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TRIBOLOGICAL CHARACTERISTCS OF SYNTHETIC HYDROGELS FOR BIOMEDICAL APPLICATIONS

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Abstract. The use of a thin layer of compliant material acting as a bearing surface in human replacement joints has recently generated considerable interest. Developments of synthetic hydrogels based on poly (2-hydroxyethyl methacrylate) (pHEMA) have been used for compliant material due to their biocompatible properties, soft consistency and low friction coefficient. This work establishes the correlation between the crosslinking density, chemical changes and tribological properties of the pHEMA / poly (methyl metacrylate-co-acrylic acid) (75:25) blend using 10 % (w/w) crosslinking agent and pHEMA / n-vinyl pirrolidone (10% (w/w)) blend with 0, 5 and 10% (w/w) of crosslinking agent. Friction and wear tests were performed in a pin-on-disc equipment using stainless steel 316L as disc counterface lubricated by distilled water. The tribological parameters investigated were the sliding speed $(0,16 \le v \le 0,5\ ms^{-1})$ *and the contact pressure* $(2,4 \le p \le 5,5$ *MPa). The friction coefficient was continuously evaluated during each test and the wear rate was quantified by weight loss. The dominant wear mechanisms were identified by Scanning Electron Microscopy.*

Keywords. *Hydrogels, Biomaterials, Biotribology, Friction, Wear*

1. Introduction

Traditionally, replacement joints are usually made of a metallic component articulating on ultra high molecular weight polyethylene (UHMWPE). Such joints operate in the mixed lubrication regime and suffer from problems of wear debris, which shorten their implant life. The UHMWPE wear particles generated at the articulating surfaces can enter the tissues surrounding the prosthesis and cause adverse cellular reactions which lead to bone resorption loosening and the need for a revision operation. Consequently, a number of studies which focus on the tribological properties of UHMWPE have been conducted [Baker, 2000, Planton, 2001, Yao, 2001, Hu, 2001, Elfick, 2001, Joyce, 2001]. An alternative approach to minimize the degeneration the UHMWPE surface is the use of a thin layer of compliant materials to form the bearing surface in total joint replacements [Caravia, 1995, Bavaresco, 2000, Freeman, 2000, Schmidt, 2000, Bavaresco, 2001]. The idea is to create a more compliant form of synthetic articular cartilage than the UHMWPE, thus reducing contact stresses and encouraging fluid film lubrication mechanisms. The hydrogels – "a polymeric material, which exhibits the ability to swell in water and retain a significant fraction of water within its structure, but which will not dissolve in water" exhibit a variety of unique behaviors for use as compliant material. The poly (2-hydroxyethyl metacrylate) (pHEMA) has been used in many biomedical applications, due to its biocompatible characteristics, high permeability to small molecules (i.e. tissue metabolites), hydrophilicity, soft consistency and low coefficient of friction [Tighe, 1994, Klempner, 1987, Pedley, 1978]. However, insufficient mechanical properties have severely limited the use of hydrogels for load-bearing applications, such as the replacement of damage or diseased tissues. Improvement of the mechanical properties of the hydrogels can be controlled by the change monomer composition (i.e. hydrophilic monomer), synthesis of blends, by the increased the crosslinking density, and polymerization conditions [Peppas, 2002, Oka, 1990, Kudela,1990, Smeathers, 1990, Corkhill, 1989]. In this work we describe the tribological properties of a series of hydrogels blends based on pHEMA when it happens the variation of the molecular structure by using the reinforcing hydrophobic polymer n-vinyl pirrolidone (NVP) and by the incorporation the poly (methyl metacrylate-co-acrylic acid) copolymer.

