Effect of radiation cross-linking on the abrasive wear behaviour of polyethylenes

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Abstract. This study explores the differences in the dry abrasive wear behavior of different polyethylenes, and compares the effect of radiation cross-linking on the wear behavior. Four different types of polyethylenes: LDPE, LLDPE, HDPE and UHMWPE were studied. Cross-linking was carried out by high energy electron beam with radiation dose of 200 kGy. The results show that in unirradiated state UHMWPE has excellent wear resistance, with HDPE showing comparable wear properties; both LDPE and LLDPE exhibit high wear rate. Cross-linking improves wear rate of LDPE and UHMWPE, however, the wear rate of HDPE and LLDPE increases with cross-linking.

1. Introduction
In general, polyethylenes possess good electrical insulation and chemical properties, and their mechanical properties are determined by the skeletal structure of the polymer chain. The different classes of polyethylenes such as low density (LDPE), linear low density (LLDPE), high density (HDPE), and ultra-high molecular weight (UHMWPE) are being used in a number of diverse applications. These can include house-wares and packaging through to cable insulation and high pressure piping [1-4]. In most cases these polymers are required to show good mechanical properties, particularly at elevated temperatures, and good abrasive wear resistance [5]. As a result, in recent years there has been a growing interest in enhancing the properties of these polymers by inducing cross-linking of the polymer chain through radiation cross-linking; and the effects of irradiation of polyethylenes have been studied extensively [6-8]. In brief, this process uses high energy radiation in the form of high energy electrons or γ-rays which generate free radicals along the polymer chain with the abstraction of hydrogen atoms [9]. These free radicals then react to form a cross-linked network structure with a corresponding change in mechanical properties. Although the cross-linking process can be performed by other methods, radiation cross-linking is a convenient process which does not result in by-products, and produces varying degrees of cross-linking without reformulation. The commercial applications of cross-linked polyethylenes include high temperature applications like insulation on electrical wires and cables, hot water pipes and tubings, heat shrinkable products, and steam resistant food packaging [10-13]. Radiation cross-linked UHMWPE has also been widely used for making orthopaedic implants [14-17].
In this study, the wear resistance under dry abrasive conditions of 4 types of polyethylenes (LDPE, LLDPE, HDPE and UHMWPE) and the effect of radiation cross-linking on wear behaviour has been investigated. The comparative data will assist in materials selection and in exploring the different ways to improve performance. The research also compares and relates the effect of the degree of crystallinity and cross-link density (gel content) induced within the polymer to subsequent changes in the wear resistance properties of these polyethylenes.

2. Experimental

2.1. Materials

The polyethylenes grades selected were: LDPE-EASTMAN 800A (Density $\rho$ 0.918 g/cm$^3$; Melt Flow Index MFI 1.7 g/10 min), LLDPE-BASF LL 18K FA ($\rho$ 0.919 g/cm$^3$; MFI 1 g/10 min), HDPE-EASTMAN H6001-A ($\rho$ 0.962 g/cm$^3$; MFI 8 g/10 min), and UHMWPE-Hoechst Celanese GUR 1050 ($\rho$ 0.930 g/cm$^3$; MFI <0.01 g/10 min).

For LDPE, LLDPE and HDPE, a Morgan injection moulding press was used for producing rectangular bars 9 mm thick, 25.4 mm wide and 100 mm long. The injection temperature was 218$^\circ$C, injection pressure 0.4 MPa and clamp pressure 98 kN (for HDPE 133 kN). The mold temperature varied from 65 -120$^\circ$C. In the case of UHMWPE, commercially available bar-stock (ram extruded) material processed by WestLake Plastics, Lenni, PA, USA was used.

Irradiation was carried out using a 2.5 MeV Van de Graff generator at a dose rate of 25 kGy per pass (1 Mrad=10 kGy), at room temperature in air. Eight passes were used to give samples a total dose of 200kGy.

2.2. Characterization

Swelling experiment was carried out according to ASTM test method D 2765 method C to measure the cross-link density (gel content). Two samples (approximately 2-2.5 mg) of each material were dipped in xylene beaker, which was placed in a copper container, and heated on a hot plate. In the case of LDPE, LLDPE and HDPE specimens, xylene was heated to 110$^\circ$C for 5 hours, while UHMWPE specimens were dipped in xylene at 130$^\circ$C for 7 hours. The different temperatures were maintained due to the fact that control UHMWPE samples took more time to dissolve and cross-linked UHMWPE samples took more time to equilibrate. The swollen gel was quickly transferred to a weighing bottle, covered and weighed. Samples were then dried in an oven at 85$^\circ$C for 24 hours and weighed. The degree of swelling was calculated from the ratio of the weights of swollen and dry samples. Flory’s swelling equation was used to determine the molecular weight between cross-links and cross-link density. The specific gravity of the diluent was taken as 0.81 Kg dm$^{-3}$ and density of the amorphous polyethylene was taken as 0.862 g/cm$^3$.

