Tribol Lett (2016)64:27
DOI 10.1007/s11249-016-0763-y

ORIGINAL PAPER

The Effect of Crosslinks on the Sliding Wear of High-Density Polyethylene

E. C. Molinari[1,2] · **M. D. Failla**[1] · **W. R. Tuckart**[2]

Received: 13 June 2016 / Accepted: 24 September 2016

Abstract The purpose of this study was to determine the influence of the molecular crosslinking in the wear resistance of a linear polyethylene (PE) sliding against a rough steel surface. A set of PEs with different degrees of crosslinks were obtained by chemical modification of a PE with varying concentrations of organic peroxide. The amount of gel, molecular weight between crosslinks (M_c), crystallinity and Vickers microhardness were determined in the crosslinked PE's. The tribological performance of the materials was evaluated under dry sliding conditions using a block-on-ring tester. The coefficient of friction and the wear rate were determined in experiments in which a sample of polymer was contacted with the peripheral surface of a steel ring rotating at constant velocity. The wear resistance of the crosslinked materials increases with the amount of gel and when M_c decreases. The crosslinked PE showed a wear rate lower than the original PE when the amount of gel was larger than 80 % of the total mass. The coefficient of friction of the PE and crosslinked material was about 0.2 regardless of the normal load applied. The analysis of the worn surfaces by optical and SEM microscopy reveals that the primary mechanism involved in wear is abrasive wear.

Keywords Polyethylene · Crosslinking · Wear · Friction

1 Introduction

Polyethylene (PE) is a widely used thermoplastic due to its balanced physical and mechanical properties, good processability and relatively low cost. Nevertheless, the PE's have relative low deformation and melting temperature that limit its use. Molecular crosslinking is a method often applied to upgrade the physical and mechanical properties and to improve the thermal stability of PE's [1–3]. Several techniques based on chemical reactive processing or radiation treatment were developed to crosslink PE's, being chemical attack by organic peroxides among the most used in the industry as it can be carried out during the processing stages in the molten state [1–3]. The O–O chemical groups of the peroxide decompose at the processing temperatures of the polymer to give oxy-radicals that subsequently remove hydrogen atoms from the molecules producing macro-radicals that may follow various chemical reactions [1–3]. The macro-radicals can participate mainly in chain-linking or chain-scission reactions, being the first the one that prevail in the case of PE's. It is well known that when PE under goes mainly chain-linking the molar mass increases with the concentration of the peroxide, until it reaches infinitely large values. If the peroxide concentration increases even further, a molecular network or gel starts forming. This phenomenon is called gelation and signals the transition between the liquid- and solid-like state. When the gel is formed, the material loses its ability to flow and part of it becomes insoluble. After gelation, some of the molecules are incorporated into the molecular network while others remain in the soluble part. If the peroxide concentration is increased above the gel point, the gel fraction increases until almost all the material is incorporated to the network [1–3].

✉ E. C. Molinari
emolinari@plapiqui.edu.ar

[1] Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET), Camino "La Carrindanga" Km 7, 8000 Bahía Blanca, Argentina

[2] Departamento de Ingeniería, Universidad Nacional del Sur, Av. Alem 1253 1° Piso, 8000 Bahía Blanca, Argentina

The properties of the crosslinked PE are determined by the degree of modification of molecular structure below the gel point, for example the average molecular weight and branching, while at higher peroxide concentrations by partition between soluble material and gel and the characteristics of the molecular network. Several papers discuss the improvement in some viscoelastic and tensile properties, thermal stability, resistance to stress cracking, to solvents and aging [1, 4–10]. However, few studies address the effect of peroxide crosslinks in relation to the wear property of the resulting polymer. Most of the studies dealing with tribological performance of peroxide-crosslinked PE were performed on ultra-high-molecular weight PE (UHMWPE) owing to the importance of this type of PE for fabricating bearing components used mostly in medical implants. There is agreement in that crosslinks help to make UHMWPE more wear resistant [11–13].

For instance, McKellop et al. [11] found that a UHMWPE crosslinked with 1 wt% of an organic peroxide (Lupersol 130) shows a mean wear rate reduction of about 93 % compared to the unmodified polymer when tested using a hip-joint simulator. Gul [14] analyzed the wear of two different UHMWPE chemically crosslinked with various concentrations of organic peroxide (Varox 130) using a bidirectional pin-on-disc wear tester, noting that the wear rate decreases linearly with the increase in crosslink density. For example, a reduction of approximately 30 % in molecular weight between crosslinks (M_c) resulted in a decrease of 67 % in the wear of one of them, while 57 % in the other. Yim et al. [15] reported that the wear resistance of a UHMWPE chemically modified with 0.5 wt% of dicumyl peroxide is 1.5 larger than the one corresponding to the pristine PE. Additionally, the authors pointed out that a correlation exists among wear rate and the ratio between the maximum contact stress and the yield stress. Muratoglu et al. [16] investigated the wear behavior of two different peroxide-crosslinked UHMWPEs using a bidirectional pin-on-disk wear tester. The authors found that the wear rate decreases proportionally with the molecular weight between crosslinks.

Studies on the tribological response of standard PEs crosslinked with peroxides show conflicting results. Rose et al. [17] performed ball-on-flat wear tests in which the polymer was the flat surface; they found that the wear resistance of HDPE could be improved by introducing crosslinks. Unfortunately, the crosslinking procedure used to modify the polymer and the parameters that characterize the structure of the material were not given in the report. In contrast, Kampouris and Andreopoulos [18] reported that the wear resistance of peroxide-crosslinked PE sliding against emery paper decreases with the gel amount. The authors used peroxide concentrations as to produce a maximum gel amount of 70–80 wt%. The wear resistance of a material having gel content of about 70 wt% was half of the pristine PE.

The few studies on the influence of crosslinking on the wear resistance of PE modified with peroxide have provided valuable information, but it is necessary to conduct additional studies on the subject since the results are somewhat contradictory. In this paper we study the tribological behavior of PE's, whose crosslinked structure was varied systematically, was evaluated by performing dry sliding tests over a steel surface. Accordingly, a high-density PE was modified with different concentration of organic peroxide ranging from 0.04 to 3.5 wt%, to produce materials having a wide difference in the amount of gel. The wear performance of the materials was evaluated by conducting friction tests using a block-on-ring machine under dry sliding conditions and at controlled ambient temperature. The experimental setup utilizes the friction between a polymer block, which is constantly loaded against the peripheral surface of a steel disc that rotates at constant speed. The wear rate was deducted from the mass loss of the specimens related to the sliding distance. The friction force was measured during the test allowing estimating the coefficient of friction (COF). The wear rate and the COF were analyzed in terms of structural parameters such as the gel fraction and the average molecular weight between crosslinks, as well as in term of the crystallinity and the hardness. The worn surface of the polymer and the steel ring surface were examined using an optical microscope and a scanning electron microscope to ascertain the wear mechanism that takes place.

2 Experimental

2.1 Material and Modification Procedure

A high-density PE from Dow-Polisur SA was used that, according to the producer, has a melt flow index of 0.38 g/10 min (190 °C/5 kg). The polymer has a weight average molecular weight of 98,000 g/mol, obtained by size exclusion chromatography combined with light scattering.

