Tribological Examination of Calcium alginate – UHMWPE blends

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Abstract**—** *Continuing our previous researches on UHMWPE (Ultra-High- Molecular-Weight Polyethylene) based implant material and its fusion with Ca-alginate, we describe new methods for preparing Ca-alginate blended UHMWPE samples and how we extended the testing of the prepared samples. If sufficient content of Ca-alginate can be achieved and the Calcium-alginate blended UHMWPE can be made, it might lead to an implant material which can promote bone formation. Earlier result shows that the Calcium–alginate contentwill be formed in the structure of UHMWPE. Using our new modified methods we can make polyethylene samples with sufficiently tough alginate content which can withstand washing and sterilization as that is shown in the paper. Since we had modified the UHMWPE specimens with Ca-alginates we carried out different types of wear testing on the prepared samples.*

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

I. INTRODUCTION

According to our earlier experience with UHMWPE implant materials, by modifying the surface properties of these materials using acrylate type monomers and thereby enhancing its wear resistance, it was our special interest to evaluate whether further surface modifying would improve the biocompatibility of the prosthetic material [1-3]. We realized quite early that the same method of bulk surface modification, which had been worked well with materials like methyl-methcrylate monomer (MMA) [4,5], would not yield a useful surface with the hydrophilic alginate material. That prompted us to work with powder type UHMWPE. We made basic experiments with GUR 4210 UHMWE powder to form an alginate coating which could trap calcium from calcium solutions; we determined the optimal sequence of the treatments, and the necessity of etching the UHMWPE powder [6].

We used GUR 1020 UHMWE powder for the majority of our experiments described here, and we carried out two different modification methods in order to form insoluble alginate layers. After preparation of the samples, morphological examinations, Ca^{2+} ion extraction tests and wear tests were carried out [7-9].

II. APPLIED METHODS AND MATERIALS

The used UHMWPE material is GUR 1020 (Average molecular weight: 4×10^6 g/mol (Mw)) powder.

Two different methods were used in order to form the calcinated alginate layer.

First method: In the first step the sodium alginate's (ISP Alginates) aqueous solution (2 wt% solution) and then the calcium chloride (2 wt% aqueous solution) was sprayed onto the polymer powder.

Second method: In the first step the sodium alginate (ISP Alginates) solution (2 wt% aqueous solution) then the calcium sulfate (2 wt% aqueous solution) was sprayed onto the polymer powder. This order of steps is considered as the "direct" order.

The methods were repeated in a reverse order as well. First, the treatment with the Ca-salt solution then the alginate spray coating.

The samples were heated at 50 °C for 1 day. The treated and untreated UHMWPE powder was compressed into sheets at 175 °C. After the forming, 20 kGy gamma irradiation followed, simulating sterilization of implant components.

III. MEASUREMENTS

We used FTIR spectra to check the alginate content on the surface of the blends.

3.1 FTIR spectra

FTIR tests were carried out by Bruker Tensor 27 instrument in ATR mode, with 64 scans.

After the alginated powders had been pressed into the sheets, FTIR measurements were carried out to check the alginate's presence in the sample. The $CaSO_4$ treated samples caused higher peaks between 1080 and 1050 cm^{-1}vawe numbers in the spectra than the $CaCl_2$ treated ones. (Fig.1.)

After both treatments ($CaCl_2$ and $CaSO_4$) the FTIR spectra showed alginate peaks between 1750 and 750 cm^{-1} wave numbers. (Fig.2.)

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.3.)

