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Thermal and Mechanical Properties of Vinyltrimethoxysilane (VTMOS) Crosslinked High Molecular Weight Polyethylene (HMWPE)

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The use of polyethylene in sliding systems for automotive industry requires adequate mechanical properties, such as high wear resistance, besides good processing properties in conventional extrusion processes. Aiming to fulfill these requirements, crosslinks were introduced in a high molecular weight polyethylene (HMWPE) grade through a process involving grafting of vinyltrimethoxysilane (VTMOS) onto the polymer chain, promoted by dicumyl peroxide (DCP). The results obtained showed that the introduction of crosslinks improved the wear resistance of HMWPE. However, the HMWPE crosslinking led to a significant decrease in the Young's Modulus, as a result of the reduction in crystallinity or the heterogeneous structure of the crosslinked samples. The tensile strength and the thermal properties were not affected.

Keywords: *high molecular weight polyethylene, mechanical properties, thermal properties, wear resistance*

1. Introduction

Poly(tetrafluorethylene) (PTFE) and ultra high molecular weight polyethylene (UHMWPE) are the first choice materials, when low friction coefficient is the main performance parameter. However, the major difference between these two polymers is that the PTFE does not have a good wear resistance, unlike UHMWPE, which is the polymeric material that presents the best resistance to abrasion index, among other thermoplastic materials. Because of that, UHMWPE has been widely used in high tech applications, where the wear and debris must be avoided[1-4].

It is worth mentioning that although UHMWPE has a good wear resistance, for some applications such as orthopedic prosthesis, satisfactory values of resistance to abrasion are only obtained by introducing crosslinks in the polymer chain, through irradiation with gamma radiation[5-9,]. However, despite of the desirable mechanical properties that UHMWPE presents the high viscosity does not allow its processing in the conventional machinery used in polymer processing.

The use of polyethylene in sliding systems for automotive industry requires adequate mechanical properties, such as high wear resistance, besides good processing properties. There is an ethylene-1-hexene copolymer (HMWPE) in the market that although presents a high molecular weight can be processed by conventional extrusion processes[1,10]. This polymer has a melt flow rate (MFR) of about 3.0 g/10 min, determined in accordance with the ASTM D1238 conditions (190°C and 21.6 kg), while the MFR of UHMWPE under the same experimental conditions is close to zero[10]. In order to obtain a suitable set of mechanical properties, it is desirable to introduce crosslinks in this polymer.

A process widely used to introduce crosslinking in polyethylene involves grafting a vinyl silane in the polymer chain and its subsequent hydrolysis, generating silanol groups. This reaction is promoted by an organic peroxide, usually dicumyl peroxide (DCP). The crosslinking occurs through condensation reactions of these silanol groups, leading to the formation of siloxane bridges (-Si-O-Si-), which restricts the mobility of the polymeric chains. An organotin catalyst is generally employed[11-26].

This crosslinking process may be performed in one single step (Monosil process) or in two steps (Sioplas process)[11]. The major difference between them is related to the procedure used for mixing the reactants. In the Sioplas process, silane and peroxide are fed together into the extruder and processed. The heating in the extrusion process promotes the peroxide degradation resulting in the grafted polymer, which is extruded and granulated. In the second step, the grafted polyethylene is mixed with the tin catalyst and extruded or injected. The obtained product is crosslinked after the extrusion in hot water, steam or moist air. In the Monosil process, silane, peroxide and catalyst are all fed together into the extruder. The length (L)/diameter (D) extruder ratio of about 30:1 allows the reactants to be reacted (grafted) during the extrusion process. After the extrusion, the polymer is crosslinked by exposing it to the steam or hot water. Other more recent technology involves the copolymerization of the silane in the polymer chain during the polymerization process[11,18-20,]. By crosslinking, some important properties of polyethylene such as: creep[12,27] and wear resistance[8,9,11,12], thermal[11,14,28] and dimensional stability[12], elastic properties[11] and impact strength[11,12] can be improved.

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From our knowledge, there is a lack of studies regarding crosslinking of the polyethylene grade used in this study and the resulting mechanical properties. Besides, in most of the studies involving silane-grafting and moisture crosslinking of polyethylene, there is no investigation of its tribological behavior. The aim of this work is to evaluate the thermal and mechanical properties resulting from the crosslinking of HMWPE by the Sioplas process. Assess the possibility of applying the obtained materials in sliding systems for automotive industry is also one of the objectives of this work. In order to accomplish this, a preliminary investigation of the tribological behavior of the crosslinked HMWPE samples was performed.

2. Experimental Procedure

2.1 Materials

The polymer used in this work was a commercial high molecular weight ethylene-1 hexene copolymer (HS5103) supplied by Braskem S. A. Specifications of this resin are presented in Table 1[1]. The dicumyl peroxide (Perkadox BC-FF) was donated by Akzo Nobel Chemicals. The vinyltrimethoxysilane (VTMOS) was supplied by D'Altomare Química Ltda. The tin catalyst used in this investigation was dibutyltindilaurate (Liocat 119) furnished by Miracema-Nuodex Indústria Química Ltda. All chemicals were used as received.