The organic peroxide used as initiator of the crosslinking reaction was 2,5-dimethyl-2,5-di(*t*-butyl peroxy) hexane provided by Akzo Nobel Argentina. The peroxide concentration ranged from 0.04 to 3.5 wt% based on the polymer mass. The polymer in the form of powder was mixed with different amounts of a solution of peroxide in acetone to give the proper concentration of peroxide in the polymer when the acetone is removed by evaporation. We used this method of impregnation because previous work showed that it produces an even and uniform dispersion of the peroxide on the polymer bulk [9].

The PE powder impregnated with the peroxide was placed into a mold that consists of two metallic plates held apart by a metallic frame of 3 mm thick and with an opening of 10 cm × 15 cm. All together were compressed between the hot plates of a hydraulic press at 170 °C for 25 min. After this time has elapsed, the mold was removed from the press and allowed to cool to room temperature. The processing time was chosen based on results of previous work and is the time required to ensure complete crosslinking reaction at the molding temperature [9]. Plates of the pristine PE were also obtained by the same molding procedure. The modified material is identified as PE#, where # is a number associated to the concentration of peroxide used to crosslink the PE. Thus, for instance, PE250 identify the material obtained using a peroxide concentration of 2.5 wt%.

2.2 Gel Content Measurements

The gel fraction of the crosslinked polymers was determined by extracting the soluble portion with hot xylene. About 0.5 g of the modified polymer was placed into a basket made from stainless steel mesh, which was immersed in xylene at 125 °C for two periods of 8 h. Fresh solvent was used in each extraction period, and nitrogen gas was continuously bubbled into the solution to prevent oxidation of the material. The samples were then dried under vacuum until reaching constant weight, and the gel fraction was estimated from the relationship between the final and the initial mass of the sample.

2.3 Swelling Measurements

Swelling measurements were done on the crosslinked polymer to obtain the molecular weight between crosslinks. A fraction of the gel of each polymer was weighted and put into xylene at 125 °C for 1 h. The amount of xylene in the gel was measured by weighing the sample just after it was removed from the solution. The molecular weight between crosslinks (M_c) was calculated according to the Flory–Rhener equation [19]:

$$M_c^{-1} = -\frac{V_r + \chi V_r^2 + \ln(1 - V_r)}{\rho_p V_0 \left(V_r^{1/3} - \frac{V_r}{2}\right)}\ (\text{g/mol})$$

M_c is the molar mass between crosslinks and V_r is the volume fraction of polymer in the swollen gel

$$V_r = \frac{1}{\left(\frac{\rho_p M_s}{\rho_s M_p}\right) + 1}$$

where M_p is the weight of the dry gel, M_s is the weight of the solvent taken up by the gel, $\rho_p = 0.806$ g/cm^3, density of the polymer, $\rho_s = 0.761$ g/cm^3, density of the solvent; $\chi = 0.31$, the solvent interaction parameter for PE swelled in *p*-xylene, $V_0 = 139.3$ cm^3, the molar volume for xylene [19]. The M_c value was not corrected by loose chain ends present in the material.

2.4 Calorimetric Measurements

The degree of crystallinity of the polymers was determined from the enthalpies of fusion measured in a Perkin Elmer (DSC) PYRIS 1 system. The calorimeter was calibrated using Indium as a standard. Specimens of about 8 mg of each polymer were sealed in aluminum pans and heated from 30 to 160 °C at a rate of 10 °C. The enthalpy of fusion of each material was calculated from the area of the endothermic peak, defined by drawing a straight line from the onset to the end of the melting range. The degree of crystallinity was estimated considering a value of 69 kcal/kg for the fusion enthalpy of pure crystalline PE [20]. The reported results for the crystallinity of the different PEs correspond to an average of the values determined for at least three samples of each polymer.

2.5 Hardness Measurements

The hardness of the samples was measured at room temperature (22 ± 2 °C) using a Hanneman D32 microhardness tester mounted on a Jena metallographic microscope and fitted with a pyramidal Vicker's tip of 136°. An indentation load of 20.5 g was applied for 2 min, following the suggestion made by Henderson and Wallance for measuring hardness in crosslinked PE [21]. Immediately after removing the load, the length of the diagonals of the mark was measured with a resolution of 1 μm. The use of a pyramidal indenter avoids complications due to the elastic recovery of the indentation since the length of the diagonals remains practically unaltered during the recovery stage [21]. The Vicker's microhardness was calculated using the standard relationship $H_v = 1.854\ P/d^2$, where P is the applied load in kg and d is the average of the diagonal lengths expressed in mm. The value of Hv reported corresponds to an average of at least 20 indentations performed to each material.

2.6 Sliding Friction Test

The wear resistance of the materials was determined using a block-on-ring tribometer in accordance with the standard ASTM G77-06 under dry conditions and at the controlled temperature of 20 ± 1 °C. A schematic representation of the arrangement used for testing the materials is shown in Fig. 1. A stationary polymer specimen was placed in sliding contact with the peripheral surface of a steel ring of

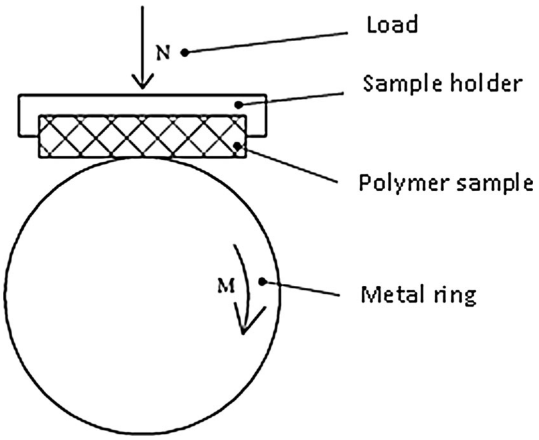

Fig. 1 Illustration of the block-on-ring assembly

35 mm diameter and 8 mm thick. The outside edge of the steel ring surface was machined to produce a surface topography characterized by having five asperity peaks per millimeter and an average surface roughness, R_a, of 14.7 µm, measured perpendicular to the sliding direction. The polymeric specimens of size 18 mm × 6 mm × 3 mm were punched out from the molded plates.

The wear tests were performed using a velocity of the rotation of the ring of 345 rpm, which corresponded to a velocity of sliding of 0.63 m/s. Before each run, the steel rings were cleaned thoroughly with acetone in an ultrasonic bath and then allowed to dry at open air.

The sample holder was rigidly attached to a pivoted arm that allowed loads to be applied to the sample by means of a dead weight. A load of 10 N was applied to all materials, while loads of 5, 15 or 20 N was also applied to some of the materials. It is necessary to point out that the analysis presented in this work was done taken the load as parameter instead of pressure, because this is not known with precision due to the geometry used, and its value changes constantly during the test when the wear proceeds.

The wear was estimated by measuring the mass loss by the sample after running the test during 1 h (sliding distance of 2276 m) to ensure that it was carried out within the steady-state region. The mass loss was determined by weighing the specimens before and after the tests to an accuracy of 1×10^{-4} g in a high-precision electronic balance. The wear rate was defined as the mass loss normalized by the sliding distance, and the value reported were obtained by averaging the results of at least five runs.