2. Experimental

2.1. Materials

Indentation creep test, water swelling (EWC) and wear tests using a pin-on-disc equipment were used to characterize the mechanical properties of hydrogels. The hydrogels blends were obtained from a mixture of 2-hydroxyetlyl metacrylate (HEMA) (Aldrich) with 10% (w/w) of linear reinforcing polymer - n-vinyl pirrolidone (NVP), benzoil peroxide (0,5 % (w/w)) as an initiator of polymerization, and trimethylol propane trimethacrylate (TMPTMMA) (Retilox) 0, 5 and 10% (w/w) as a crosslinking agent. The pHEMA/poly (methyl metacrylate-co-acrylic acid) (pHEMA/poly (MMA-co-AA)) were prepared using the poly (methyl metacrylate-co-acrylic acid) (75:25). The poly (MMA-co-AA) (10 % (w/w)) was dissolved in the HEMA monomer after which benzoil peroxide (0,5 % (w/w)) and TMPTMMA (10 % (w/w)) crosslinking agent were added to the solution under agitation before the polymerization. Both hydrogels blends were prepared by thermal polymerization (70 – 85°C) by 4 hours.

2.2. Indentation creep test

The Indentation creep test was performed using a Material Test System (MTS- Teststar II). The samples were immersed in distilled water and indented using a spherical tip with a diameter of 3.2 mm. A load of 4.935N (0.5kgf) was applied on the sample for 180s. The indentation height (h) was measured through time (t).

The indentation creep modulus was calculated using the equation described by KEMPSON [13] (Eq. 1).

$$E = \frac{9 \cdot 10^4 p}{16\sqrt{r}} \left[\frac{1 - \exp(-0.42 \cdot e / a)}{h} \right]^{3/2} \qquad (1)$$

E = creep modulus [kgf/m^2]
p = load [kgf]
r = indenter radius [cm]
e = sample thickness [cm]
h = indentation height [cm]
$a = \sqrt{(2rh - h^2)}$ [cm]

2.3. Equilibrium water content (EWC)

For the equilibrium water content (EWC) determination, dried samples of the hydrogels were immersed in deionized/distilled water at room temperature and the EWC was calculated by weight difference usually expressed by Eq. 2.

EWC = (weight of wet gel – weight of dried gel) / Weight of wet gel x 100 (2)

The swollen gel weight was measured allowing the hydrogels to reach equilibrium state in distilled water, which was indicated by their constant final weight.

2.4. Preparation of Coating

Friction and wear tests were accomplished by using solid porous substrates of ultra high molecular weight polyethylene (UHMWPE) pins (cylindrical shape), coated with pHEMA/n-vinyl pirrolidone (pHEMA/NVP) and pHEMA/poly (MMA-co-AA). The porous substrates were immersed in a mixture of monomer, initiator and crosslinking agent. The system went through thermal polymerization for 4 hours (70-85°C). After that, it was placed in water for the removal of the residual monomer and initiator. Thus, the hydrogels were formed on the surface and inside the pores of the substrates, assuring its mechanical fixation.

2.5. Wear Tests Using Pin-on-Disc Equipment

The tribological characterization was performed at room temperature in pin-on-disc equipment, Plint TE67, using stainless steel 316L as disc counterface. The sliding occurred in distilled water, with two sliding speeds (0.16 and 0.5 ms^{-1}), and variable contact pressure ($2.4 \leq p \leq 5.5$ MPa). The contact surfaces of the discs were polished with silicon carbide paper followed by finishing with 1 μm diamond paste. The final surface roughness of the discs, as measured by profilometry, was 0.03 μm Ra. The discs were washed, first with detergent and water and then with absolute ethyl alcohol. After that, the solvent was evaporated in hot air flow. The friction coefficient was evaluated during each test and the wear rate of the pins was quantified by weight loss. A lubricant-containing vessel was used, where a control static pin was immersed to estimate the weight gain due to absorption of distilled water.

2.6. Scanning electron microscopy

The dominant wear mechanisms were identified by Scanning Electron Microscopy - SEM (JEOL JXA 860A) equipment. The surfaces samples were fixed in a metallic support and gold sputtered using Sputter Coater BAL-TEC SCD equipment.

