EXPERIMENTAL DETERMINATIONS OF THE TITANE ALLOY, TI12MO, BEHAVIOUR, WITH BIOMEDICAL APPLICATION

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Genunchiul este cea mai mare şi cea mai complexă articulaţie a corpului uman. Este insa si cea mai vulnerabilă articulaţie, din cauza solicitărilor mari cărora le este supusă, fără să fie protejată în acelaşi timp, de jur împrejur, asemenea altor articulaţii, de mase mari musculare.Ingineri, biologi si chirurugi se confruntă cu o sarcină deosebită atunci când proiectează proceduri, componente şi sisteme pentru înlocuirea ţesutului vătămat peste limite, de boală sau traumă. Selecţia corectă a materialului pentru proteze şi a altor dispozitive folosite în chirurgia de implantare are un aspect critic şi reprezintă o adevarărată provocare. Lucrarea de faţă studiază comportamentul tribologic şi de rezistenţă al aliajului nou de titan Ti12Mo, ce poate fi utilizat în realizarea implantelor articulare

The knee is the largest and most complex joint of the human body .It is also the most vulnerable joint, due to large loads to which it is subjected, without being protected by large muscular masses, like other joints. Engineers, biologists and surgeons face a special task when they design procedures, components and systems to replace damaged tissues beyond any limits, caused by disease or trauma. A proper selection of the material for prostheses and other devices used in implant surgery represents a critical issue and quite a challenge. This paper studies the tribological and strength behavior of a new titanium alloy, Ti12Mo that can be used for joint implants.

Keywords: titanium alloy, synovial fluid simulated „ex vivo”, HEMA, visualization in „vitro”

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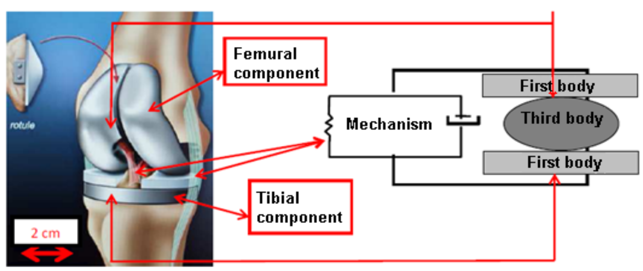
1. Introduction

Studies on joint implants must be undertaken with caution because of the biological specificities and tribological function of the joint in vivo. The biological experiments on living tissues give results depending on the physicochemical properties of the environment in which they are performed. The tribological behavior of the contact depends on the mechanical properties of the system and on the properties of the materials in contact.

Consequently, a tribological study should consider the tribological triplet assembly [1], which consists of: the mechanism that requires local loads, the first bodies that border the contact and the third body that separate the first bodies.

2. Proposed model for the tribological system

In Fig. 1 are illustrated the tribological triplet elements starting from a prosthetic joint: the joint implant surfaces are considered to be the first bodies, meanwhile the synovial fluid is the third body. The musculoskeletal – ligament system plays the role of the mechanism.



a) b)

Fig. 1.The knee joint: a) knee joint protheses; b) the tribological triplet for the joint

In this study, samples of the new titanium alloy (Ti12Mo), glass (from CVI Melles Griot) and rigid HEMA (**HEMA is 2-hydroxyethyl methacrylate** from "Corneal Industrie ",) were used as "first body" of the tribological system.(table 1)

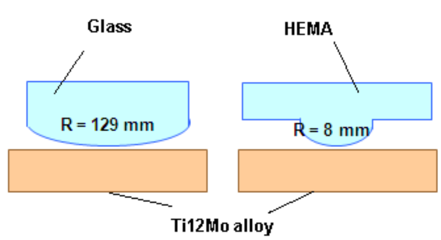


Fig. 2. The form of the contact bodies

The knee joint is very complicated to reproduce. This proposed theoretical model is a new one for this joint type (new titan alloy, Ti12Mo). The tribological couple sphere-plane is close to the real joint. (Figure 2)

The couple's form was selected to obtain constant pressure between the two bodies. This method permits to compare the experimental results for different tribological couples. ((Ti12Mo/glass, Ti12Mo/HEMA)

The titanium alloy samples are small plane cylinders, with a transparent counterface made of borosilicate glass (130mm radius) or HEMA (8 mm radius). (Fig. 2 and table 1)

Table 1.