During the test, the force of friction was measured by a transducer mounted to the arm and recorded with a data acquisition system. This allowed obtaining the COF according to the standard ASTM G115.

The surface of the rings and the worn surface of the polymers were observed by optical microscopy and scanning electron microscopy (SEM) to assess the wear processes involved. The surface of the materials was coated with gold by vacuum evaporation technique and observed using a SEM JEOL EVO 40-XVP.

3 Results and Discussion

3.1 Gel Content and Swelling Results

The HDPE was modified using concentrations of organic peroxide from 0.04 to 3.5 wt%. The modification reactions are assumed to proceed following the general scheme proposed for free radical mechanism [3]. The peroxide decomposes when it is exposed to heat, and alkoxy radicals are formed. These radicals can remove hydrogen atoms from the macromolecules to form macro-radicals that may follow different reaction pathways; the main reaction is the combination producing molecular crosslinks. The soluble fraction and swelling measurements performed give information about the gel content and the average molecular weight between crosslinks by calculation using the Flory–Rhener equation [19]. Table 1 summarized the structural properties together with crystallinity and hardness of the materials studied.

The evolution of gel with the peroxide concentration is presented in Fig. 2. As can be observed, the material remains soluble and no gel fraction could be detected when the polymer was modified with a concentration of peroxide of 0.04 wt%. Nevertheless, it is expected that the peroxide attack produces a material with branched structure having larger weight average molecular weight and broader molecular weight distribution than the pristine PE [9]. A rather small amount of gel (~2 wt%) was detected in PE008 signaling the incipient formation of a molecular network. Further increment in peroxide concentration causes an increment in the amount of gel that reaches a value close to 100 wt% when 1.5 wt% of peroxide was used to modify the PE. At this peroxide concentration, most of the molecules were incorporated into the network and the soluble material is too low to be measurable. Additional increment in peroxide concentration does not seem to change the amount of gel that remains in about 100 wt%. These observations are in concordance with results reported by other authors when cross linking linear PE's with organic peroxides [7, 18, 23]. In Fig. 2 it is also included the molecular weight between crosslinks as a function of the concentration of peroxide. It can be seen that M_c decreases with the peroxide content indicating the formation of a network with increasing crosslinking density. M_c reaches a value of about 1700 g/mol at peroxide concentration of 2.5 wt% when the gel amounts ~100 wt% that indicates the formation of a highly dense molecular network.

Table 1 Parameters obtained from structural and mechanical characterization

Material	Concentration of peroxide (wt%)	Gel content (wt%)	M_c (g/mol)	Crystallinity (wt%)	H_v (kg/mm^2)
PE	0	0	–	55	3.8
PE04	0.04	0	–	54	3.5
PE08	0.08	~2	–	54	3.4
PE15	0.15	25	–	53	3.2
PE30	0.30	77	16,600	45	2.6
PE50	0.50	80	15,600	42	2.7
PE100	1.00	97	6800	41	2.4
PE150	1.50	~100	2300	38	1.9
PE250	2.50	~100	1700	40	2.1
PE350	3.50	~100	2200	44	2.1

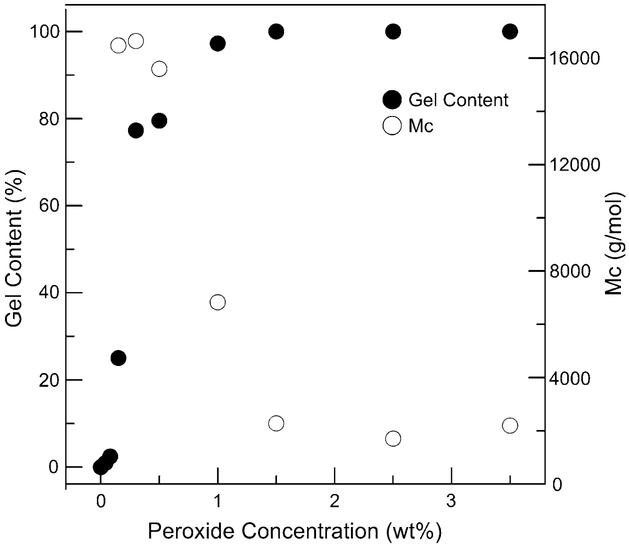

Fig. 2 Gel content and molecular weight between crosslinks, M_c, as a function of the peroxide concentration

It has been considered that the junction of the molecular network results from a combination of chemical crosslinks and trapped physical entanglements. The last type of junction may dominate the network as suggested by some authors taking into consideration that the physical entanglements accounts for a large proportion of the network junctions, about 2/3 of the total, in crosslinked PE [24]. This is consistent with that the M_c for materials having ~100 % of gel is close to the molecular weight between entanglements 1200–1400 g/mol that is proposed for linear PEs [25]. The M_c reaches a stable value, still seems to go through a minimum, when the PE was modified with the higher concentrations of peroxide. At this point, the molecular network may impose restrictions to the mobility of free radicals due to constraint in diffusion of molecular segments that can hamper chain-linking reactions. In consequence, the macro-radicals may be able to follow other reaction pathways, for instance scission reactions that might be responsible for the observable change in the diminishing trend of M_c with the peroxide concentration.

3.2 Crystallinity and Vickers Microhardness

The thermal behavior of the PE and the modified material was analyzed by calorimetry following the procedure presented in the experimental section. The thermograms obtained for all the samples were characterized by a well-defined endotherm of fusion. The modified polymers display a clear decay in the heat of fusion and a reduction in the temperature of fusion with the peroxide content.

The crystallinity level as obtained from the heat of fusion is presented in Table 1 and plotted against the peroxide concentration in Fig. 3. The decrease in crystallinity with the amount of gel is observed in the figure, which is

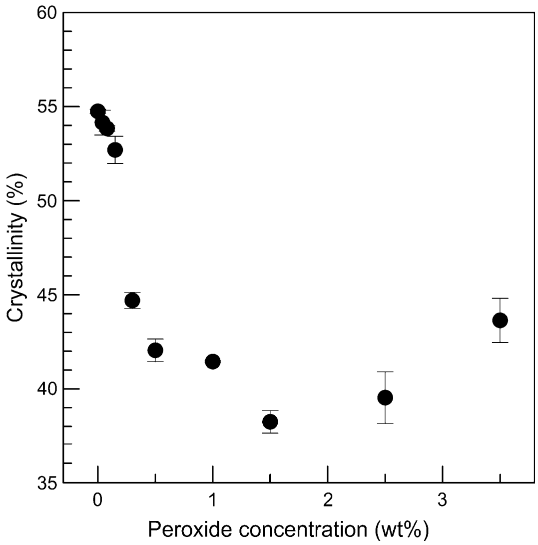

Fig. 3 Crystallinity as a function of peroxide concentration

expected to occur because the modification process involves the fusion of the PE to induce chemical modification which is followed by crystallization of a crosslinked network. The formation of chain linkages as a consequence of the peroxide attack reduces the sequence of crystallizable chain segments and restricts its diffusion in the melt, that in turn affects the reorganization and chain folding of the polymer chains during the crystallization process [26, 27]. As a result, the increment in the density of crosslinks, or equivalently decreasing the molecular weight between crosslinks, causes the formation of crystal with smaller size and less perfect and reduces the crystallinity of the polymer as the peroxide concentration increases. The lower levels of crystallinity (38–40 %) were obtained when the PE was modified with 1.5–2.5 wt% of peroxide and the amount of gel is about 100 wt%. The results are in agreement with earlier reports that found crystallinity level of about 40 wt% when the gel attained is close to 90 wt% after crosslinking linear PE with an organic peroxide [7]. The occurrence of some molecular chain scission at this level of modification as commented above may be the contributing factor for the small change in the crystallinity trend observable at the highest concentrations of peroxide. The molecular scission could favor the freedom of movement of molecular segments that promote further crystallization.