3. Results and Discussion

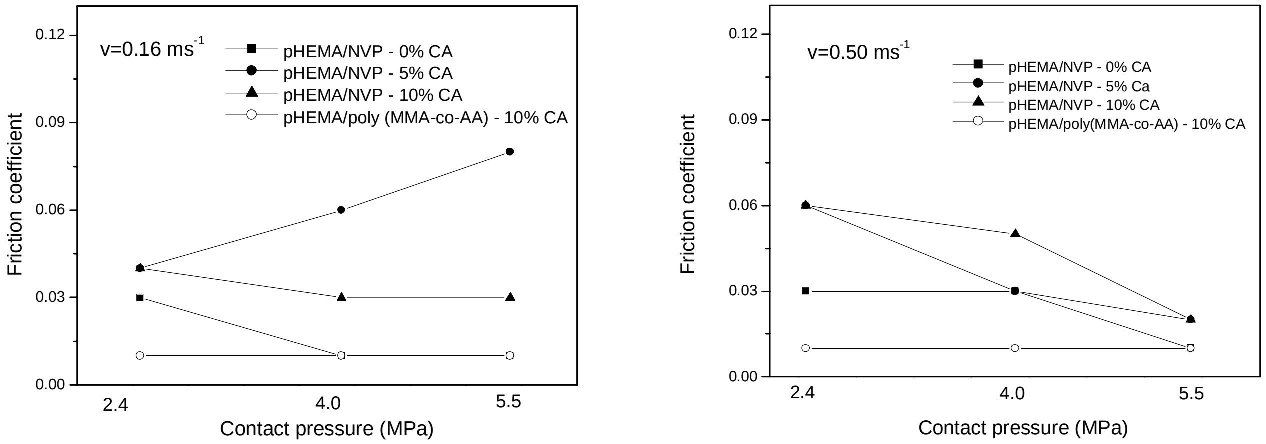
The hardness of the hydrogels was modified as a function of the crosslinking agent and of the type of reinforcing polymers. Table 1 shows the indentation creep modulus (E) and EWC measured for the pHEMA/NVP (10% w/w) with 0, 5 and 10% (w/w) of crosslinking agent (CA), and for the pHEMA/poly (MMA-co-AA)) with 10 % (w/w)) of CA.

Table 1. Indentation creep modulus (E) and EWC for the pHEMA/NVP (10% w/w) with 0; 5 and 10% (w/w) of crosslinking agent (CA), and for the pHEMA/poly (MMA-co-AA)) with 10 % (w/w)) of CA.

Hydrogel blend - CA (%)	Indentation Creep Modulus (E = MPa)	EWC (%)
pHEMA / NVP - 0	4,0	38
pHEMA / NVP - 5	9,7	30
pHEMA / NVP - 10	15,0	25
pHEMA/poly (MMA-co-AA) - 10	7,0	32

The increase of the crosslinking agent concentration caused an increase in the value of the indentation creep modulus and a decrease in the equilibrium water content of the pHEMA/NVP hydrogels. With the increase in crosslinking agent concentration, there was an increase of the crosslinking density in the polymeric network, causing a decrease in its flexibility. Consequently the hardness of the material was improved and, in that way, the absorption of water was hindered. The pHEMA/(poly (MMA-co-AA) blend presented value of indentation creep modulus smaller than the values presented by the pHEMA/NVP with 5 and 10% (w/w) of crosslinking agent and EWC similar ($\approx$ 32%) to the pHEMA / NVP hydrogel with 5% (w/w) of CA.

The effect of the changes of reinforcing polymer and the crosslinking density of the polyHEMA/NVP (10% w/w) and pHEMA/poly (MMA-co-AA) (75:25) hydrogels in the friction coefficient (μ) and wear rate for different values of contact pressure (p=2.4; p=4.0 and p=5.5 MPa) and sliding speed (v=0.16 ms^{-1} and v=0.50 ms^{-1}) is shown in figures 1 and 2, respectively.