Proprieties of the tribological coupling

Material / Proprieties	Ti12Mo	Glass	Rigid HEMA	Cortical bone
Young modulus E ,(GPa)	74	69	1	8-30
Poisson's ratio(ν)	0.3	0.2	0.2	0.4-0.6
Counterface radius (mm)	0	130	8	

2.1. Lubricant selection – third body

The third body of the real joint contact is the synovial fluid, which is colorless, transparent and viscous with the aspect of "albumen" [3]. The liquid lubricates the joint surfaces and facilities the sliding between them during the movement [4]. The synovial fluid volume present in normal conditions in a healthy joint is about 0.5- 4 ml, depending of the size of the joint.

The synovial fluid composition is: protein 20 mg/ml; albumin – 7-18 mg/ml; globulin – 0.5-2.9 mg/ml; glucose – hyaluronic acide -3mg/ml; lipids (phospholipids) – 3 mg/ml [6].

2.2. Lubricants used experimentally as third body

During the friction tests carried out in this study three lubricants have been used as third body:

Physiological saline solution

The used physiological saline solution is a buffer solution (TRIS=hydroxymethyl aminomethane) which permits to maintain constant the pH during the experiments at a value of 7.2 (physiological value). 150mM of NaCl were dissolved in this solution in order to obtain the physiological osmotic pressure. [5, 6]

Lipid vesicles

In order to highlight the role of the lipids in the tribological performance of the implants, a solution based on lipids vesicles at physiological pH was synthesized [5, 6]. It is known that the lipids are insoluble in aqueous solutions.

For this reason, the extrusion technique was used to disperse, uniformly their size and also to avoid their precipitation.

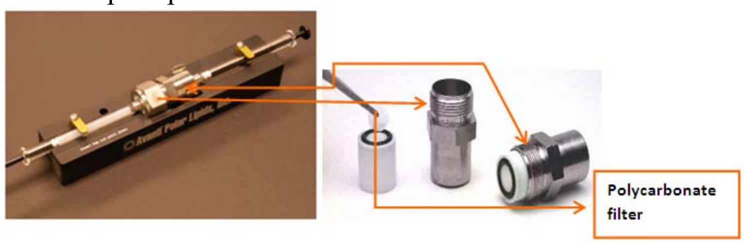


Fig. 3. Extruder

The used lipids were DPPC type (DPPC=1,2-dipalmitoyl-sn-glycero-3-phosphocholine). These are found in liquid state at 45ºC, so their extrusion must be performed at the same temperature. The extruder (Figure 3) is a device composed of two syringes containing the solution of lipids,with is a polycarbonate filter between them. The solution is passed through the filter from one syringe to the other, 19 times [7]. Filters of 0.4mm and 0.2mm were used. At the end of the extrusion operation unilamellar liposomes of uniform size were obtained.

Synovial fluid simulated ex-vivo

To reproduce the biological operating conditions, the joint lubricant(synovial fluid) was synthesized, simulating the pH, the physiological osmotic pressure, the molecular composition, and more than that the molecular complexes which exist in the synovial liquid in vivo [5, 6].

3. Samples preparation -”first body”

The Ti12Mo samples were manufactured at I.N.S.A.(Institute National des Sciences Appliqués), Rennes, France, in the Laboratory of Chemical Sciences

The samples surfaces were polished by lapping (polish with abrasive paste of different grits) until a roughness smaller than 0.4 µm was obtained. The used paste was OPS (OPS=colloidal silica emulsion) type with a pH of 9.8, and the grit was 0.04 µm.

Samples of same size, with a diameter of 12 mm and height of 3 mm were obtained.

4. Experimental Setup

The experimental determinations were performed in the following successive steps: the morphological and physicochemical investigation of the surfaces before friction, friction tests and the morphological and physicochemical investigation of the surfaces after friction.

4.1. Investigation methods of the friction surfaces from a morphological and physicochemical point of view

Contact angle determination

Contact angle method permits the determination of the samples surface superficial tensions (Fig. 4). This method gives information about physicochemical properties (degree of wetting, adsorption, chemisorptions, adhesion, and hydrophilic character) of the studied surfaces (table 2).

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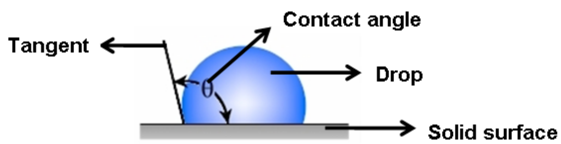


Fig.4 Contact angle measurement (θ)

Table 2.