Table 1. Specifications of HMWPE (Braskem-HS5103)[1].

Properties	ASTM Method	Values
Melt flow index (MFI) (190°C/21.6 kg)	D 1238	2.2 g/10 min
Density	D 1505/ D 792	0.952 g/cm^3
Yield strength	D 638	25 MPa
Tensile stress at break	D 638	30 MPa
Flexural Modulus	D 790	1200 MPa
Durometer Hardness (Shore D)	D 2240	66

2.2 Grafting procedure

Mixtures of HMWPE, DCP (0.01wt%) and VTMOS (0.5, 1.0 and 1.5 wt%) were processed in a AXPlásticos single screw extruder at 50 rpm. The extruder had a screw diameter of 30 mm and a length/diameter ratio of 32:1. The temperature profile in the extruder from the feed to the metering zone was set to 190/220/240/260/280°C. The extruded samples were mixed with the tin catalyst (0.05 wt%) and reprocessed in the extruder using the same experimental conditions above described. The samples were then immediately stored in a oven at 60°C to prevent atmospheric absorption of water. Dried extruded granules were then compression molded in a hot Carver Press at 190°C for 5 min to make sheets of 2 mm thick for water crosslinking reactions[1].

2.3 Water crosslinking reactions

In order to provide the crosslinking reaction in the HMWPE, the silane-grafted sheet samples were immersed in a hot water bath at 80°C, for a period of 24 h, in a Quimis equipment, Model Q 215-2[1].

2.4 Characterization

The following analysis were used to characterize the materials obtained:

2.4.1 Fourier transform infrared (FTIR) spectroscopy

FTIR spectra for crosslinked HMWPE films were recorded in the region of 4000-600 cm^{-1} using the Varian infrared spectrometer, Excalibur Series 100, equipped with a diamond crystal attenuated total reflectance (ATR) accessory. Films of 0.2 mm thick were obtained by compression molding in a Carver Press at 200°C for 5 min.

2.4.2 Gel content

The gel content of the HMWPE crosslinked samples was determined according to ASTM-D2765. The samples with about 0.3 g were allowed to swell and the soluble fractions were extracted in Xylene at (120 ± 2)°C for 24 h. The samples were then dried to a constant weight at a vacuum oven at (60 ± 1)°C. The gel content was determined by calculating the percentage of the sample weight remaining related to the sample initial weight.

2.4.3 Dynamic mechanical analysis (DMA)

The Storage Moduli (E') of the HMWPE samples were determined in a Q 800 dynamic mechanical analyser (DMA) (TA Instruments) by employing a tensile configuration. Specimens with 16 mm x 4 mm x 2.2 mm dimensions were prepared by compression molding in a Carver Press at 190°C for 5 min. Temperature was swept from 30^0 to 190°C at 3°C / min with a modulating strain of 0.2% at 1 Hz. The Storage Modulus (E´) was reported as a function of temperature. E´ values in the rubbery plateau region were then obtained at 180°C for each sample.

2.4.4 Differential scanning calorimetry (DSC)

The thermal properties of HMWPE and VTMOS crosslinked HMWPE samples were evaluated by DSC using a Perkin Elmer 7 Series Thermal Analysis System. Polymer samples of 4.5-7 mg were encapsulated in standard aluminum pans. An indium standard was used to calibrate the temperature scale and enthalpy of melting. The endotherms were determined at a heating rate of 10 °C / min over a range of 30° to 200°C under nitrogen atmosphere. The degree of crystallinity of the samples was calculated from the enthalpy of melting, assuming a value of 293 J/g for a melting enthalpy of a 100% crystalline polyethylene.

2.4.5 Thermogravimetric analysis (TGA)

The thermal stability of the samples was evaluated by TGA. The analyses were performed from 25 to 700°C at a heating rate of 10°C/min under nitrogen flow. The initial temperature of loss of weight (T_{onset}) and the temperature, in which the loss of weight was maximum were measured.

2.4.6 Tensile testing

Tensile properties were measured using a Shimadzu Universal Testing Machine, Model AG-I with a 5 kN load cell. Tests were conducted in accordance to ASTM D 638 using Type V test specimen dimensions. A crosshead speed of 2 mm/min was employed.