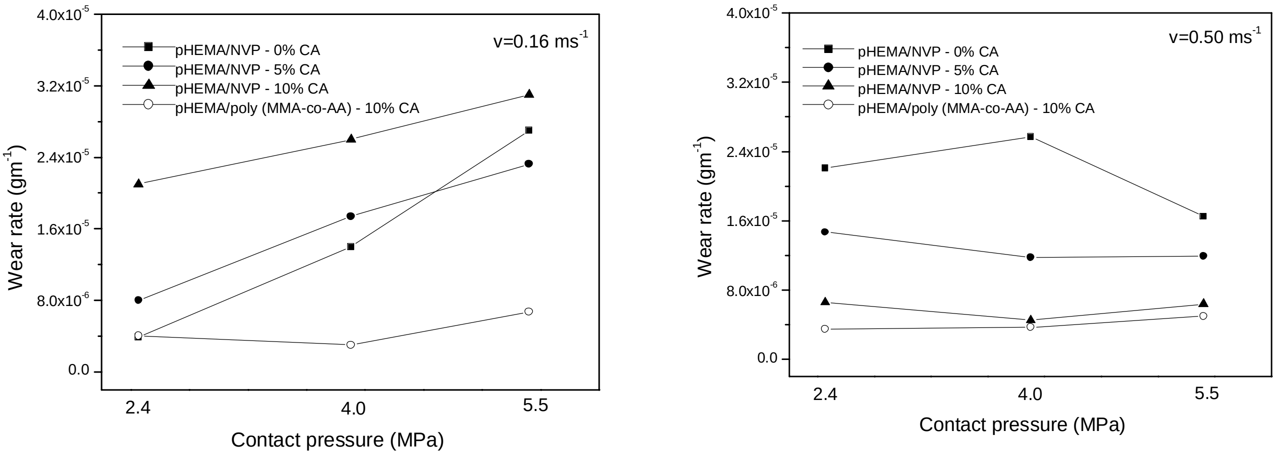


(a) (b)

Figure 1. Friction coefficient *vs.* contact pressure (MPa) for hydrogels tested at different sliding speeds: v=0.16 ms^{-1} (a) and v=0,50 ms^{-1} (b).

Figures 1 and 2 show the changes of the tribological behavior of the hydrogels synthesized with poly (MMA-co-AA) and with NVP. Independently of the test conditions and of the indentation creep modulus (E), the pHEMA/(poly (MMA-co-AA) hydrogels presented better tribological properties, with low friction values ($\mu \approx 0,01$) and wear rate in the order of 10^{-6} gm^{-1}.