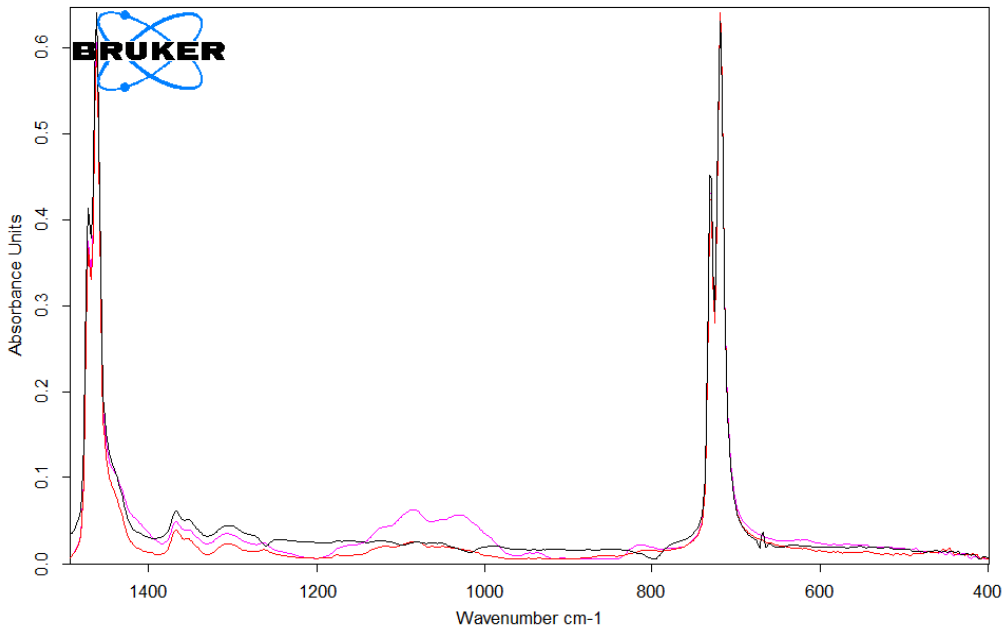

FIGURE.1: FTIR SPECTRA ON PRESSED UHMWPE ALGINATE BLEND SHEETS
(Black – GUR1020; Magenta – GUR1020-CaSO4-alginated blend, Red – GUR1020-CaCl2-alginated blend)

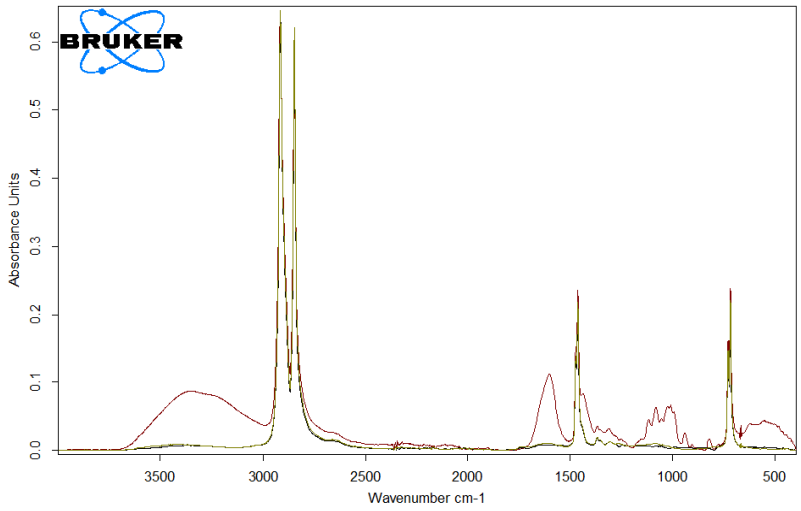

FIGURE.2: FTIR SPECTRA ON PRESSED AND IRRADIATED UHMWPE CACL2-ALGINATED BLEND SHEETS

(Black – GUR1020; Red – GUR1020-$CaCl_2$-alginated blend, Gold – GUR1020-$CaCl_2$-alginated blend after irradiation treatment)