Differential scanning calorimetry (DSC) of the control and radiated samples was carried out on a Perkin–Elmer DSC 7a model to determine the degree of crystallinity and melting points of the different materials. The heating rate was 10$^\circ$C/min. Results were also used to ascertain any degradation taking place in the samples. The heat of fusion of the materials was compared with the heat of fusion of 100% crystalline polyethylene, taken as 289 J/g.

2.3. Wear test

The wear rate of the control and 200 kGy radiated polymer samples was compared using a pin-on-disc wear testing machine under dry abrasive conditions. The polymer was machined to a cylindrical shape to form the “pin” which had a diameter of 5 mm and length 10 mm. The pin was held against a SiC abrasive paper (600 grit size) attached to the disc using a load of 1 Kg. The test was performed with a sliding speed of 1 m/s for a total sliding distance of 730 m. A new SiC paper was used for each polymer sample tested. No lubricant was used and no attempt was made to clean the abrasive paper from transferred debris. In some tests the pin suffered from extreme wear and a shorter sliding
distance had to be used. The wear rate was determined by recording the change in pin weight as a function of sliding distance.

3. Results

Table 1 shows the molecular weight between cross-links and the cross-link density of the four different types of radiated polyethylenes measured by the swelling experiment. Highest cross-link density is achieved in UHMWPE, followed by LLDPE, LDPE and HDPE, respectively. The degree of crystallinity and onset melting point measured by DSC analysis are shown in Table 2. The comparison of the degree of crystallinity of unirradiated samples shows that percent crystallinities of LDPE and LLDPE are in the same range of is 33-34%, while HDPE has the highest crystallinity 67%. UHMWPE lies in between at about 50% crystallinity. Cross-linking does not produce appreciable change in the degree of crystallinity and melting points of LDPE, LLDPE and HDPE. The small variation can be attributed to measurement error. While in the case of UHMWPE appreciable increase in crystallinity is observed.

Table 1. Molecular weight between cross-links (g/mole) and cross-link density (moles/m³) of the control and cross-linked polyethylenes measured by the swelling experiment

| Sample ID       | Mol. Wt. between cross-links, g/mole | Cross-link density, moles/m³ |
|-----------------|-------------------------------------|-----------------------------|
| LDPE 200 kGy    | 33430 (±10550)                      | 27.1 (±8.57)                |
| LLDPE 200kGy    | 18700 (±328)                        | 46.1 (±0.81)                |
| HDPE 200 kGy    | 42420 (±1620)                       | 20.3 (±0.78)                |
| UHMWPE 200 kGy  | 16220 (±4440)                       | 55.2 (±15.12)               |

Table 2. Degree of crystallinity (%) and the onset melting point (°C) of the control and cross-linked polyethylenes measured by the DSC analysis

| Sample ID       | Degree of Crystallinity, % | Onset Melting Temperature, °C |
|-----------------|----------------------------|-----------------------------|
| LDPE Control    | 33.7                       | 104.4                       |
| LDPE 200 kGy    | 32.1                       | 100.6                       |
| LLDPE Control   | 33.4                       | 110.2                       |
| LLDPE 200kGy    | 33.7                       | 110.0                       |
| HDPE Control    | 67.3                       | 128.2                       |
| HDPE 200 kGy    | 68.8                       | 132.3                       |
| UHMWPE Control  | 49.7                       | 130.0                       |
| UHMWPE 200 kGy  | 60.7                       | 132.9                       |
The comparison of the wear behavior of the control unirradiated samples of 4 polyethylenes is presented in Figure 1. A distinct behavior is shown by LDPE and LLDPE in contrast to HDPE and UHMWPE; both the former suffer high wear. The transfer of material on the abrasive paper was also different in the two categories. In LDPE and LLDPE fine flake like wear debris were transferred onto the abrasive paper, but not as a continuous transfer film; the pin suffered from extreme wear and lip formation was observed. Whereas in the case of HDPE and UHMWPE little loose debris were produced leading to smooth and continuous transfer film on the abrasive surface. This play a significant role in reducing further wear of the polymer surface, and provides a counter-surface with low coefficient of friction. Lip formation was not observed in these materials. The comparison of 200 kGy irradiated specimen with the control also exhibit two distinct behaviours (Figure 2). In LDPE and UHMWPE wear resistance improves with irradiation, while in LLDPE and HDPE the wear resistance degrades with irradiation. The most wear resistant material in this study is radiated UHMWPE, and on the other extreme the least wear resistant material is control LDPE.

![Figure 1. Weight loss (g) versus sliding distance (m) curves for unirradiated (Control) polyethylenes measured from a pin-on-disc wear test under dry abrasive conditions](image)

4. Discussion
To explain the differences in behavior of the different polyethylenes, it is important to understand the skeletal structure of these materials. LDPE has a highly branched structure with crystallinity ranging from 30-40%, as opposed to HDPE which has a linear structure and crystallinity as high as 75% [4, 18]. LLDPE has controlled amount of short branches of the desired length, with little or no long-chain branching making it different from LDPE, however, degree of crystallinity remains about the same. As its name suggest UHMWPE has very high molecular weight linear molecules, which leads to lower crystallinity (typically 45 % [19]) and higher entanglement densities. The differences in behavior are due to the relative amounts of crystallinity and entanglement density, with chain branches and higher molecular weight promoting higher entanglement density and lower crystallinity.