2.4.7 Sliding wear testing

The sliding wear tests were performed in an equipment developed by the Brazilian company NFP Automotive to perform tests with conventional and new developed materials. This equipment is composed of a cart like compartment, which has a steel base where the sample to be tested with dimensions of 150 mm x 15 mm x 2 mm is placed. This base is disposed on linear bearings and connected to a motor that rotates at a frequency range of 50 to 60 rpm by an articulated rod. A polished carbon steel AISI 1020 pin with 10 mm diameter is positioned on the prepared sample in the cart. This pin is kept in a vertical position by an aluminum base connected to a load cell (MK Controle, Model CSA -10 kg), which is supported by a bearing type rod in a steel base. The aluminum base has a support, where weights may be allocated allowing the reproduction of a sliding movement between two materials subject to a stress. The pin imposes a stress on the sample and the sliding force between them is recorded by the load cell during the entire movement and during all desired cycles. In this work, a force of 74 N was applied to the pin and the friction forces were acquired at each 600 cycles. These experimental conditions were adopted based on tests performed on gearboxes for heavy trucks used in NFP automotive[1]. In order to determine the abrasion resistance, the specimens were weighted before and after the test.

3. Results and Discussion

In order to obtain a material with improved wear resistance and good processability, crosslinks were introduced in a high molecular weight polyethylene grade. The crosslinking method employed is based on the grafting of a vinyl silane onto the polymer chain and the formation of siloxane bridges, through moisture crosslinking. The main features of the products obtained are described below.

3.1 Evidence for grafting and crosslinking reactions

Figure 1 shows the mechanism leading to the crosslinking of polyethylene and the involved reactions[14,18-20,29-31]. The changes in the content of structures I-III and the occurrence of oxidation products, whose absorption bands are reported in Table 2 are often used to monitor the crosslinking process[14].

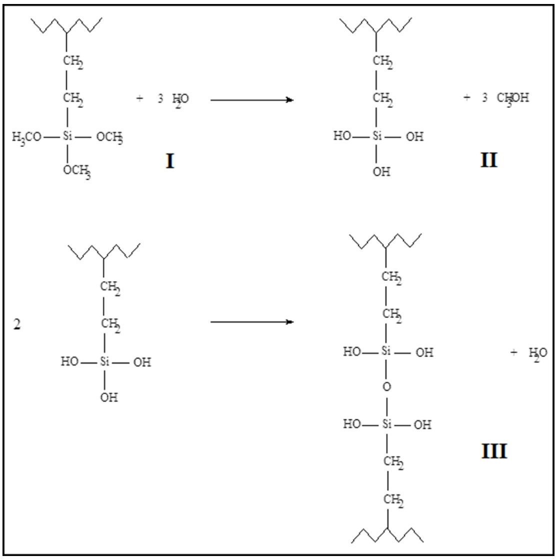

Figure 1. Silane crosslinking of polyethylene.

Table 2. Absorption frequencies used to follow the crosslinking reactions of polyethylene.

Structure	Wavenumber (cm^{-1})	References
-Si-CH	773	28
-Si-CH$_2$	1244	25, 28
-Si-OCH$_3$	1080,1090, 1092, 1192	17-19, 25, 26
-Si-OH free	3691	17
Hydrogen Bonded	3549 (3431)	17
-Si-O-Si-	1030, 1003	17, 27
-C=O	1720	17

In this work, FTIR technique was used to ensure that silane grafting and crosslinking reaction ocurred as a result of the Sioplas process. Figure 2 shows the FTIR spectra of HMWPE before and after crosslinking with 1.5 wt% of VTMOS, promoted by 0.01 wt% of DCP in the presence of 0.05 wt% of a tin catalyst. Quite similar spectra were obtained for HMWPE crosslinked with 0.5 and 1.0 wt% of VTMOS.

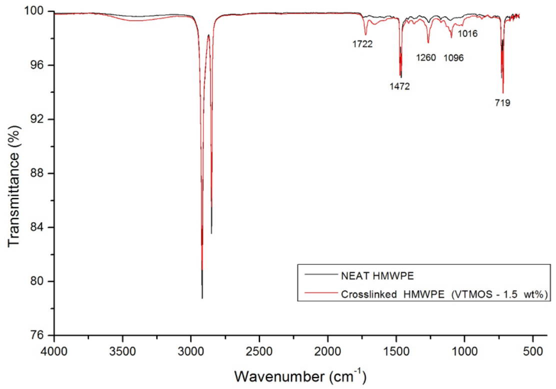

Figure 2. FTIR spectra of HMWPE and HMWPE crosslinked with 1.5 wt% of VTMOS.

There is an absorption peak at 1096 cm^{-1} related to the Si-O-C stretching vibration of the silane group. According to Ahmed et al.[32], the absorption peaks at 1192 and 1092 cm^{-1} are characteristic of the methoxy groups Si-OCH$_3$ and any siloxane crosslinks (Si-O-Si) that are formed during extrusion. There is also a peak at 1260 cm^{-1}, related to the Si-CH$_2$ group and other around at 1722 cm^{-1} corresponding to the absorption of carbonyl groups, C=O. The Si-O-Si absorption peak usually appears as a shoulder on the larger band related to the Si-O band of the Si-O-CH$_3$ structure. This larger peak can influence the absorption value of the Si-O-S linkage[20]. The peak at 1016 cm^{-1} may be assigned to the Si-O-Si asymmetric streching[31]. In this work, the peaks related to silane grafting and crosslinking reactions became more evident as the concentration of silane was increased. The absorption bands at 2916, 2848 and 719 cm^{-1} correspond to polyethylene CH$_2$ asymmetric stretching, CH$_2$ symmetric stretching and rocking deformation[29].