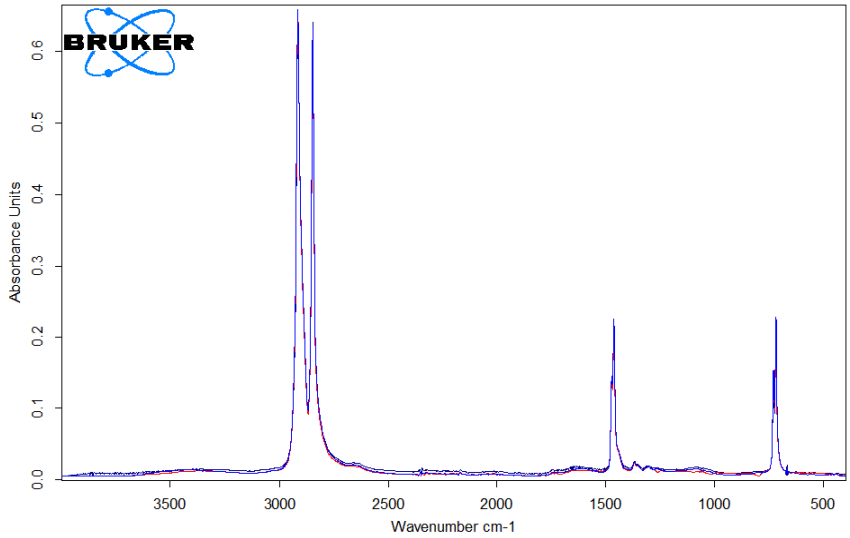

FIGURE.3: FTIR SPECTRA ON IRRADIATED UHMWPE ALGINATED BLEND SHEETS AFTER IRRADIATION TREATMENT

(Red – GUR1020; Blue – GUR1020-$CaCl_2$-alginated blend, Dark blue – GUR1020-$CaSO_4$-alginated blend)

3.2 Tribological tests

We also used the samples for the wear tests which had been prepared using the "direct" order, first alginate- than Calcium treatments.

Unidirectional wear test were carried out on samples using a CSM pin-on-disc tribometer. The pin material was 6Cr100 chromium bearing steel 6 mm diameter polished spherical surface with a surface roughness of Ra~0.01 μm. The loading normal force was 10 N, the rotation speed was 10 cm/s and the wearing distance was 1000m. The tribological tests were performed along a circle with a radius of 8 mm at room temperatures.

The resulting traces of wear on for the samples were measured using 3+Surtronic wear profile measurer, and from which the deformed volume was calculated (Fig.4. and Table 1.).

TABLE 1
THE DEFORMATION RESULTS ON ALGINATED UHMWPE BLENDS

Material	Deformed volume (μm^3)
UHMWPE	192.43
$CaCl_2$-alginated UHMWPE	54.51
$CaSO_4$-alginated UHMWPE	102.18

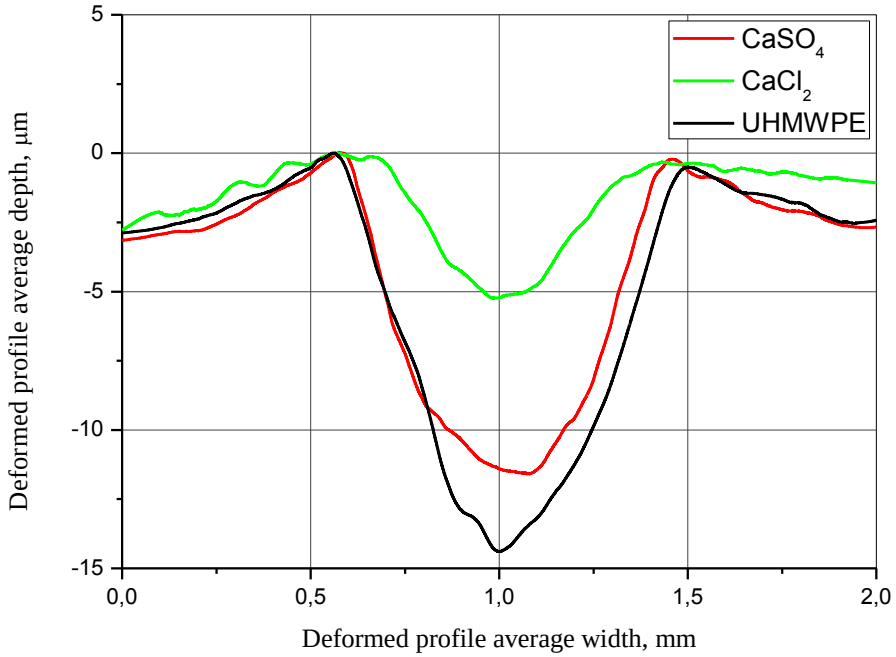

FIGURE.4: PROFILE CURVE MEASUREMENT RESULTS ON IRRADIATED UHMWPE ALGINATED BLEND SHEETS
(Black – GUR1020, Green – GUR1020-$CaCl_2$-alginated blend, Red – GUR1020-$CaSO_4$-alginated blend)

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

The profile curves show these differences as well, the normal UHMWPE deformed path is wider and deeper than the sample paths containing Ca-alginate.