The interpretation of contact angle measurements

Contact angle (θ)	Surface type	Example
~0	Super-hydrophilic	UV radiation TIO_2
<30	Hydrophilic	Glass
30-90	Intermediary (for θ≈30 – hydrophilic surface;θ ≈90 hydrophobic surface)	Aluminum
90-140	Hydrophobe	Plastic
140>	Superhydrophobe	Lotus leaf

The measurement of the contact angle was performed using a goniometer type Data physics OCA20. The device allows the determination of dynamic and static contact angle (with the drop placed on the surface or captive on a tilt support on flat or inclined surfaces (0 °-180°). The interface pressure is between 0.01 and 2000 mN/m ± 0.05 mN/m. The liquid which forms the drops on the sample surface was distilled water. This was fragmented in successive drops by a syringe attached to the device. The syringe is drive by the existing software of the device. The drop must be left for a few minutes to stabilize its form. With the device software, the angle between the surface and the tangent at the drop, in both lateral sides of the drop was directly measured. The measurements were resumed at different moments to describe also the influence of the titanium oxide layer formed at the samples immediate contact with the environment. For each sample 10 measurements were performed and their average value was considered as the final result of the contact angle.

Morphological study of the surface

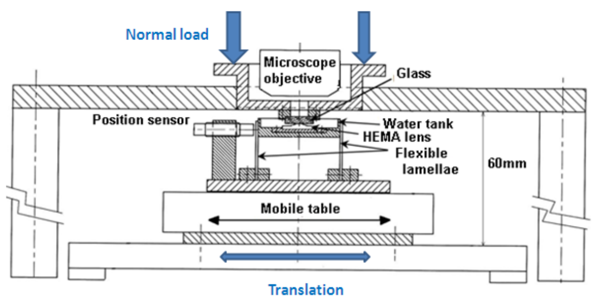
The sample surface morphology and the chemical composition of the outer layer were analyzed by SEM using a FEI XL30 microscope. The surface roughness and texture have a strong influence on the results obtained from different measurements, for the example the ones for the contact angle. For this reason, the SEM method gives important information for data interpretation.

Profilometry

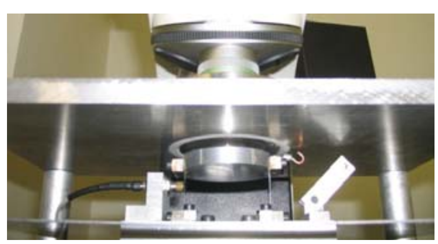
Profilometry measurements were performed on an Altisurf 500 profilometer. Surface analysis led to the determination of the average surface roughness Ra, before and after friction tests.

4.2. Experimental friction device

The tribological mechanism of the joint model of the knee prosthesis is simulated using an experimental device which allows a tribological investigation of the contact through friction measurements and through in situ visualization.



a)device scheme



b) experimental device

Fig. 5. Experimental device

Initial configuration of the experimental mechanism

The experimental device was conceived to allow the "ex-vivo" reproduction of the mechanical parameters. (Fig. 5)

The support with the titanium sample and the flexible lamellar system are fitted on a mobile motorized table. The normal force is applied using masses of circular form. The optic microscope (Leica DMLM) grants the observation of the contact through the transparent counterface. This observation is realized in situ during friction, and it can be made in white (classic), green and blue light (fluorescence). When the green or blue light are used, the acquisition parameters must be maintained constant, to be able to compare de different quantities of fluorescents lipids present in contact. The position sensor is fixed near the flexible lamellae and operates on Foucault currents, capturing the elastic strain of the lamellae during the movement. In this way, the tangential force of the whole set-up is measured

Description of the experiment

With the aid of the device described above, determinations for the samples placed on the mobile table were performed, at different velocities and different intervals of time.

The friction coefficient is obtained through the measurement of the tangential force using the experimental configuration illustrated in figure 3. This measurement is realized using a position sensor based on Foucault currents which register a tension proportional to the deformation of the flexible lamellar system (f). The elastic strain is proportional with the tangential force. The calibration was made with marked masses, which permitted to obtain a value of the proportionality constant (K_e) between force and tension, of an order of 0.1 N/V [8].