The variation of microhardness with the crystallinity is shown in Fig. 4. The line in the figure was drawn just to signal trend. It can be seen that the hardness shows a tendency to increases with increasing crystallinity level. Previous studies involving PEs have observed a similar relationship between hardness and crystallinity, although direct proportionality between them is not observed over a wide range of crystallinity [28–30].

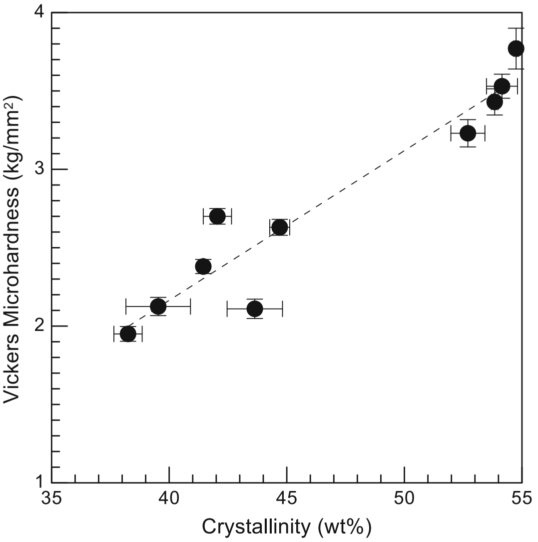

Fig. 4 Vickers microhardness as a function of crystallinity

3.3 Tribological Behavior

Preliminary experiments showed that the wear rate and COF measured for a given material varied appreciably after performing consecutive trials using the same ring. As illustrative example, Fig. 5 includes the wear rate and COF measured for PE008 as function of the number of trials. It can be observed that the values of these properties decrease continuously up to the fourth trial after which they level off. A similar behavior was observed for all the materials.

Examination of the contact surface of the steel ring with an optical microscope reveals that the topography of the surface is altered after the first consecutive tests. As illustrative example, Fig. 6 displays microphotographs of a zone of the contact surface of the ring as seen before testing (Fig. 6a) and after the ninth trial experiment (Fig. 6b). The dark areas in the photography are the ridges, while the gray ones are the valleys of the grooves produced after machining the steel by a turning process. The arrows point the crest of the ridges which appears as very light gray areas in the photography. It can be observed a notable increase in the size of these areas after performing the set of experiments consecutively. These changes indicate that the asperity of the grooves becomes smoother and flatter after testing. Other authors have reported that PE rubbing against a steel surface produces a smoothing of the metal surface which reduces wear of the polymer [22].

Thus, the large variation in the wear rate and COF observed after the first trials can be ascribed to the modification of the surface of the steel. After the fourth or fifth round, the topography of the metal surface does not seem subject to change; at least detectable with a light

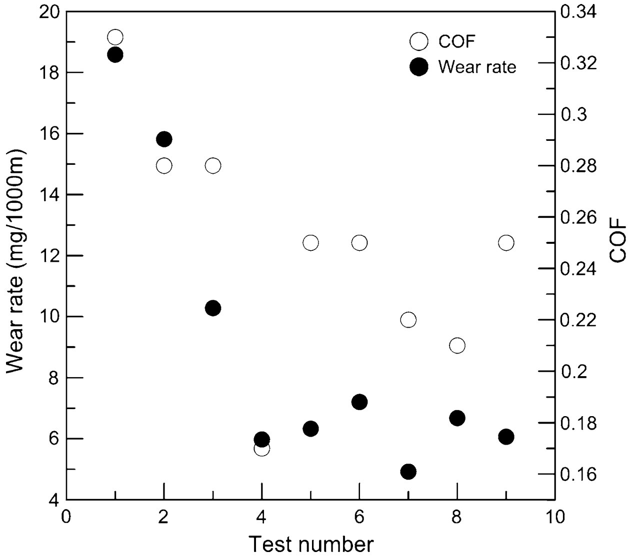

Fig. 5 Wear rate and COF as a function of the number of trials for PE-008

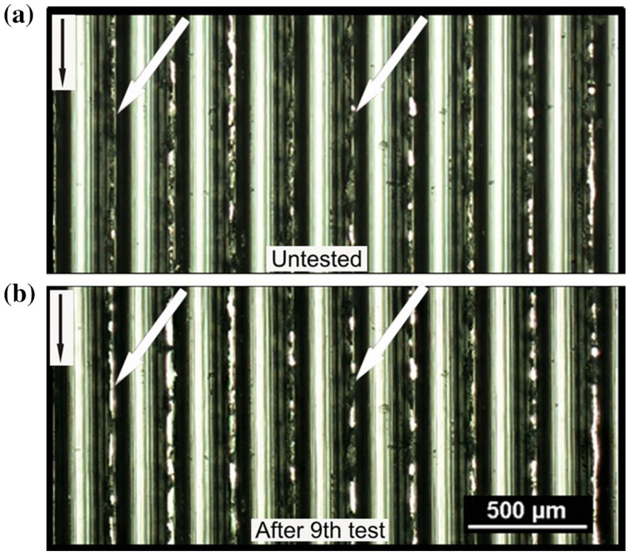

Fig. 6 *Top* view of a zone of surface of the steel ring obtained with an optical microscope: **a** before testing and **b** after the ninth trials

microscope, which may explain that the tribological properties do not change significantly in value as shown in Fig. 5. Taken into account this observation, the values of the properties reported here correspond to an average of at least five independent measurements, which were performed after making five consecutive tests using the same ring each time.

The wear rate as a function of the peroxide concentration evaluated at load of 10 N is shown in Fig. 7.

In this figure it can be seen that the wear rate increases rapidly with the peroxide concentration up to a concentration of 0.08 wt%, PE008 shows a wear rate about three times larger than PE. Further increment in peroxide concentration produces a monotonic decrease in wear rate.