3.2 Effect of the VTMOS concentration on the gel content and on the storage moduli (E') of the HMWPE samples.

Table 3 shows the gel content of samples of HMWPE crossslinked with different concentrations of VTMOS. Table 3 also shows the values of Storage Modulus (E') obtained from DMA analysis.

The gel content increases with the increase of silane concentration. These results are in agreement with those obtained by other researchers[14,16,33]. There are evidences that high concentrations of silane grafted polyethylene are obtained using low concentrations of peroxide or with the increasing of peroxide concentration using low concentrations of silane. These studies indicate that, on basis of the processing conditions adopted, there is a optimum ratio between silane and peroxide concentration that provides the better efficiency of the graftization process[11].

According to Tamboli et al.[13], the main difference between thermoplastic and crosslinked polymer is that, at the temperature above the crystalline melting point, crosslinked polymer behaves as a soft rubber, while thermoplastic has no significant strength above melting temperature.

Table 3. Gel content and Storage Modulus (E') of HMWPE and VTMOS crosslinked HWMPE.

VTMOS (wt%)	Gel Content (%)	Error	E' (MPa) at 180°C
0	0.98	0.25	-
0.5	8.69	1.35	0.4331
1	29.23	0.43	0.5565
1.5	57.54	3.62	0.7241

Figure 3 presents the DMA curves of HMWPE and VTMOS crosslinked HMWPE samples.

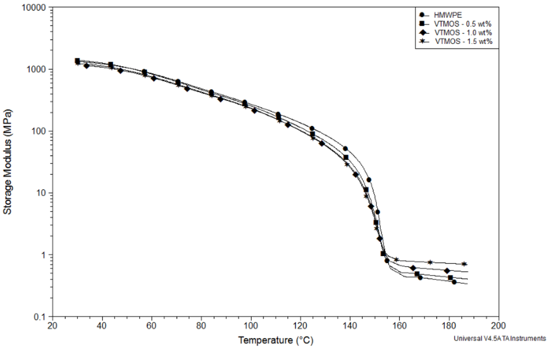

Figure 3. DMA curves of HMWPE and VTMOS crosslinked HMWPE samples

The profile of DMA curve of HMWPE is not affected by the introductions of crosslinks as shown in Figure 3. However, from 100°C, the samples processed with VTMOS present a slightly greater reduction of the E`values than the E' value presented by the HMWPE. A pronounced drop in E' is observed around 140°C due to the melting of the polymer. Compared to the HMWPE, the silane HMWPE crosslinked samples present higher and constant E´ values in high temperatures. Even, the DMA curve of HMWPE tends to flatten at higher temperatures. This finding has been attributed to the formation of unintended crosslinks caused by moisture intrusion into the polymer both pre and pro extrusion[18]. An increasing of the pseudoequilibrium modulus (E') in the rubbery plateau region with the increasing of VTMOS concentration is also observed (Table 3).

3.3 Thermal properties

Table 4 presents the following thermal properties of the materials under study: melting temperature (T_m), crystallization temperature (T_c), degree of crystallinity (X_c), the temperature of the beginning of degradation (T_{onset}) and the temperature at which the rate of thermal degradation is maximum (T_{max}).

The thermal properties of HMWPE are not greatly affected by the introduction of crosslinks, as the silane

Table 4. Thermal properties of HMWPE and VTMOS crosslinked HMWPE samples.

VTMOS (wt%)	T_m (°C)	T_c (°C)	X_c (%)	T_{onset} (°C)	T_{max} (°C)
0	132.6	119.3	64.2	461.6	480.6
0.5	131.8	119.2	61.4	461.9	482.2
1.5	131.4	118.4	60.8	463.6	482.9

polyethylene crosslinking occurs basically in the amorphous regions leaving the crystalline phase unchanged or slightly modified. Although the energy of the Si-O-Si linkages is high, 779 kJ/mol, the introduction of crosslinks hardly affect the polyethylene thermal stability, especially in a nitrogen atmosphere[21]. Similar results have been found by others researchers[12,15].

3.4 Tensile mechanical properties

Table 5 shows the tensile mechanical properties of HMWPE and VTMOS crosslinked HMWPE samples.