The obtained proportional constant depends on the assembling and dismounting conditions of the device, so the calibration must be made for each performed experiment. The loads used at calibration are removed and the sample is fixed on the support. Then the lubricant is placed and the cylindrical device, which carries out the loading too, is installed (his masse is 240.99 grams). With the assembly made, it was moved to make possible the visualization with the optic microscope. The sensitivity, the linearity range and the sensor position for force values between -1N and 1N, has a measurements incertitude of 5.10^{-4}N. The ratio between the normal force imposed by gravity and the measured tangential force represents the measured friction coefficient. The variation of this coefficient is registered during the experiments, achieving thus the "friction curve" for each sample. As the translation movement of the mobile table is alternative, the friction curve presents positive and negative parts, each coinciding with a movement direction.

Contributions to the optimization of the device

Starting with the year 2008 [9], the mobile table, an integral part of the experiment device was motorized and adapted to be driven by a computer software.

In this study, the plots of the calibration and friction curves were made by computer software, but in the same time on graphic support. In order to have the same information on the computer and on the paper, adequate acquisition parameters were inputted in the operating software.

So for one hour recording, one hundred points were registered with a updating period of the signal image of 0.01 seconds, and the signal acquisition was made at 1Hz frequency. The friction curve points are registered in a "txt" file and can be processed with Microsoft Office Excel.

5. Results

5.1. Characterization of the Ti12Mo alloy surfaces before friction tests

Samples surfaces characterization of the new alloy was made by: contact angle measurements, from which physicochemical properties can be, deduced, scanning electronic microscopy (SEM) for topography and profilometry in order to determine the surfaces roughness (Ra) before friction.

Table 3.

Surface characterization before friction tests

First bodies	Contact angle (θ)	Roughness (Ra, μm)
HEMA	30° ± 2°	0.0198
Glass	25° ± 2°	0.0063
Ti12Mo	40° ± 2°	0.015

The results from table 3 show that glass and HEMA surfaces are hydrophilic, very smooth, without morphological particularities in SEM. Titan surfaces have a bigger contact angle, but remain also hydrophilic.

It is known that the titan and its alloys surfaces form a TiO_2 layer of some nanometers at atmosphere contact [10]. The thickness of this layer makes the titan implant to have a superior biocompatibility [11-14]. Furthermore a thin layer of TiO_2 makes the surface to be more hydrophilic; meanwhile a thicker layer makes it less hydrophilic [15]. The thicker oxide layer increase the proteins absorption, for example, for each increase with 200 nm, the protein absorption ratio albumin/fibrogen augments seven times[16].

5.2. Characterization after friction of the new titan alloy Ti12Mo by the role of the third body

5.2.1 Ti12Mo alloy- physiological serum – glass counterface

The results obtained during in situ viewing and measurement of the friction coefficient show that at the beginning, small wear particles from the contact bodies can be detected. During friction, these particles generate striae on the samples surface. The striae are filled with particles which flattened more and more in contact, leading to a smooth form of the friction trace at the end of the test. The friction coefficient obtained in this case is 0.5.

The analysis of the studied surfaces attest the presence of a considerable wear in case of the glass sample (nearly 6μm of glass thickness was lost during friction) and a lesser one for the titan sample (striae of about 1μm in depth).

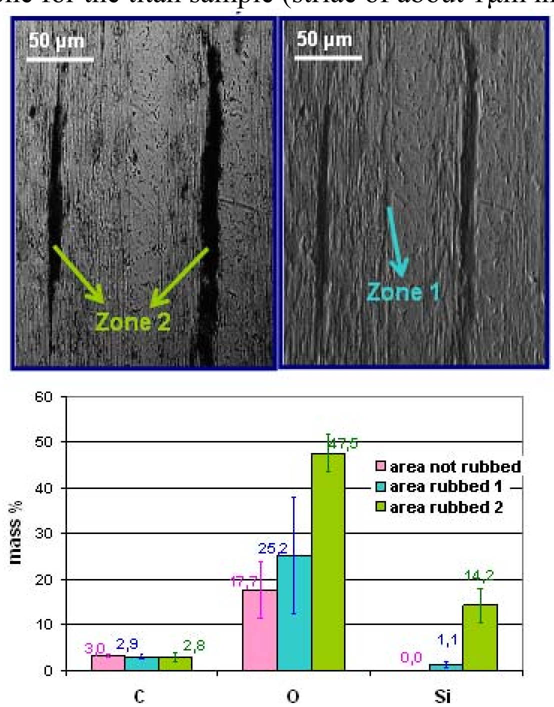


Fig. 6. SEM analysis on the titan surafce

The analysis of optic and electronic microscopy (visualization and EDX- energy-dispersive X-ray spectroscopy) shows that the glass surface presents strips due probably to the detachment of the glass particles that remained in contact and created a abrasive wear and the titan particles (highlighted with EDX probe) of some micrometers. The titan surface presents lamellae due probably to the superficial tribological transformation of the titan (zone 1 –figure 6) and striae due to the abrasive wear of the glass particles (zone 2 – big concentration of Si revealed by the EDX analysis – figure 6).