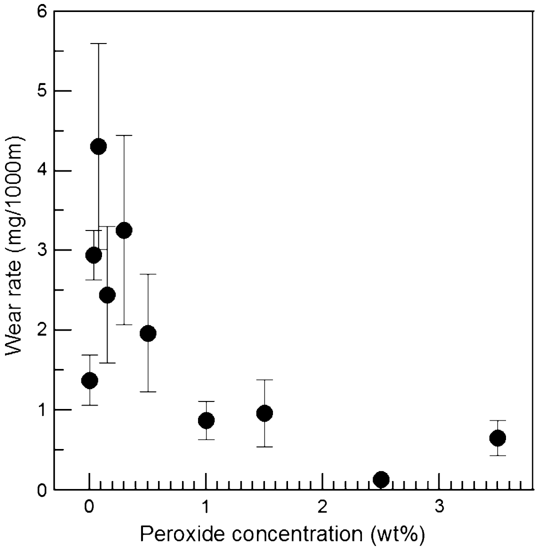

Fig. 7 Wear rate as a function of peroxide concentration

The wear rate of PE is consistent with the wear results reported by Trevor for linear PE of equivalent molecular weight that was measured in abrasive conditions although under somewhat different conditions than the one used here [31]. The reduction in wear resistance observable in the PEs modified with the lowest peroxide doses is contrary to what is expected taken into account the different factors that play some role in the wear behavior of PE. It has been reported that an increases in the molecular weight and a decreases in crystallinity can result in a decrease in wear of PEs [31, 32]. However, our results indicate that the wear rate increases when the crystallinity slightly decreases as can be deducted from the results present in Table 1. In addition, from previous studies it is known that the molecular weight of the modified PE increases with peroxide concentration until the critical concentration of gel formation is reached [9, 10].

The higher wear resistance of PE relative to those material crosslinked with the lower concentrations of peroxide can be explained at least in part by considering the effect that has the transference of material to the counterface on the wear of polymers. It is known that wear of linear PE sliding over steel surface generally decreases if the sliding occurs repeatedly over the same contact surface, which is linked to the transfer of a thin film of polymer over the metallic surface [32–34]. When PE was tested, there was evidence of the formation of a deposit of material on the metal surface, while this was not observed in any of the crosslinked PE. Figure 8 shows SEM images of the steel surfaces that were involved in rubbing against PE. In Fig. 8a it is possible to identify material occlude in grooves, whereas the light gray areas in Fig. 8b correspond to material deposited irregularly on the steel surface.

This deposited material on the metallic counterface may provide some protection to the PE from the harsh roughness of the steel surface. In the case of crosslinked polymers, not transfer material to the metal surface was detected, indicating that this phenomenon does not occur or that the transferred material does not adhere firmly to the surface to survive after repeated sliding. The molecular crosslinks seem to hamper the transference of material to the counterface in the crosslinked PE's.

In addition to the material transfer to the counterface, the molecular orientation that occur in surface regions along the sliding direction is considered responsible for improving the wear resistance of linear PE, whereas this is adversely affected when such orientation is limited [34]. On this respect, it is worth to mention that the higher wear resistance recognizable in linear PE relative to the low-density counterparts has been linked to the branched molecular structure of the latter, which limits molecular

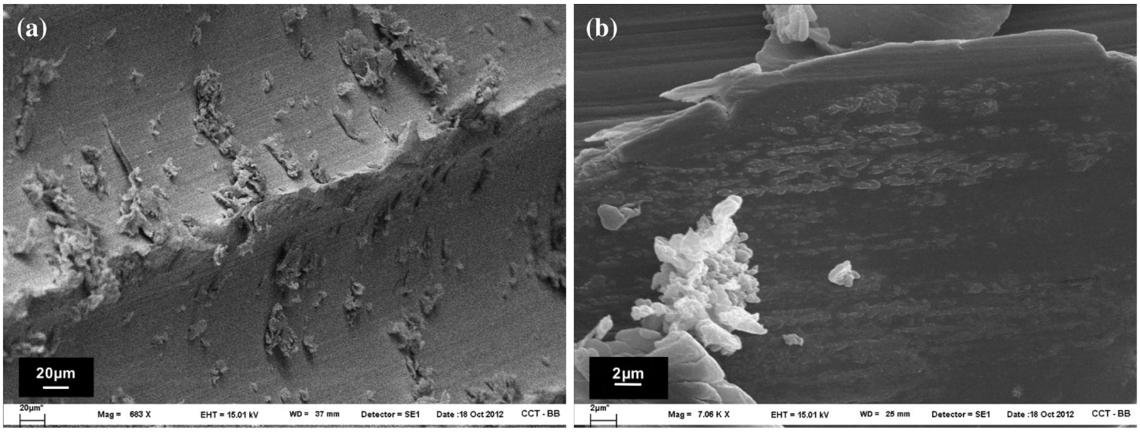

Fig. 8 SEM micrographs of the steel counterface after testing PE: **a** ×800, **b** ×7000

orientation near the contact surface. Previous studies showed that when a linear PE is modified with concentrations of peroxide lower than the one required to form a gel, the molecular weight of the polymer increases while a fraction of the molecules acquires a complex branched structure [9, 10]. It was found that these structural changes affect the mechanical response to tensile forces of the polymers, for example, the drawability of the material decreases with increasing peroxide concentration [9, 10]. Thus, the reduction in wear resistance that occurs at the lowest peroxide concentration may also be related to the presence of long-chain-branched structure in the material that limits the molecular orientation that may occur at the contact surface layer.

Returning to the analysis of data results presented in Fig. 7, it can be observed in the figure that when the concentration of peroxide exceeds 0.08 wt%, the wear rate diminishes continuously with the concentration of peroxide. Materials modified with concentrations of peroxide >0.5 wt%, wear less than the original PE, being PE250, the material obtained by crosslinking PE with 2.5 wt% de peroxide, the one with the largest wear resistance, which is about ten times greater than that of PE. It is interesting to note that the wear rate of PE250 is comparable in magnitude to the value of the wear rate reported for some UHMWPE's obtained under rather different conditions of sliding friction [35–37]. The wear rate does not seem to vary significantly when the concentration of peroxide increases over 2.5 wt%.

The trend of the wear with the peroxide concentration of crosslinked PE contrasts with the results reported by Kampouris and Andreopoulos [18]. They found that the wear resistance of crosslinked PE increases with the amount of gel by rubbing the polymers against sandpaper, the maximum amount of gel achieved in these cases was 70 % by weight. However, our results are consistent with these authors in the fact that the wear resistance of the crosslinked PE is lower than the original PE when the amount of gel in the material is ≤70 wt%.

The lower wear resistance of crosslinked PEs with respect to the starting PE has also been observed by other authors. For instance, Shen and Dumbleton [4] examined the wear of a set of UHMWPE crosslinked with gamma ray with doses up to 1000 Mrad by means of a thrust washer wear test. At normal loads below the critical one to produce a sharp increase in wear, wear decreases with either radiation dose or the amount of gel, but the irradiated samples show higher wear rate than the original PE. The authors proposed that material transfer and hardness are the two competing factors in determining the wear behavior of the materials [4]. Inhibition of the formation of a transfer film on the contact surface was considered by the authors as causing the lower wear rate in crosslinked PE, while the increase in hardness with the degree of crosslinking could explain the tendency of a declining rate of wear with doses in irradiated PE [4].