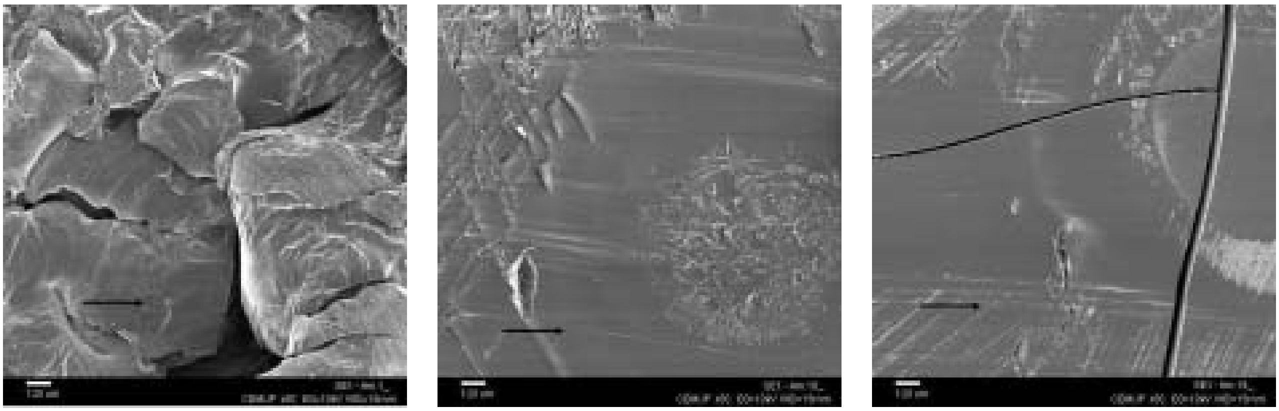
Recent works (Gong et al, 1999, 2002) showed that the tribological behavior of polymeric hydrogels in contact with solid surfaces is complex due to their structure and specific properties and that the friction force will depend on the chemical and physical characteristics of the interaction (attractive or repulsive) at the contact sites between the mating surfaces, as well as on the contact pressure and sliding speed. Furthermore, the frictional force substantially changes with the change in the chemical structure of the hydrogel, such as the charge crosslinking density, the solvent content and the chemical properties of the solid counterface. It is also known that the incorporation of acid groups (COO-), in this case, coming from the acrylic acid, increases the concentration of negative load at the surface, which hinders the loss of water of the polymeric network changing their superficial properties (Malmonge, 1997). It is believed that this superficial change generating a repulsive effect at the interface between the mating surfaces promotes their better behavior response. However, it is observed that the tribological behavior of the blends synthesized with NVP showed significant dependence on the sliding speed and contact pressure. When the pHEMA/NVP hydrogels are submitted to low sliding speed (v=0.16 ms^{-1}) the hydrogels synthesized with 0% (w/w) of CA presented the best tribological properties (Fig. 1 (a) and Fig. 2(a)), as they are more compliant materials, with larger capacity to absorb the normal load. The increase of CA concentration causes a structural change on the hydrogels, which increases their wear rate (Fig. 2(a)) by lack of compliance. For higher sliding speed (0.50 ms^{-1}) the friction values decreased with the increasing of the contact pressure for all of the compositions of pHEMA/NVP hydrogels. It is believed that in the low sliding speed conditions the hydrodynamic effect was insufficient to generate an effective lubricant film between the mating surfaces and the direct contact was kept during the sliding motion, whereas the sliding conditions corresponding to v=0.50 ms^{-1} promotes the establishment of an hydrodynamic lubrication regime. These effects, together with the increasing of the crosslinking density, explain the reduction of the wear rate of more resistant hydrogels (5% and 10% (w/w) CA) (Fig. 2(b)), although with a small increase of the corresponding friction values (Fig. 1(b)).



(a) (b)

Figure 2. Wear rate *vs.* contact pressure (MPa) for hydrogels tested at different sliding speeds: v=0.16 ms^{-1} (a) and v=0,50 ms^{-1} (b).

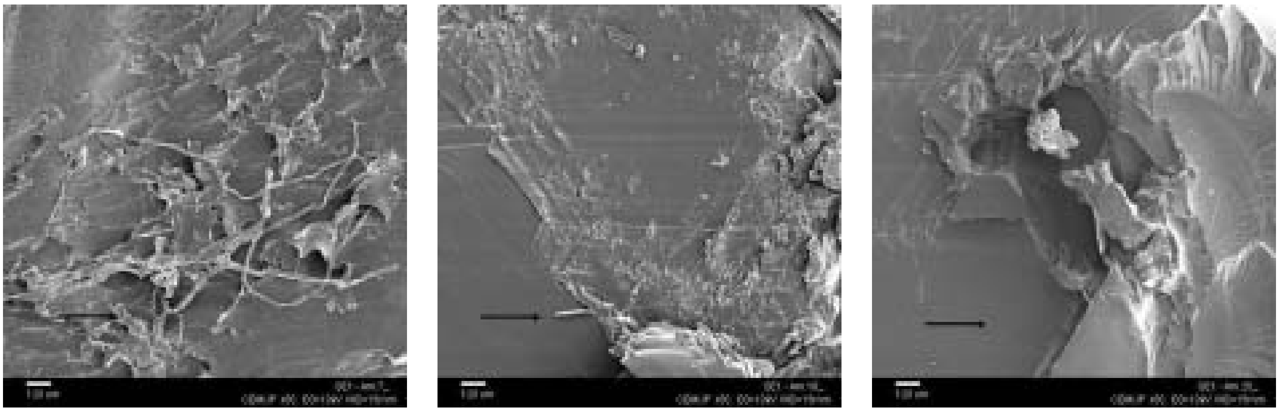
The morphological wear features of the pHEMA/NVP (10% w/w) hydrogels synthesized with 0, 5 and 10% (w/w) CA after testing at v=0.16 ms^{-1} are shown in Figs. 3 and 4, respectively for p=2.4 MPa and p=5.5 MPa. For pHEMA/NVP hydrogels in the low sliding speed regime (v=0.16 ms^{-1}), it is observed that the less crosslinked hydrogel (0% (w/w) CA) is characterized by high plastic deformation (Fig. 3(a) and 4(a)), denoting adhesion as the dominant wear mechanism. However, with the increase of hardness, for hydrogels crosslinked with 5% and 10% (w/w), abrasive wear starts to be important and plowing grooves are evidenced at the worn surfaces (Fig. 3(b), 3(c) and 4(b), 4(c)).