3.3 Cross-shear wearing test

This type of measurement was important for us because the movement of the hip cause complex worn surface[1-3,10]. We chose a pentangle as the way to find out what happens at the cross points (Fig.5.). A CNC turning-lathe was used to make the measurement. The pin material was 6Cr100 chromium bearing steel 6, 75 mm diameter polished spherical surface with a surface roughness of Ra~0.01 μm. The loading normal force was 10 N, the speed was 1200 mm/min on a 55 mm distance with 5000 period. After all the periods we analysed the cross points of the pentangle with a microscope. In case of this type of wear measurement could be reproducing the real wear mechanism like in the hip joint. So we can analyse the debris size and shape could be possibly presence in case of these new materials. The debris size is important because these debris is irritated the phagocytes up to 10 μm [1,11-16].]

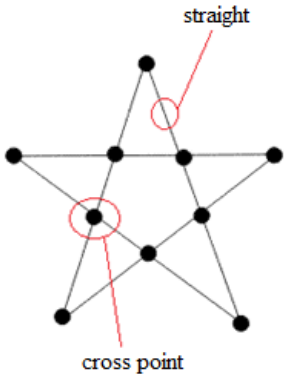

FIGURE 5: THE PENTANGLE CROSS SHEAR WEAR PROFILE

We made 25 x 25 mm samples for the measurements. After measuring 200x enlargement pictures had been formed to make debris analysis. Equal surfaces were used to evaluate how many debrises had got off from the surface of the cross point (Fig.6.).The reason why the debrises get offis that the bounds can not move any more and are getting weak by the time and finally brake. The size of the worn arewas smaller in case of the both Ca-alginated UHMWPEsamples than the virgin UHMWPE one (Table 2). An analyser process was used to determine the precise data's [17].

TABLE 2
RESULTS OF COMPUTER ANALYSIS

Sample	Average worn surface (μm^2)	Average worn surface in %	Worn area (piece)	Average diameter of worn area (µm)
UHMWPE	31,057.35	11.73	29.50	49.98
$CaCl_2$-alginated UHMWPE	50,250.33	18.98	53.67	35.99
$CaSO_4$-alginated UHMWPE	19,005.76	7.18	36.50	28.21

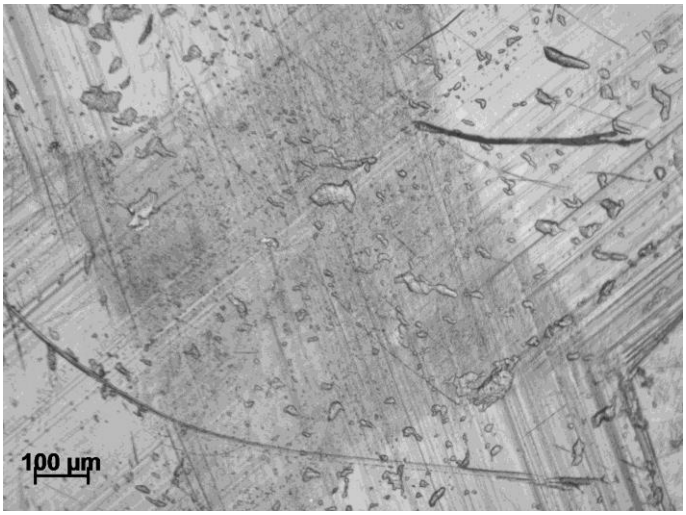

FIGURE 6: A MICROSCOPE RECORD ABOUT THE CROSS PATH ON THE UHMWPE SAMPLE

The overall analysed surface was 264,804 μm^2. We experienced the biggest worn surface in case of the $CaCl_2$-alginated UHMWPE sample. Both blends showed lower resistance against wearing in the amount of the worn area but they had smaller diameters than in the UHMWPE sample (Fig.7.). The smaller worn area could determine that the debris size could be smaller as well.