The results obtained shows that the HMWPE crosslinking led to a significant decrease in the elasticity modulus. However, the increasing of VTMOS concentration and gel content have not promoted any increasing in the Young´s Modulus of the crosslinked samples. This result was not expected as the mobility of the polymeric chains is restricted by the introduction of crosslinks[25]. Some researchers has attributed the decrease of the Young`s Modulus with the increase of the crosslinking density to a decrease in HMWPE crystallinity[13,34]. According to Tamboli et al[13], reduction in crystallinity occurs because crosslinking takes place in the amorphous phase. Decrease in the degree of crystallinity and crystalline thickness promotes a decrease of the Young's Modulus. Khonakdar[34] et al. in a study of high density polyethylene crosslinked with di-tert butyl cumyl peroxide (BCUP) verified that the glass transition temperature decreased with the increase of peroxide concentration. This result was attributed to the reduction in crystallinity and the expected increase in free volume as a result of restriction in chain packing. These researchers verified a decrease in the tensile modulus with the increase of peroxide concentration.

Table 5. Tensile mechanical properties of HMWPE and VTMOS crosslinked HMWPE samples.

VTMOS (wt%)	Young's Modulus (MPa)	Error (MPa)	Tensile Strength (MPa)	Error (MPa)
0	1259.9	79.9	21.6	0.5
0.5	1072.5	67.2	19.7	1.7
1.0	1041.8	93.8	21.8	0.4
1.5	918.3	69.3	21.3	1.0

The decrease of the elasticity modulus may also be considered a result of the heterogeneous structure of the crosslinked samples, composed by regions in which there are highly crosslinked centers and a large fraction of effectively uncrosslinked chains[15].

In this study, there was a slight decrease in the HMWPE degree of crystallinity with the increase of VTMOS concentration (Table 4). However, it is not possible to say for sure that this observed decrease in the modulus was due to this gentle decrease of HWMPE crystallinity. The heterogeneous structure of crosslinked samples may also be responsible by the reduction of the HMWPE elasticity modulus with the increase of the crosslinking density.

Table 5 shows that the HMWPE yield tensile strength was not affected by the reticulation process. This result is in agreement with those obtained by other researchers[11]. The increase in tensile strength seems to be caused basically by the -C-C- crosslinks, whereas the effect of siloxane bridges on this property is considered secondary. However, other studies indicate the tensile strength increases gradually with increasing of silane concentration from zero to 1.5 phr. This result has been attributed to the formation of a crosslinked structure considered very stable due to the high bond energy of the siloxane links[33].

3.5 Tribological properties

The friction and wear are often hard to predict from the material properties. Therefore, it is usually necessary to perform friction and wear tests for developing a tribo engineering system for a specific application. During test, it is important to simulate the conditions at which the system will be submitted because many variables, such as: contact pressure, temperature, sliding velocity, roughness of the rubbing surfaces, relative motion, among others affect wear and friction. The polymer molecular structure, viscoelastic behavior, surface texture and processing properties also have influence of the polymer tribological properties. Therefore, it is very important to simplify tests in order to exclude variables not significant for a given application[35,36].

In polymer friction, the main mechanisms of wear are adhesion, abrasion and fatigue. According to Lancaster[37], abrasive wear has been defined as wear by displacement of material from surfaces in relative motion caused by the presence of hard protuberances, or by the presence of hard particles, either between the surfaces or embedded in one of them. However, the wear of polymers is very complex and frequently none of the friction mechanisms of failure can be achieved without participation of others.

In this work, as mentioned earlier, sliding wear tests were performed in an equipment developed by the Brazilian company NFP Automotive[1]. In this company, there is a demand to perform tests with conventional materials as well as some new proposed materials. The tribological tests are performed in order to evaluate if a material could be used for the development of steering columns and i-shaft systems for transportation segments. A significant small wear is desirable to ensure low friction over high number of cycles that corresponds to the life span of these automotive parts. The mass loss is usually an indication that the test material is not suitable for the desired application.

Figure 4 presents the relationship between the tribological pairs under study and the slip cycles.

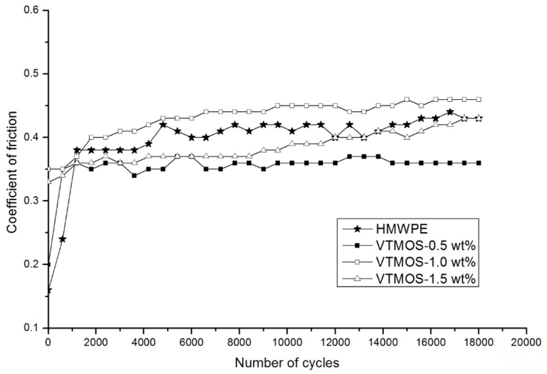

Figure 4. Relationship between the coefficient of friction of the HMWPE/Carbon Steel 1020 and VTMOS crosslinked polyethylenes/ Carbon Steel 1020 friction pairs and the slip cycles.

The variation of wear rate with operating time involves three distinct stages: a running-in period, a steady-state period and a severe wear period. At the starting of the experiment, the friction force is low due to the initial contact between the two materials that constitute the tribological system. As the friction continues, the softer material becomes worn and remains in contact with the harder material. The roughening of the surface of the softer material causes the ploughing and there is an increase of the coefficient of friction between the two materials. After a certain period, the increase of roughness and other parameters may reach a steady value and then, the values of the coefficient of friction remains constant. At this time, the friction force becomes independent on the force acting on the softer material[36].