The crosslinked PE analyzed here shows a decreasing trend of the hardness with the concentration of peroxide, see Table 1. Therefore, the difference in hardness values between the materials does not seem to be useful to explain the wear trend with the peroxide concentration. However, it should be noted that by the effect of friction, the temperature in the surface layers of polymer may be greater than the temperature of the environment in which the tests were performed, which could lead the material to be softer. Some evidence of surface heating was obtained by analysis of the worn surfaces as will be shown later. Thus, the actual hardness of the material in contact with the steel surface might be lower than the values reported in Table 1, as these were measured at room temperature (22 ± 2 °C). On this basis, it can be speculated that the material near the contact surface might acquire rubber-like characteristics during the test and its properties become less influenced by the crystallinity. It is plausible that the material acquired a rubber-like characteristics in which case an increment in the hardness with the degree of crosslinking can be expected, as it happens in the case of rubber-like materials. Thus, the observed diminishing trend of the wear with the concentration of peroxide or gel amount might be justified.

For elastomeric material, the molecular weight between crosslinking, M_c is one of the molecular parameter that determines mechanical properties. For instance, when M_c decreases, the elastic modulus and the hardness increases while the maximum elongation decreases. Therefore, we have tried to correlate M_c with the wear rate. In Fig. 9 the wear rate is plotted as a function of M_c.

A correlation between wear rate and M_c for crosslinked PEs was already put forward by Gul [14] and Muratoglu et al. [16]. These authors studied the wear behavior of UHMWPE's crosslinked by organic peroxide, carrying out pin-on-disk wear experiments under bidirectional motion using serum as the lubricating medium. The cited authors reported that the wear of the materials decreases with peroxide concentration from the value corresponding to the original PE, and that a linear relationship exists between M_c and wear rate. The dashed line on the graph in Fig. 9 represents the best fit of the data using a linear regression. It can be seen that the data does not adhere well to a linear relationship as suggested. But, it has to be taken into account that the test setup used by us is very different to that used by Gul [14] and Muratoglu et al. [16]. In addition, our M_c data cover a wider range than those reported by them, which goes from about 10,000 to 5000 g/mol. Nevertheless, the results presented here are similar to those found by Gul [14] and Muratoglu et al. [16] in which a decrease of approximately 28 % in the value of M_c causes a diminution in the wear rate of about 74 %, while, in our case, the wear rate decreases about 86 % when M_c is reduced in about 25 % (values obtained by comparing data for PE150 and PE250).

To further extend the study, some of the materials were tested using normal loads of 15 or 20 N. Figure 10 shows the wear rate as a function of normal load for: PE; PE008, the material with an incipient molecular network; PE050 and PE100, materials with 80 and 97 wt% of gel, respectively; and PE250, which has about 100 wt% of gel. It can be seen in Fig. 10 that the wear of PE and PE250 does not seem to be noticeable affected by changes in the normal load. On the other hand, the load seems to affect the wear process of PE008, PE050 and PE100 as the wear rate of those material shows a decreasing trend with the load. PE008 displays the greatest decrease in wear rate being the wear higher than the original PE at all loads.

The worn surfaces of the PE's were examined by SEM in order to evaluate the wear mechanisms involved. Figure 11 shows images of worn surfaces of PE, PE008 and PE250 that were chosen as illustrative examples. The analysis of the topography of the worn surfaces reveals that abrasion is the main phenomena that occurs in all the cases, where scratching, tearing and wavelike formation are visible. When the materials were tested with 10 N, parallel deep furrows can be seen on the surfaces along the abrading direction, Fig. 11a–c, which are due to the plow action of the hard asperities of the steel counterbody surface. In the case of PE008 and PE250, Fig. 11b, c, respectively, there is evidence of material plastically deformed displaced sideways of the furrows in the form of more or less elongated strings attached to the surface. Additionally, scratches promoted by cutting are noticeable. In the case of PE250, Fig. 11c, the surface damage is in the

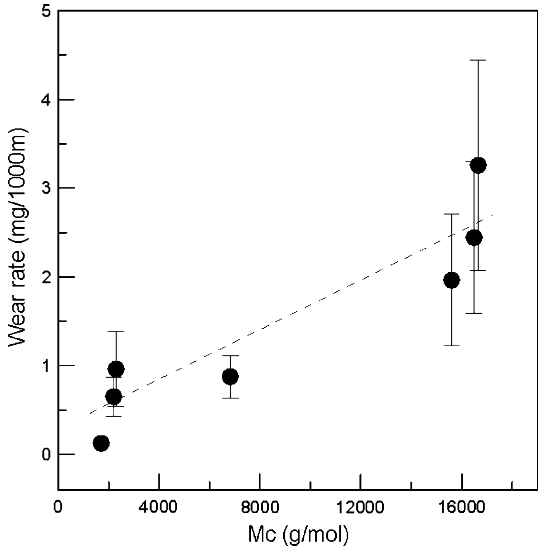

Fig. 9 Wear rate as a function of M_c

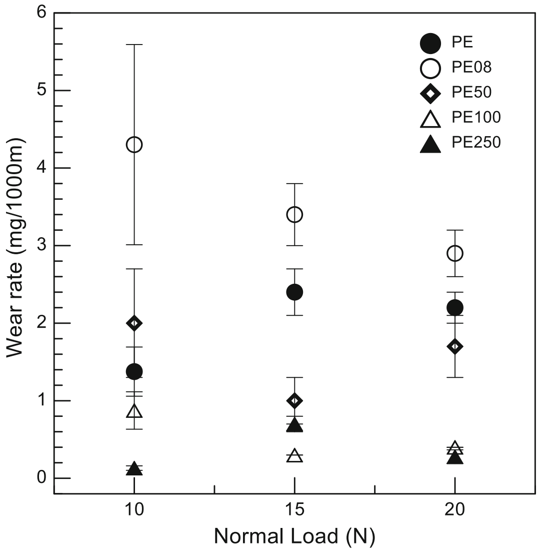

Fig. 10 Wear rate as a function of normal load for PE and some of the crosslinked PE's