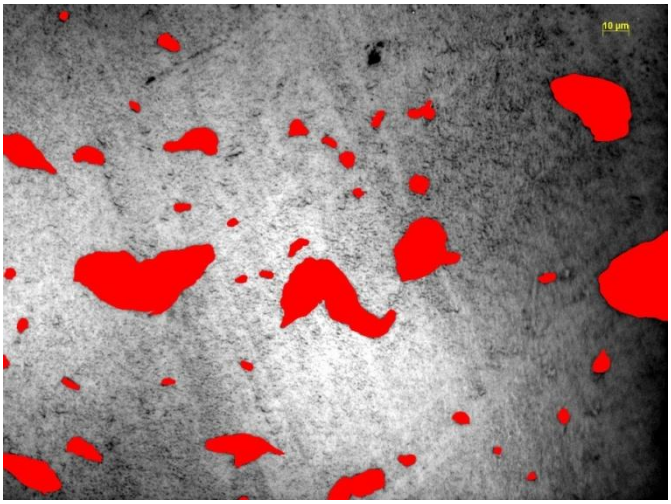

FIGURE 7: IMAGE OF $CaSO_4$-ALGINATED UHMWPE SAMPLEAFTERTHEANALISERPROCESS

The resulting traces of wear on for the samples were also measured using 3+Surtronic wear profile measurer, and from which the deformed volume was calculated (Fig.8. and Table 3).

TABLE 3
RESULTS OF THE PROFILE MEASURING METHOD

Sample	Average width (mm)	Average depth (µm)	The deepest point(µm)
UHMWPE	1.50	16.5	18
$CaCl_2$-alginated UHMWPE	1.50	19.5	21
$CaSO_4$-alginated UHMWPE	1.38	19.5	21

The results show that the average width and depth of the profiles are almost equal and the same could be observed in case of the deepest points. The cross-shear wear resistance properties of the alginate treated samples are as good as the virgin material. It may be because higher amount of volume got off from the surface in case of the alginated ones.

The debris came off from the surface because they cannot resist this type of various forces and they cannot orientate more. The bounds get weaker and after all they broke.

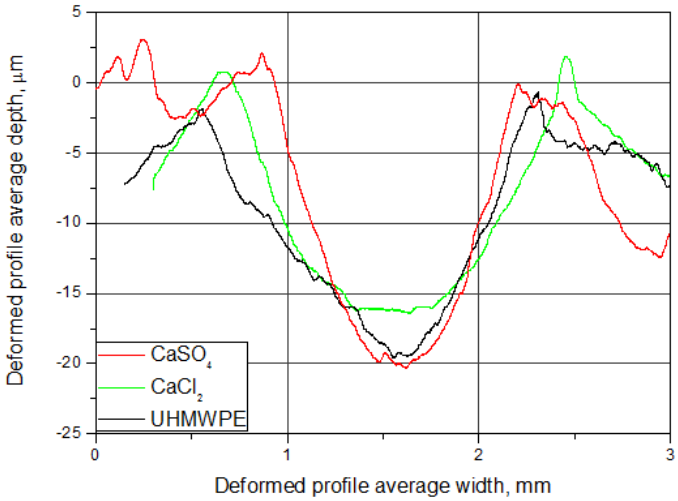

FIGURE 8: PROFILE CURVE MEASUREMENT RESULTS ON IRRADIATED UHMWPE ALGINATED BLEND ON THE CROSS PATH
(Black – GUR1020, Green – GUR1020-$CaCl_2$-alginated blend, Red – GUR1020-$CaSO_4$-alginated blend)

IV. SUMMARY

UHMWPE has beneficial properties and provides advantages for utilization in human body as a raw material for joint prosthesys. Using Ca-alginate as blend for could be introduces positive effect on the mechanical behavior of the polymer. This paper evaluates the two different types of UHMWPE - Ca-alginate blends unidirectional and cross-shear wear tribology properties. The unidirectional wearing properties could be increased with the both Ca-alginate treatments. The debris sizes also decreasing in the cross-shear pathes, but the deformed cross -section profiles of paths are not decreased efficiently. Our experiments were carried out on GUR 1020 UHMWPE powder. We would also like to carry out these tests on production UHMWPE hip joint cups too, to check that the alginate is able to adhere to the surface of a processed hip joint cup. All of these measurements and experiments were done as preparative ones to make one time real prosthetic material.

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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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