5.2.2. Ti12Mo alloy – lipid vesicles – glass counterface

The analysis of the measurements of the friction coefficient and the visualization in situ shows that at the beginning of the friction, the lipids have the tendency to concentrate out of the contact (zone with the form of arc, more definitive and visible in the fluorescent image – figure 7). During friction, the lipids re-enter in contact and form brighter small arcs. The formation of these arcs involves the adhesion between the two bodies in contact due to the presence of the meniscus formed by the lipids membranes. The friction curve also shows zones of stick-slip. The friction coefficient obtained in this case is 0.5.

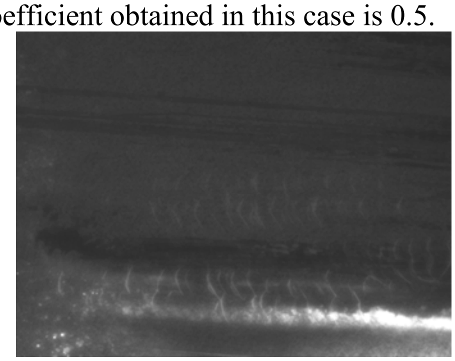


Fig..7. Titan sample visualization with fluorescent optic microscopy

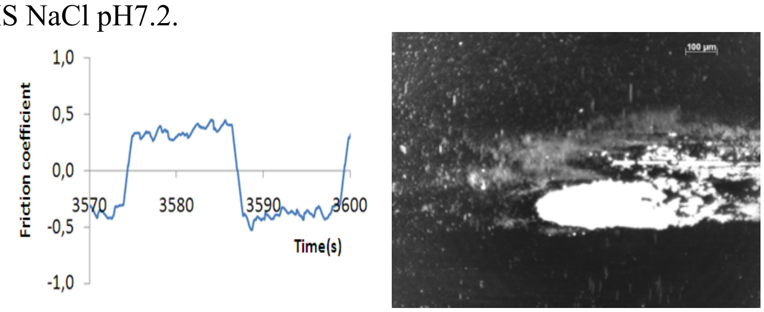
The visualization with fluorescent optic microscopy of the surfaces after friction shows the presence of wear striae on the glass surface, parallel to the friction direction. Also fluorescent particles can be observed, which give the impression that they are elongated and perpendicular on the friction direction. This can be due to the titan particles transferred from the glass by lipids membranes winding and attaching.

The characterization of the rubbed surfaces attests the presence of a considerable wear on the glass sample (about 5µm thick) and a less important wear for the titan sample (delicate striae of about1 µm depth).

The analysis with the optic and electronic microscope evidences on the glass surface the appearance of the rays due to the detachment of the glass particles which remain in contact and creates abrasive wear. The glass particles are smaller than those visualized in the case of TRIS. The transfer percentage is about 40% under that for the TRIS. Also thicker particles are present, having a smoother contour and containing more carbon than titan. These can be due to the glass particles which have detached during friction, and there were re-bound on the glass through the lipids membranes. This can explain their high percentage of carbon. On the titan surface one can notice the appearance of lamellae due to the superficial tribological transformation of the titan and striae formed by abrasive wear generated by the glass particles.

5.2.3. Ti12Mo alloy – synovial fluid ex-vivo – glass counterface

The visualization and measurement of the friction coefficient in situ show that at the beginning of friction the synovial substitute stays in the contact zone and forms lamellae oriented in the friction direction (Figure 8). During friction, the lipids accumulate more and more in contact zone, increasing the density of the lamellae, forming an almost continuous layer. For this case, the friction coefficient obtained is 0.3. The formation of these lamellae and of the molecular absorbed layer makes the friction coefficient to remain constant during the test. The friction coefficient is twice smaller than in case of physiological saline solution, TRIS NaCl pH7.2.



a b

Fig. 8. a) Friction coefficient graphic (0.3) ;b) Image obtained by fluorescent optic microsocpy – blue light , at the end of friction

Analyzing the rubbed surfaces it was observed that the glass wear is strongly decreased in the presence of the synovial fluid. Regarding the titan sample , one can notice two trace of wear thicker than those present in the case of TRIS and lipids (striae of about 0.5 µm in depth). Between these two traces, no presence of wear can be observed (Fig. 9).