(a) (b) (c)

Figure 3. SEM worn surfaces of the pHEMA/NVP (10% w/w) hydrogels synthesized with: 0% (w/w) of crosslinking agent (CA) (a), 5% (w/w) of CA (b) and 10% (w/w) of CA (c) (v=0.16 ms^{-1}; p=2.4 MPa).

In addition, the hydrogels with more crosslinking density also presented cracks perpendicularly oriented to the sliding motion. It is important to refer that the extensive cracks that can be seen in Figure 3 (c) were caused during the coating process with gold for SEM characterization after the tribological test.



(a) (b) (c)

Figure 4. SEM worn surfaces of the pHEMA/NVP (10% w/w) hydrogels synthesized with: 0% (w/w) of crosslinking agent (CA) (a), 5% (w/w) of CA (b) and 10% (w/w) of CA (c) (v=0.16 ms^{-1}; p=5.5 MPa).

Figures 5 and 6 show the worn surface morphology of the pHEMA/NVP hydrogels after testing at high sliding speed (v=0.50 ms^{-1}) for p=2.4 MPa (Fig 5) and p=5.5 MPa (Fig 6). Similarly to low sliding speed regime, the most compliant hydrogel presented adhesive wear as dominant mechanism of surface damage (Figs. 5(a) and 6(a)) and the hydrogels synthesized with 5 and 10 (w/w) of CA are characterized by abrasion and cracks perpendicularly oriented to the sliding direction (Figs. 5(b), 5(c), 6(b) and 6(c)).

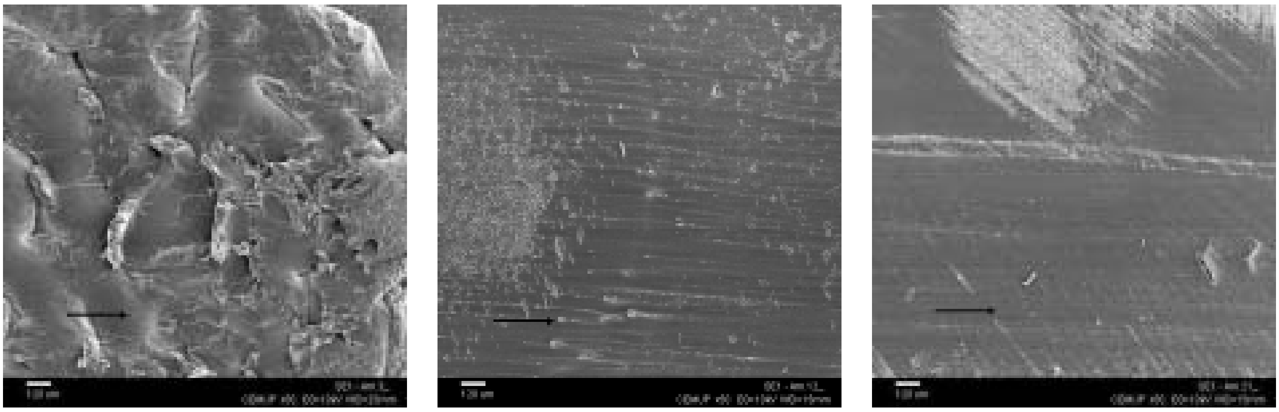

(a) (b) (c)

Figure 5. SEM worn surfaces of the pHEMA/NVP (10% w/w) hydrogels synthesized with: 0% (w/w) of crosslinking agent (CA) (a), 5% (w/w) of CA (b) and 10% (w/w) of CA (c) (v=0.50 ms^{-1}; p=2.4 MPa).

