear profile measurer, and the deformed volume was calculated from the results.

TABLE 1
THE DEFORMATION RESULTS ON ALGINATED UHMWPE BLENDS

Material	Deformed volume (μm^3)
UHMWPE	192.43
CaCl2-alginated UHMWPE	54.51
CaSO4-alginated UHMWPE	102.18

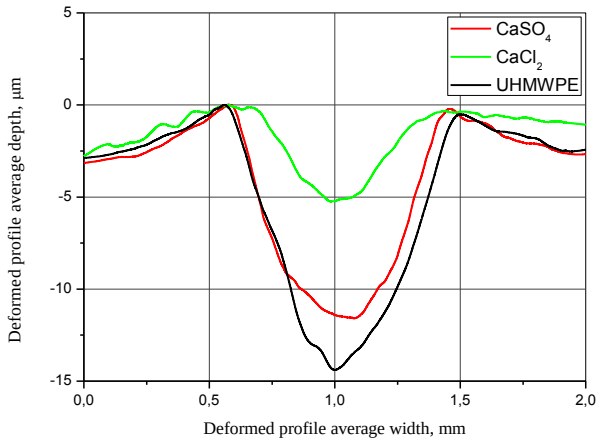

FIGURE 4. Profile curve measurement results on irradiated UHMWPE alginated blend sheets after irradiation treatment
(Black – GUR1020, Green – GUR1020-CaCl2-alginated blend, Red – GUR1020-CaSO4-alginated blend)

The results showed that the $CaSO_4$ treatment had reduced the wear deformation to the half of the original, while the $CaCl_2$ treatment had reduced it further to the quarter of it.

The profile curves showed these differences as well. The normal UHMWPE deformed paths are wider and deeper than the Ca-alginate containing samples paths.

3.3 ICP measurements for determining Ca(II) ion release

Migration behavior of the Calcium (II) ions was evaluated using extraction method, where the samples were kept in distilled water and also in isotonic salt solutions for 24 and 48 hours. The change in Ca2- content was measured using SF-ICP-MS method. The Sector Field Inductive Coupled Plasma Mass Spectrometry uses Radio frequency (RF) plasma to vaporize and ionise the solution containing the materials of interest and introduces it to a mass spectrometer using magnetic sectors to diverge the ions flying trough by mass. These instruments have much higher resolution than the simpler mass spectrometers using quadruple analyzators.

The ICP measurements were carried out on all of the samples which were made by both "direct" and reversed order methods.

The ICP measurements' results show Calcium can migrate from the blend materials. The dissolved Calcium's quantity depends on the previous treatment.

TABLE.2.
The results of ICP measurements on UHMWPE and Ca-alginated-UHMWPE blends

Material	Calcium content (mg/l)
UHMWPE	0.0534
CaCl2-alginated UHMWPE direct order	2,5140
CaCl2-alginated UHMWPE reversed order	4.1795
CaSO4-alginated UHMWPE direct order	0.8477
CaSO4-alginated UHMWPE reversed order	0.5902

The results show that the blends formed using $CaCl_2$-algination could emit more Ca^{2-}-ions to the water or isotonic salt solutions than UHMWPE blends made using $CaSO_4$-algination. The method of sample preparation (using direct order or reversed order layer preparation) did not influence the amount of released Ca^{2-} ions only the quality of the Ca ion source materials ($CaCl_2$ or $CaSO_4$ salt).

3.4 Estimation of the degree of cross linking by determination of the gel content

This measurement was carried out by an international standard ISO 10147:2011 which is especially made for polyethylene materials.

As it is above the samples were irradiated by gamma radiation with 35 kGy energy. We wanted to know how bounds affected by the treatments. The procedure is to make test pieces and boil them in a solvent for specified time and temperature. The mass of the test pieces were measured before and after immersion. The degree of crosslinking is expressed as the percentage by mass of the insoluble material. The following apparatus was required in order to carry out the test: reflux condenser, round bottom flask of at least 500 ml capacity, heating mantle (boiling range: 137°C to 144°C), cage for holding the sample pieces during the test. The solvent was xylane, an isomeric mixture with a purity of 98 % volume fraction.