In the first part of the tribological test, an increase in temperature and the formation of a transfer film is often noticed. This film is formed by the polymer particles that lie between the asperities at the steel pin surface. The formation of a transfer film occurs for most polymers, except for the highly crosslinked and some glassy polymers. Transfer film has important effects on the tribological behavior of polymers. In general, the thinner and more uniform and continuous the transfer film is, the lower the coefficient of friction. During the stationary test stage, however, oscillations of the coefficient of friction may occur due to local breakdown and recovery of the transfer film[35,36,38,39].

The mechanism of improvement in the wear resistance of the ultra high molecular weight polyethylene (UHMWPE) by increasing the crosslinking density seems to be basically dependent on the decreased conformational segmental mobility of the polymeric chains. This restricted mobility of the chains leads to a significant reduction in the surface deformation and orientation, which are the primary precursors of wear particle generation[40].

Figure 4 shows that a steady value of coefficient of friction is achieved by both, the HMWPE/ Carbon Steel 1020 and HMWPE crosslinked with 0.5wt% of VTMOS/ Carbon Steel 1020 friction pairs. However, the stationary value of the dynamic coefficient friction of this sample / Carbon Steel pair is lower than that presented by the HMWPE/ Carbon steel friction pair. This result may be an indication that the crosslinking of HMWPE with this low concentration of silane improves the wear resistance of this polymer. The coefficient of friction of HMWPE/ Carbon Steel pair seems to achieve a constant friction coefficient from 4800 cycles. However, this coefficient of friction begins to oscillate and appears to increase again from 15000 cycles. These oscillations may be attributed to changes in the sample, such as degradation.

Some empirical correlations established for the abrasive wear shows the wear rate is proportional to the inverse of the double strain energy in the elastic region of the tensile curve for the softer material[35]. Therefore, the evaluation of the resilience of the materials under study becomes interesting.

Figure 5 shows the resilience of HMWPE and VTMOS crosslinked HMWPE samples.

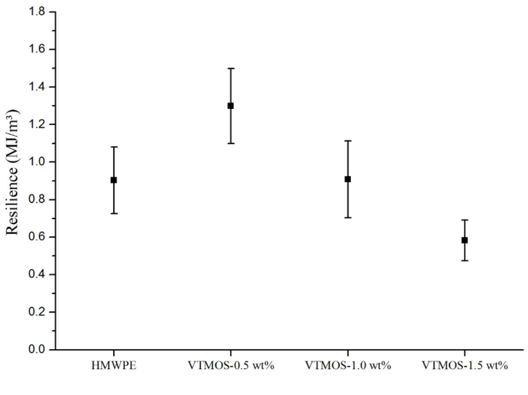

Figure 5. Resilience of HMWPE and VTMOS crosslinked HMWPE samples.

The resilience of the polyethylene crosslinked with 0.5 wt% of VTMOS is higher than that of the HMWPE. Thus, this crosslinked sample has more capacity to sustain the stresses caused by the contact with the asperities without significant permanent deformation. This result might be a plausible explanation for the increased resistance to wear this sample presents compared to that presented by the HMWPE.

Inspection of Figure 4 shows that at the starting of the sliding test the HMWPE crosslinked with 1.0 wt% of VTMOS/steel pair and the HMWPE crosslinked with 1.5 wt% of VTMOS/ steel pair exhibit a coefficient of friction around 0.34 and 0.33. This result perhaps may be attributed to the higher gel content and hardness of these samples.

A steady value of the coefficient of friction was not achieved during the sliding test of the crosslinked HMWPE with 1.0 and 1.5 wt% of VTMOS / steel tribological systems (Figure 4). These results may be an indication that the restricted mobility of the polyethylene chains with higher crosslinking density (Table 3) may be hampering the formation of the transfer films. In order to obtain more reliable results it is necessary to perform a experiment with a higher number of cycles or with an increasing of the normal force.

Table 6 shows the loss of mass of HMWPE and VTMOS crosslinked HMWPE samples during the wear sliding test. It is possible to see that in the experimental conditions used in this work the VTMOS crosslinked HMWPE samples/ Carbon Steel 1020 tribosystems presented higher wear resistance than the HMWPE/ Carbon steel 1020 tribosystem.

Table 6. Loss of mass of HMWPE and VTMOS crosslinked HMWPE samples during the wear sliding test.