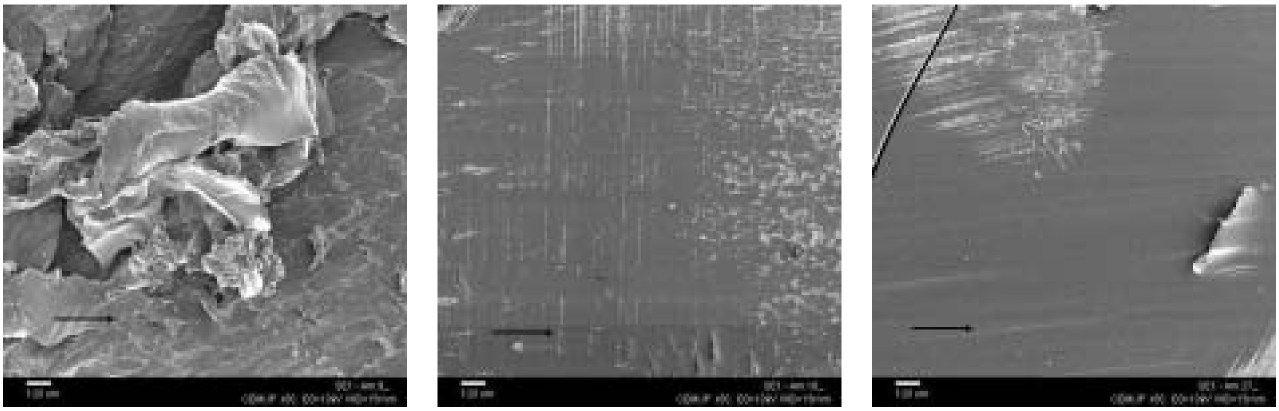
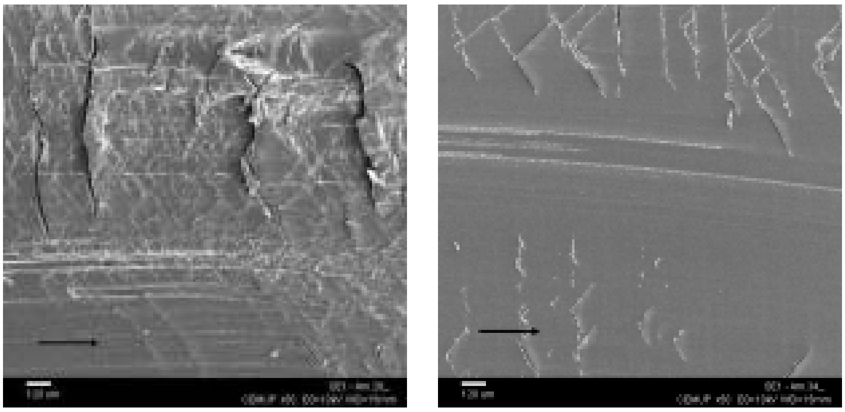

(a) (b) (c)