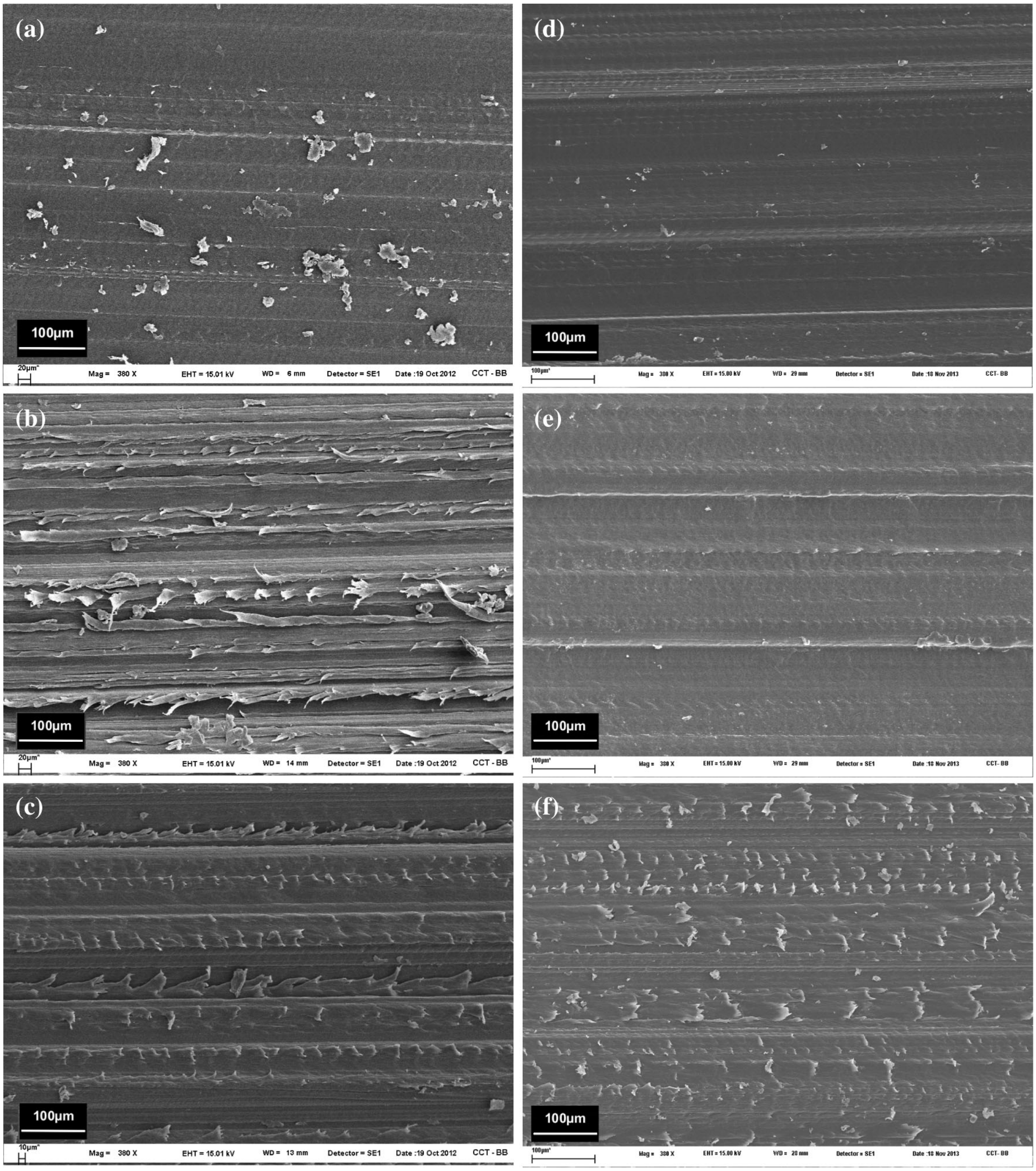

Fig. 11 SEM micrograph of the worn surfaces. Sliding direction parallel to the *horizontal*. **a** PE–10 N, **b** PE008—10 N, **c** PE250—10 N, **d** PE—15 N, **e** PE008—15 N and **f** PE250—15 N

form of a more or less periodic parallel tears pattern in the direction of motion.

Scratches and a wavelike pattern can be noticed on the surface of the samples tested with 15 N, photography in Fig. 11d–f. The wavelike abrasion pattern observed in the worm surfaces resembles the Schallamach waves, which is a characteristic damage observed in worn surfaces of rubbery materials [34]. One possible explanation for the occurrence of this phenomenon is that friction may promote an increase in temperature during the test, softening the polymer surface and resulting in the generation of a periodic tear which is possibly caused by fatigue. The characteristics of the worn surface of PE and PE 250 are similar to those produced when these materials were tested with 10 N, indicating that the load does not seem to affect the wear mechanism in accordance with the insensitivity of the wear rate to changes in load. On the other hand, it is notorious the difference in the topography between the worn surfaces resulting after testing PE008 with 10 and 15 N. All these features suggest that the complex

Table 2 COF

Material	10 N	15 N	20 N
PE	0.18	0.22	0.17
PE004	0.20	–	–
PE008	0.25	0.24	0.20
PE015	0.16	–	–
PE030	0.20	–	–
PE050	0.27	–	–
PE100	0.19	–	–
PE150	0.22	–	–
PE250	0.22	0.25	–
PE350	0.23	–	–

mechanism of wear shown by PE008 is changing with the load, which is a possible reason for the downward trend in the rate of wear with the load shown by this material.

The values of the COF are presented in Table 2. The friction coefficient measured for PE falls in the range of values reported for this parameter, between 0.13 and 0.25, for the friction pair steel-PE [37–40]. In general, the results show that the COF of PE is slightly lower than those of the crosslinked PE's when they are compared at a given load, and no significant difference in the friction coefficient between the crosslinked PE's is evident. The lower friction coefficients of PE can be attributed to the transferred material on the counterpart metallic during the friction test. The deposition of material was negligible small in the crosslinked PE's. The load does not seem to affect noticeably the friction coefficient of the materials.

4 Conclusion

In this study, a set of crosslinked PE's were synthesized by crosslinking a linear PE with the aim of evaluating the influence of the molecular network on the wear resistance of the materials when sliding against a rough steel surface. From this, the following conclusions can be drawn:

- The molecular crosslink increases with the concentration of peroxide distinguished as an increment in the gel and a reduction in the molecular weight between crosslinks. Fully crosslinked materials, with about 100 wt% of gel, were obtained at the largest peroxide concentrations. The Vickers microhardness increase monotonically with crystallinity. However, it was not possible to establish a direct correlation between the wear of the crosslinked material with either the crystallinity or the hardness.
- The wear rate of crosslinked PE's decreases with the concentration of peroxide, that is, with increasing the gel amount and decreasing the molecular weight between crosslinks. When the amount of gel reaches a value larger than 80 % of the total mass, there are no significant differences in wear resistance between the PEs. Therefore, such high crosslink level is needed to obtain materials with wear resistance greater than the original PE. The crosslinks of PE slightly increases the COF of the material, but this parameter does not appear to be affected by the degree of crosslinking because the crosslinked materials showed similar values of friction coefficient.
- The wear and friction of the PE are dominated by the deposition of material on the steel counterface, while the crosslinks produced in the molecular structure of PE hamper the formation of a stable material deposit and transfer to the counterface. On the polymers worn surfaces, the more frequent surface morphologies due to abrasion damage were scratching, tearing and wavelike formation.