The test pieces were prepared in accordance with the following instructions. Each test piece shall comprise a slice or shaving, having a thickness of 0,2 (± 0,02) mm, taken from the cross section of the sample includes the full wall thickness. The mass of the test pieces must be 0,2 g. This part of the preparation was handmade by a mechanical machine. 8 to 12 slices were made on average in case of every sample after they had been placed into a stainless cage. The mass of the test pieces were measured before placing into the cage and with the cage as well. Finally the cages were placed into the round-bottomed flask and filled them with xylane and 1 % mass of 1076 irganox antioxidant was added as the last step. The process lasted 8 hours after the solvent was boiling.

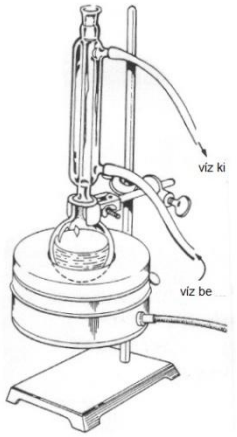

FIGURE 5. Schematic figure of the measure method

After the procedure the test pieces must be dried by placing them for at least 3 hours in a vacuum oven, kept at 90(±2)°C under vacuum (negative pressure) for at least 0,85 bar. This is approximately 0,15 bar absolute pressure or less. Finally it is allowed to cool ambient temperature and weight the residue or the cage.

TABLE 3
DATA'S BEFORE THE PROCESS

Sample	Cage mass (g)	Mass of sample (g)
5	4,0865	0,1988
7	4,0355	0,2036
Virgin	3,9574	0,2028

This was important because we wanted to experience the degree of the crosslinking of the samples against the virgin material. The difference might cause mechanical and physical changes in the material. We needed 120 g xylane and 1 g of antioxidant.

TABLE 4
DATA'S AFTER THE PROCESS

Sample	Sample mass (g)	Sample mass after process (g)	Crosslinking percent (%)
5	0,1988	0,1543	77,615
7	0,2036	0,133	65,324
Virgin	0,2028	0,1418	69,921

The results show that in case of sample number 5 ($CaCl_2$ direct order) we experienced more than 10% higher crosslinking percent than the virgin material. We can think after this data that the raw material and the calcium solution could make bounds between each other. In case of sample number 7 ($CaSO_4$ direct order) we experienced lower crosslinking percent. The less percent may mean less bounds between the raw material and the alginate solution.

$$\text{crosslinking percent} = \frac{\text{mass of the sample after boiling}}{\text{mass of the sample before boiling}} \times 100\% \quad (1)$$

The higher percent means a more seristable and more homogene material. That was the cause why the sample 5 had higher resistance against linear tribological test

IV. CONCLUSION

The completed treatments proved they are suitable for fixating Calcium(II) ions on UHMWPE polymer surfaces. The polymer powder is capable to bind with the surface of the sodium alginate and is able to hold the created calcium alginate during processing and after the 35 kGy irradiation process. The radiation did not affect the behavior and properties of the

alginate salts. The presence of calcium alginate on the surface was proved with great confidence using FTIR measurements. The wear tests and the extraction experiments are still in progress.

It was also proved, that the created Ca-alginate layers can release the bonded Ca(II) ions in time which under specific conditions can promote bone growth or at least make the implants more tissue and bone friendly, thus more acceptable by their surroundings. It is also important to do further experimental work on the kinetics of the Ca(II) ion release process, and to work on the promotion of calcium uptake into the neighboring tissues.

All of these measurements and experiments were done as preparative ones to make one time real prosthetic material. We worked with GUR 1020 UHMWPE powder and we also would like to carry out these experiments on a production UHMWPE hip joint cup to check whether the alginate layer is able to add to the surface.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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