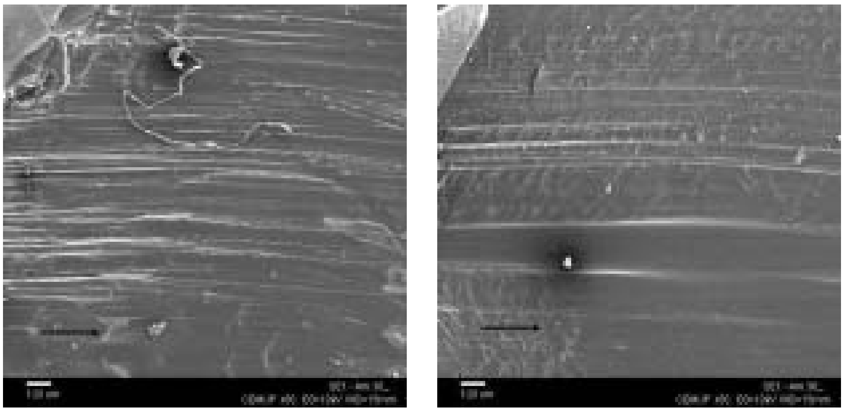
Figure 6. SEM worn surfaces of the pHEMA/NVP (10% w/w) hydrogels synthesized with: 0% (w/w) of crosslinking agent (CA) (a), 5% (w/w) of CA (b) and 10% (w/w) of CA (c) (v=0.50 ms^{-1}; p=5.5 MPa).

Figures 7 and 8 present the morphological wear features of the pHEMA/ poly (MMA-co-AA) hydrogels synthesized with 10% (w/w) CA after testing at v=0.16 ms^{-1} (Fig. 7) and v=0.50 ms^{-1} (Fig. 8) under p=2.4 MPa (Figs. 7(a) and 8(a)) and p=5.5 MPa (Fig. 7(b) and 8(b)). In all test conditions the worn surface of hydrogels synthesized with MMA-co-AA) revealed features of cracked surfaces together with some traces of abrasion marks. Corroborating these observations for pHEMA/poly (MMA-co-AA) hydrogels, no significant changes were found for friction and wear results at different test conditions (Figs. 1 and 2)



(a) (b)

Figure 7. SEM worn surfaces of the pHEMA/poly (MMA-co-AA) (75:25) blend synthesized with 10% (w/w) of CA, $v=0.16\ ms^{-1}$ $p=2.4$ MPa (a) and $p=5.5$MPa (b).



(a) (b)

Figure 8. SEM worn surfaces of the pHEMA/poly (MMA-co-AA) (75:25) blend synthesized with 10% (w/w) of CA, $v=0.50\ ms^{-1}$ $p=2.4$ MPa (a) and $p=5.5$MPa (b).

4. Summary

In this work, the effect of the changes of reinforcing polymer and crosslinking density on the tribological properties of pHEMA based hydrogels was studied. Same being the polymeric base (pHEMA) common for all hidrogéis and to be in larger proportion in the mixture was verified that the modifications accomplished in the composition of the materials were significant. It was verified that although the pHEMA/poly (MMA-co-AA) hydrogel is characterized by smaller indentation creep modulus (E), this material exhibited better tribological properties, independently of the contact pressure and of the sliding speed ($\mu \approx 0.01$ and wear rate $=10^{-6} gm^{-1}$). It is believed that the superficial changes caused by the addition of coming negative groups of the acrylic acid have generated repulsion between the mating surfaces. The blends synthesized with NVP showed significant dependence with the increase of sliding speed and contact pressure. It was verified that in the low sliding speed regime ($v=0.16\ ms^{-1}$) the soft and more compliant hydrogel presented the lower wear rate. However, for experimental conditions that favoured the occurrence of hydrodynamic effect ($v=0.50\ ms^{-1}$), the more resistant materials, with smaller capacity of water absorption, presented the better tribological response. The morphological characterisation of the worn surfaces by SEM allowed to conclude that the most compliant hydrogels (0% (w/w) CA) presented adhesive wear as the main wear mechanism. As the crosslinking density of hydrogels increased, the capacity of absorption of water was reduced and the dominant wear mechanism was abrasion. The friction coefficient was relatively low ($0.01 \leq \mu \leq 0.03$) and the wear rate of hydrogels was in the range of $10^{-6}\ gm^{-1}$ to $10^{-5}\ gm^{-1}$. The hydrogels synthesized with the poly (MMA-co-AA) presented features of a cracked surface in all of the test conditions.

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