References

1. Chodak, I.: Properties of crosslinked polyolefin-based materials. Prog. Polym. Sci. (1995). doi:10.1016/0079-6700(95)98859-N
2. Peacock, A.J.: The chemistry of polyethylene. J. Macromol. Sci. Part C Polym. Rev. (2001). doi:10.1081/MC-100107860
3. Lazar, M., Rado, R., Rychly, J.: Crosslinking of polyolefins. Adv. Polym. Sci. (1990). doi:10.1007/3-540-52159-3_8
4. Shen, C., Dumbleton, J.H.: The friction and wear behavior of irradiated very high molecular weight polyethylene. Wear (1974). doi:10.1016/0043-1648(74)90149-5
5. Stachowiak, G.W., Batchelor, A.W.: Engineering Tribology, 2nd edn. Butterworth Heinemann, Boston (2001)
6. De Boer, J., Pennings, A.J.: Crosslinking of ultra-high molecular weight polyethylene in the melt by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne: 2. Crystallization behaviour and mechanical properties. Polymer (1982). doi:10.1016/0032-3861(82)90222-1
7. Narkis, M., Raiter, I., Shkolnik, S., Eyerer, P., Siegmannz, A.: Structure and tensile behavior of irradiation and peroxide-crosslinked polyethylenes. J. Macromol. Sci. Part B Phys. (1987). doi:10.1080/00222348708248057
8. Khonakdar, H.A., Morshedian, J., Wagenknecht, U., Jafari, S.H.: An investigation of chemical crosslinking effect on properties of high-density polyethylene. Polymer (2003). doi:10.1016/S0032-3861(03)00363-X
9. Pérez, C.J., Cassano, G.A., Vallés, E.M., Failla, M.D., Quinzani, L.M.: Rheological study of linear high density polyethylenes modified with organic peroxide. Polymer (2002). doi:10.1016/S0032-3861(02)00076-9
10. Pérez, C.J., Cassano, G.A., Vallés, E.M., Quinzani, L.M., Failla, M.D.: Tensile mechanical behavior modified with organic peroxide. Polym. Eng. Sci. (2003). doi:10.1002/pen.10136
11. McKellop, H., Shen, F.W., Lu, B., Campbell, P., Salovey, R.: Development of an extremely wear-resistant ultra high molecular weight polyethylene for total hip replacements. J. Orthop. Res. (1999). doi:10.1002/jor.1100170203
12. Kurtz, S.M., Pruitt, L.A., Jewett, C.W., Foulds, J.R., Edidin, A.A.: Radiation and chemical crosslinking promote strain hardening behavior and molecular alignment in ultra high molecular

weight polyethylene during multi-axial loading conditions. Biomaterials (1999). doi:10.1016/S0142-9612(99)00038-1
13. Lewis, G.: Properties of crosslinked ultra-high-molecular-weight polyethylene. Biomaterials (2001). doi:10.1016/S0142-9612(00)00195-2
14. Gul, R.M.: The effects of peroxide content on the wear behavior, microstructure and mechanical properties of peroxide crosslinked ultra-high molecular weight polyethylene used in total hip replacement. J. Mater. Sci. Mater. Med. (2008). doi:10.1007/s10856-008-3368-7
15. Yim, C.I., Lee, K.J., Jho, J.Y., Choi, K.: Wear resistance of some modified ultra-high molecular weight polyethylenes and its correlation with tensile properties. Polym. Bull. (1999). doi:10.1007/s002890050486
16. Muratoglu, O.K., Bragdon, C.R., O'Connor, D.O., Jasty, M., Harris, W.H., Gul, R., et al.: Unified wear model for highly crosslinked ultra-high molecular weight polyethylenes (UHMWPE). Biomaterials (1999). doi:10.1016/S0142-9612(99)00039-3
17. Rose, R.M., Cimino, W.R., Ellis, E., Crugnola, A.N.: Exploratory investigations on the structure dependence of the wear resistance of polyethylene. Wear (1982). doi:10.1016/0043-1648(82)90048-5
18. Kampouris, E.M., Andreopoulos, A.G.: The effect of the gel content of crosslinked polyethylene on its physical properties. Eur. Polym. J. (1989). doi:10.1016/0014-3057(89)90240-1
19. Hendra, P.J., Peacock, A.J., Willis, H.A.: The morphology of linear polyethylenes crosslinked in their melts. The structure of melt crystallized polymers in general. Polymer (1987). doi:10.1016/0032-3861(87)90215-1
20. Quinn, F.A., Mandelkern, L.: Thermodynamics of crystallization in high polymers: poly-(ethylene). J. Am. Chem. Soc. (1958). doi:10.1021/ja01546a003
21. Henderson, P.J., Wallace, A.J.: Hardness and creep of cross-linked polyethylene. Polymer (1989). doi:10.1016/0032-3861(89)90251-6
22. Böhm, H., Betz, S., Ball, A.: The wear resistance of polymers. Tribol. Int. (1990). doi:10.1016/0301-679X(90)90055-T
23. Peacock, A.J.: Computer aided calculation of crosslinking efficiency. Polym. Commun. **25**, 169–171 (1984)
24. Smedberg, A., Hjertberg, T., Gustafsson, B.: The role of entanglements in network formation in unsaturated low density polyethylene. Polymer (2004). doi:10.1016/j.polymer.2004.05.005
25. Wood-Adams, P.M., Dealy, J.M., DeGroot, A.W., Redwine, O.D.: Effect of molecular structure on the linear viscoelastic behavior of polyethylene. Macromolecules (2000). doi:10.1021/ma991533z
26. Mandelkern, L.: Crystallization of Polymer. Cambridge University Press, Cambridge (2002)
27. Kunert, K.A., Soszyfiska, H., Pislewski, N.: Structural investigation of chemically crosslinked low density polyethylene. Polymer (1981). doi:10.1016/0032-3861(81)90237-8
28. BaltáCalleja, F.J., Fakirov, S.: Microhardness of Polymers. Cambridge University Press, Cambridge (2000)
29. Simis, K.S., Bistolfi, A., Bellare, A., Pruitt, L.A.: The combined effects of crosslinking and high crystallinity on the microstructural and mechanical properties of ultra high molecular weight polyethylene. Biomaterials (2006). doi:10.1016/j.biomaterials.2005.09.033
30. Flores, A., Ania, F., Baltá-Calleja, F.J.: From the glassy state to ordered polymer structures: a microhardness study. Polymer (2009). doi:10.1016/j.polymer.2008.11.037
31. Tervoort, T.A., Visjager, J., Smith, P.: On abrasive wear of polyethylene. Macromolecules (2002). doi:10.1021/ma020579g
32. Anderson, J.C.: High density and ultra-high molecular weight polyethenes: their wear properties and bearing applications. Tribol. Int. (1982). doi:10.1016/0301-679X(82)90111-6
33. Bahadur, S., Stiglich, A.J.: The wear of high density polyethylene sliding against steel surfaces. Wear (1981). doi:10.1016/0043-1648(81)90021-1
34. Briscoe, B.J., Sinha, S.K.: Wear of polymers. Proc. Inst. Mech. Eng. Part J J. Eng. Tribol. (2002). doi:10.1243/135065002762355325
35. Unal, H., Sen, U., Mimaroglu, A.: Dry sliding wear characteristics of some industrial polymers against steel counterface. Tribol. Int. (2004). doi:10.1016/j.triboint.2004.03.002
36. Yim, C.I., Lee, K.J., Jho, J.Y., Choi, K.: Wear resistance of some modified ultra-high molecular weight polyethylenes and its correlation with tensile properties. Polym. Bull. (1999). doi:10.1007/s002890050486
37. Friedrich, K., Schlarb, A.K.: Tribology of Polymeric Nanocomposites. Academic Press, Elsevier (2008)
38. Matsubara, M., Watanabe, K.: The wear properties of high density polyethylene irradiated by gamma rays. Wear (1967). doi:10.1016/0043-1648(67)90005-1
39. Briscoe, B.J., Pogosian, A.K., Tabor, D.: The friction and wear of high density polythene: the action of lead oxide and copper oxide fillers. Wear (1974). doi:10.1016/0043-1648(74)90081-7
40. Tuckart, W., Molinari, E., Rossit, D., Failla, M.: Friction and wear behavior of irradiated polyethylene sliding against a rough steel surface. Tribol. Lett. (2014). doi:10.1007/s11249-014-0344-x