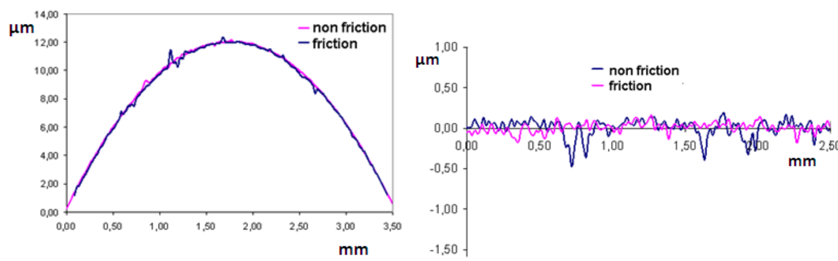


Figure.9 Profilometrie measurements before and after for a)glass;b)Ti12Mo alloy

Using the electronic scanning microscope we can draw the next observations. On the glass surface one can observe the presence of small titan particles, having a transfer percentage of 80% smaller than the one detected in case of TRIS. Also thicker particles, with irregular contour and containing more carbon are present on the glass surface. This can be due to the formation of thin continuous layers of synovial molecules, which explains their high carbon percentage. The titan surface presents wear traces, due to the detachment of some glass particles. Between the two wear traces a layer formed through the absorption of the synovial molecules and having a high carbon percentage can be noticed.

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5.2.4. Ti12Mo alloy – synovial fluid ex-vivo- HEMA counterface

Observing the surface and monitoring the friction coefficient in situ, it was noticed that at the beginning of the test, the synovial substitute stays in contact and forms lamellae perpendicular orientated on the friction direction. During friction, these lamellae enfold, creating rollers which are elongated and accumulate at the contact limit. The friction coefficient obtained in this case is 0.5 (Fig. 10).The rollers and lamellae are adherent at the bodies in contact. This phenomenon imposes the change in the sense of the friction and the measurement of the adhesion stress which is about 0.2N for rollers and 0.12 N for lamellae.

The images taken by fluorescent optic microscope attest the presence of rollers of about some µm in diameter and some centimes of µm, in length on the glass surface and lamellae which tend to roll up on the HEMA.

The analysis of the rubbed surfaces confirms that the wear of the titan samples is practically zero in the presence of the synovial substitute and HEMA counter face.

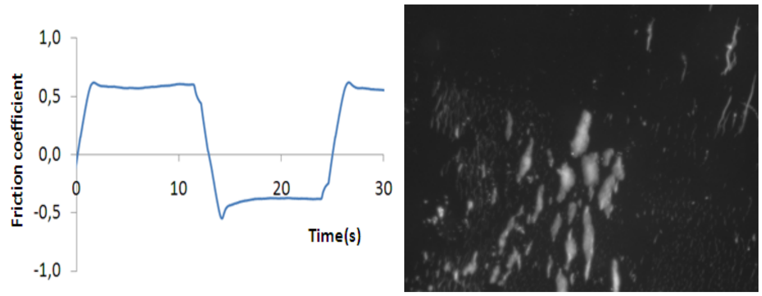

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Fig.10. a) Friction coefficient graphic (0,5) with adhesion stress (0,2N –rollers) ;b) Image in fluoresent optic microscopy – blue light , at the end of friction

The SEM analysis showed that the HEMA surface present organic rollers, which contain an important percentage of carbon, and the titan one presents organic lamellae and rollers.

6. Conclusions and perspectives

The Ti12Mo alloy was elaborated in order to obtain in its structure dominant beta phase, which allows a Young's modulus of 74 GPa, closer to the one for the bone.

The performances of the Ti12Mo alloy shows that from a mechanical resistance and tribological point of view, tested in simulated biological environment, are closer to the ideal situation of a real knee coupling.

Correlating the analysis before and after friction can be stated that: when the Ti12Mo alloy is tested in simulated synovial fluid, the wear in contact drops considerably; The presence of a glass or polymer counterface changes the accommodation mode of velocity, encouraging the formation of the third body in shape of lamellae on the glass surface and rollers on the HEMA counter face. This phenomenon generate adhesion stresses, visible on the friction curves in case of HEMA, in the contact zone, which can explain the enfolding of the lamellae in adherent rollers to the rubbed surfaces.

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