VTMOS (wt%)	Initial mass	Final mass	Loss of mass (%)
0	3.166	3.140	0.82
0.5	3.021	3.021	0
1.0	3.315	3.315	0
1.5	3.443	3.443	0

4. Concluding Remarks

The results obtained indicate the gel content and crosslinkink density of HMWPE increase with the increasing of VTMOS content. The thermal properties were not much affected by the crosslinking density. The tensile modulus of HMWPE decreased with the introduction of crosslinks. Maybe, this result may be explained by the observed tendency of reducing the degree of crystallinity of HMWPE with increasing of the crosslink density or by the heterogeneous network formation. The yield tensile strength of HMWPE, however, was not affected. The preliminary investigation of the tribological behavior of the HMWPE/ steel 1020 pair and HMWPE crosslinked samples/ Carbon Steel 1020 pairs indicated that the functionalization of HMWPE with VTMOS improved the wear resistance of HMWPE in the experimental conditions adopted in this work. In order to obtain more reliable results for the tribological properties, in the next steps of this study, experiments with a higher number of cycles or with an increasing of the normal force should be performed.

5. Acknowledgments

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6. References

1. Moraes LRC. *Processos de formação de ligações cruzadas de polietileno de alto peso molecular*. [Dissertation]. Nova Friburgo: Universidade do Estado do Rio de Janeiro; 2015.
2. Fischer LW. *Selection of Engineering Materials and Adhesives*. Boca Raton: CRC Press; 2005.
3. Baena JC, Wu J, Peng Z. Wear Performance of UHMWPE and Reinforced UHMWPE Composites in Arthroplasty Applications. A Review. *Lubricants*. 2015;3(2):413-436.
4. Selyutin GE, Gavrilov YU, Voskresenskaya EN, Zakharov VA, Nikitin VE, Poluboyarov VA. Composite Materials Based on Ultra High Molecular Polyethylene: Properties, Application Prospects. *Chemistry for Sustainable Development*. 2010;18:301-314.
5. Medel FJ, García-Álvarez F, Gómez-Barrena E, Puértolas JA. Microstructure changes of extruded ultra high molecular weight polyethylene after gamma irradiation and shelf-aging. *Polymer Degradation and Stability*. 2005;88(3):435-443.
6. Pruitt LA. Deformation, yielding, fracture and fatigue behavior of conventional and highly cross-linked ultra high molecular weight polyethylene. *Biomaterials*. 2005;26(8):905-915.
7. Oral E, Neils AL, Rowell SL, Lozynsky AJ, Muratoglu OK. Increasing irradiation temperature maximizes vitamin E grafting and wear resistance of ultrahigh molecular weight polyethylene. *Journal of Biomedical Materials Research. Part B Applied Biomaterials*. 2013;101B(3):436-440.
8. Kurtz SM, Muratoglu OK, Evans M, Edidin AA. Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty. *Biomaterials*.1999;20(18):1659-1688.
9. Muratoglu OK, Bragdon CR, O' Connor DO, Jasty M, Harris WH. A novel method of cross-linking ultra-high-molecular-weight polyethylene to improve wear, reduce oxidation, and retain mechanical properties. *Journal of Arthroplasty*. 2001;16(2):149-160.
10. Globichem. *High density polyethylene HS5103* [Internet]. 2016. Available from: <http://www.globichem.com/pdf/polyethyene-pe/hdpe/HDPE%20-%20HS5103.pdf>. Access in: 2/11/2016.
11. Morshedian J, Hoseinpour PM. Polyethylene crosslinking: Silane Method: A Review. *Iranian Polymer Journal*. 2009;18(2):103-128.
12. Sirisinha K, Sungmanee B. Silane Crosslinking of High Density Polyethylene as Catalyzed by Tin and Amine Catalyst. *Journal of Chemical Engineering and Chemistry Research*. 2014;1(6):365-372.
13. Tamboli SM, Mhaske ST, Kale DD. Crosslinked polyethylene. *Indian Journal of Chemical Technology*. 2004;11:853-864.
14. Melo RP, Aguiar VO, Marques MFV. Silane Crosslinked Polyethylene from Different Commercial PE`s: Influence of Comonomer, Catalyst Type and Evaluation of HLPB as Crosslinking Coagent. *Materials Research*. 2015;18(2):313-319.

15. Celina M, George GA. Characterization and degradation studies of peroxide and silane crosslinked polyethylene. *Polymer Degradation and Stability*. 1995;48(2):297-312.

16. Shah GB, Fuzail M, Anwar J. Aspects of the crosslinking of polyethylene with vinyl silane. *Journal of Applied Polymer Science*. 2004;92(6):3796-3803.

17. Kuan HC, Kuan JF, Ma CCM, Huang JM. Thermal and mechanical properties of silane-grafted water crosslinked polyethylene. *Journal of Applied Polymer Science*. 2005;96(6):2383-2391.

18. Ghosh-Dastidar A, Sengupta S, Flory A, Cogen JM. Effect of Silane Grafting Level and Crosslinking Structure on Properties of Moisture Crosslinkable Systems. In: *Proceedings of the 57th International Wire&Cable Symposium*; 2008 Nov 9-12; Providence, RI, USA. IWCS; 2008. p. 138-145.