The lower cross-link density achieved in HDPE is due to the fact that cross-linking mainly occurs in amorphous regions which are very small in HDPE. The cross-link densities achieved in UHMWPE are very high as compared to other materials due to its higher molecular weight leading to larger entanglement densities and larger potential cross-linking sites. LDPE show similar behavior but lower cross-link densities; this is due to smaller average molecular weight of LDPE as evident by its large melt flow index (MFI); a smaller MFI indicates a higher molecular weight. As compared to HDPE, LDPE has higher cross-link density at similar radiation dose as also reported in earlier studies [12]. This is mainly due to the lower crystallinity and higher branch content of LDPE as compared to
The higher cross-link densities achieved in LLDPE as compared to LDPE can also be due to its higher molecular weight, as shown by its lower MFI.

Figure 2. Comparison of the wear behavior of unirradiated (Control) and 200 kGy radiated samples of (a) LDPE, (b) LLDPE, (c) HDPE, and (d) UHMWPE
The DSC analysis confirms that the degree of crystallinity is in range of that expected from literature. The crystallinity and melting point did not changed much with cross-linking in LDPE, LLDPE, and HDPE, which verifies the absence of degradation in molecular weight by oxidation and radiation damage, since any such change would increase the degree of crystallinity. The exception is UHMWPE where appreciably high increase in crystallinity is observed due to degradation in molecular weight. The reason is that free radicals produced during radiation exposure in UHMWPE can survive for a long time due to diminished molecular motion because of its high molecular weight; as oxygen diffuses in the material the radicals are consumed leading to further degradation in molecular weight. The lower molecular weight fragments produced are able to reorganise and crystallize more readily [8]. Since the samples were analysed after two to three years of storage enough time was available for the diffusion of oxygen and subsequent degradation. The technique employed to avoid this problem is to melt anneal UHMWPE after radiation exposure to extinguish any free radicals present and add antioxidants such as vitamin E [20, 21].

The comparison of the wear behavior of control polyethylenes show that LDPE and LLDPE experience very high wear rate as compared to HDPE and UHMWPE, which show comparable and very small wear rate. This observation can be explained on the basis of the smooth transfer film produced in the two later cases leading to reduced friction coefficient and reduction of further wear. The production of this continuous transfer film can be further explained on the basis of high strain to failure and toughness generally observed in HDPE and UHMWPE.

Cross-linking improves the wear resistance of LDPE and UHMWPE, and degrades it in LLDPE and HDPE. Wear mechanisms of polyethylenes can be divided in the following categories; adhesive, abrasive, and surface fatigue wear. Adhesive and surface fatigue wear involves the removal of polymer by the harder counterface asperities after many interactions, while abrasive wear involves the ploughing of polymer by the surface asperities of a harder material and is associated with rough surfaces [22, 23]. Wear test used in this study is likely to produce abrasive wear due to absence of any lubricant and presence of an abrasive counter surface. The decrease in wear rate of radiated LDPE and UHMWPE is due to the formation of extensive cross-link network structure in these cases. This network structure is produced by the cross-linking of large number of entanglements produced by the very high molecular weight of UHMWPE and by the branched structure of LDPE. The cross-links in the network structure will obstruct the formation of wear debris by resisting the uncoiling of the physical entanglement; leading to an improved wear behavior. Due to the linear molecular structure of HDPE the network formation due to cross-linking will not be extensive leading to decreased wear resistance with radiation. The unexpected decrease in the wear resistance of radiated LLDPE, in spite of high cross-link density, can be due to degradation in mechanical properties such as toughness.

5. Conclusions
The results provide a comparison of the properties of different types of unirradiated and radiated polyethylenes. It shows that UHMWPE has the highest cross-linking efficiency, followed by LLDPE, LDPE and HDPE, respectively. The degree of crystallinity does not change appreciably with irradiation since it is carried out at room temperature, except in case of UHMWPE where some degradation in molecular weight due to diffusion of oxygen causes an increase in crystallinity.

Wear test results show that control LDPE exhibits the highest wear rate closely followed by LLDPE. In contrast control HDPE and UHMWPE exhibit very low wear rate due the formation of a continuous transfer film. Radiation cross-linking decreases the wear rate in LDPE and UHMWPE, while increases the wear rate in HDPE and LLDPE. Therefore, cross-linking is only a promising method to improve the wear properties of the former two materials. This effect is due to the formation of extensive network structure aided by the high entanglement density present in LDPE and UHMWPE. Under dry abrasive conditions the most wear resistant material investigated in this study is radiated UHMWPE.
6. Acknowledgment
Authors like to acknowledge help of the following colleagues and students in GIK Institute, Topi, Pakistan: Mr. Fahd N. Khan and Mr. Adeel Raza for conducting the swelling experiment, and Mr. Khawaja Zakaullah for conducting the DSC analysis.

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