19. Cameron R, Lien K, Lorigan P. Advances in silane crosslinkable polyethylene. *Wire Journal International*. 1990;23(12):56-58.

20. Hjertberg T, Palmlöf M, Sultan BA. Chemical reactions in crosslinking of copolymers of ethylene and vinyltrimethoxy silane. *Journal of Applied Polymer Science*. 1991;42(5):1185-1192.

21. Sen AK, Mukherjee B, Bhattacharyya AS, De PP, Bhowmick AK. Kinetics of silane grafting and moisture crosslinking of polyethylene and ethylene-propylene rubber. *Journal of Applied Polymer Science*. 1992;44(2):1153-1164.

22. Wong WK, Varral DC. Role of molecular structure on the silane crosslinking of polyethylene: the importance of resin molecular structure change during silane grafting. *Polymer*. 1994;35(25):5447-5452.

23. Huang H, Lu HH, Liu NC. Influence of grafting formulations and extrusion conditions on properties of silane-grafted polypropylenes. *Journal of Applied Polymer Science*. 2000;78(6):1233-1238.

24. Barzin J, Azizi H, Morshedian J. Preparation of Silane-Grafted and Moisture Crosslinked Low Density Polyethylene. Part II: Electrical, Thermal and Mechanical Properties. *Polymer-Plastics Technology and Engineering*. 2007;46(3):305-310.

25. Oliveira GL, Costa MF. Optimization of process conditions, characterization and mechanical properties of silane crosslinked high-density polyethylene. *Materials Science and Engineering: A*. 2010;527(18-19):4593-4599.

26. Narkis M, Tzur A, Vaxman A, Fritz HG. Some properties of silane-grafted moisture-crosslinked polyethylene. *Polymer Engineering & Science*. 1985;25(13):857-862.

27. Lachtermacher MG, Tatizawa, N, Ramos VD, inventors. Petróleo Brasileiro AS, assignee. *Polietileno de alta densidade modificado por reação com peróxido para a fabricação de filmes e fibras*. Brazil Patent PI09048847. 2011 Aug 2.

28. Sun KR, Park IG, Nam YS, Song Y, inventors. LG Chem Ltd, assignee. *Crosslinked polyehtylene resin composition*. Korea Patent EP 3045496 A1. 2016 Jul 20.

29. Pessanha AB, Rocha MCG, Silva AHMFT. Introdução de ligações cruzadas no LLDPE através do processo de extrusão reativa de graftização do vinil-trimetóxi-silano (VTMS) na cadeia polimérica: Efeito das condições de processamento e do sistema reacional. *Polímeros*. 2011;21(1):53-58.

30. Shieh YT, Chuang HC, Liu CH. Water crosslinking reactions of silane-grafted polyolefin blends. *Journal of Applied Polymer Science*. 2001;81(7):1799-1807.

31. Shieh YT, Tsai TH. Silane grafting reactions of low density polyethyelene. *Journal of Applied Polymer Science*. 1998;69(2):255-261.

32. Ahmed GS, Gilbert M, Mainprize S, Rogerson M. FTIR analysis of silane grafted high density polyethylene. *Plastics, Rubber and Composites*. 2009;38(1):13-20.

33. Yussuf AA, Kosior E, Alban L. Silane grafting and crosslinking of metallocene-catalysed LLDPE and LDPE. *Malaysian Polymer Journal*. 2007;2(2):58-71.

34. Khonakdar KA, Morshedian J, Wagenknecht U, Jafari SH. An investigation of chemical crosslinking effect on properties of high density polyethylene. *Polymer*. 2003;44(15):4301-4309.

35. Gustafsson E. *Investigation of friction between plastic parts*. [Dissertation]. Göteborg: Chalmers University of Technology; 2013.

36. Chowdhury MA, Nuruzzaman DM, Roy BK, Samad S, Sarker R, Rezwan AHM. Experimental investigation of friction coefficient and wear rate of composite materials sliding against smooth and rough mild steel counterfaces. *Tribology in Industry*. 2013;35(4):286-296.

37. Lancaster JK. Abrasive wear of polymers. *Wear*. 1969;14:223-239.

38. Besnea MAC, Trufasu DC, Andrei G, Bastiurea M, Rodeanu MS. Estimation of Wear Behavior of Polyphenylene Sulphide Composites Reinforced with Glass/Carbon Fibers, Graphite and Polytetrafluoroethylene by Pin-on-Disc Test. *Tribology in Industry*. 2015;37(1):88-96.

39. Xie T, Zhou ZH, Xu ZX, Yu JW, Jiao MH. Characteristics of the transfer film and tribological properties of Oxide/PTFE composites. *Advanced Materials Research*. 2013;631-632:172-175.

40. Muratoglu OK, O'Connor DO, Bragdon CR, Delaney J, Jasty M, Harris WH, et al. Gradient crosslinking of UHMWPE using irradiation in molten state for total joint arthroplasty. *Biomaterials*. 2002;23(3):717-724.