Influence of Gamma Radiation at Low Dose on Some of Mechanical Properties of (HDPE/HIPS) Blends

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ABSTRACT

To solve different problems related to the radiation stability of polymeric articles and purposeful radiation-induced modifications of polymeric materials, the effect of low dose of gamma irradiation on some mechanical properties, at room temperature and in the presence of oxygen, on blends of high density polyethylene (HDPE) and high impact polystyrene (HIPS) has been studied.

Thermal – mechanical mixing was used to prepare binary polymeric blends from (HDPE / HIPS) with different compositional ratios, i.e. (100/0, 90/10, 80/20) using single screw extruder. The exposure of these blends to dose of Cs-137 gamma radiation at 0.2 kGy improves the mechanical properties. Scanning electron microscopy (SEM) has been used to investigate the effect of gamma irradiation on the surface morphology of the polymer material. It is noticed that after the radiation treatment; tensile strength, modulus of elasticity and hardness of used (HDPE/HIPS) at all blends ratio have been increased due to partial cross linking.

Keywords: Gamma irradiation; Polymers; Mechanical properties.

تأثير جرعة قليلة من اشعة كاما على بعض الخواص الميكانيكية لخليط من (HDPE/HIPS)

الخلاصــة

لحل المشاكل المختلفة المرتبطة باستقرارية المواد البوليمرية عند تعرضها الى الاشعاع والحث على تطوير خصائص المواد البوليمرية باستخدام الاشعاع ،تمت دراسة تأثير جرعة قليلة من اشعة كاما على بعض الخصائص الميكانيكة لخلائط من البولي اثيلين العالي الكثافة HDPE والبولي ستايرين

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عـالي الصـدمة HIPS .ولقـد تـم تحضـير خلـيط (HDPE/HIPS) بنسـب وزنيـة مختلفـة تشـمل (100/0)،(90/10)و(80/20) باستخدام ماكنة البثق احادية اللولب و تعريضها الى جرعة مقدارها 0.2 KGY من اشعة كاما المنبعثة من المصدر Cs-137.وكما تم استخدم المجهر الالكتروني الماسح لتشخيص التاثير الحاصل في طوباغرافية سطح المادة البوليمرية المستخدمة نتيجة تعرضها للاشعاع حيث ان بعد التشعيع اظهرت النتائج العملية ان مقاومة الشد ، معامل المرونة والصلادة لجميع النماذج المستخدمة ازدادت ولكل نسب الخلط المستخدمة وذلك نتيجة التشعيع تميل الى تشكيل روابط عرضية بين السلاسل ثؤثر على خصائصها الميكانيكية.

INTRODUCTION

The use of radiation in the processing of polymers is gaining more and more interest because it can be suggested as an alternative to the traditional chemical methods [1] to modify the molecular structure of polymers. The possibility of processing the final shape of the polymeric material in the solid state opens up new opportunities to obtain materials with well-tailored properties [2].

Polymeric materials based on commodity thermoplastics are attractive, not only for their low cost, but also for their technical performance, versatility of processing-transformation, and simplicity of recycling. Blends and composites take advantage of synergetic combinations of the difference in properties of resins. As an example of this trend, it is enough to mention the advance of polymer blends in replacing engineering resins in the automotive industry; Polyethylene (PE) is widely used in various fields because of its excellent properties such as softness, elasticity and insulation. They are also used in nuclear power plants and are exposed to ionizing radiation for a long time. Since aliphatic polymers are very sensitive to radiation, synthesis and development of radiation-resistant polymeric materials are strongly desired. Blending of synthetic and natural polymers is a well-known method of modifying properties of polymer. It is an economically viable and versatile way to prepare new engineering materials and to overcome deficiency in some material characteristics. However, most of the polymer blends are immiscible on the molecular scale and form heterogeneous systems that affect their mechanical behavior. There have been a few attempts to improve the miscibility by using radiation to modify one or both polymers [3].

The effects of irradiation on PE have been studied extensively. It is reported that oxidative degradation becomes a major process during gamma irradiation, particularly at low dose- rate gamma irradiation. However, there have been suggestions in literature [4] that cross-linking may still be an important process during the low dose rate gamma irradiation and that peroxides can act as an initiator for radiation-induced crosslinking of PE.

The effects of radiation on polymer structure, and consequently on its physical characteristics, are well known in the plastics industry. The literature on the mechanisms behind these effects shows two opposite trends, depending on irradiation conditions: cross linking of the polymer molecules, which increases the mechanical strength and oxidative degradation, which generally causes material weakening. Which

tendency will be predominant seems to be related to the amount of oxygen available on the material and the capability to replace the oxygen as it is consumed by chemical reactions with radicals produced during irradiation.

A discussion of the effect of radiation on mechanical strength as a consequence of the balance between cross-linking and oxidative degradation is presented in many publications. Wündrich (1985) presents a review of the literature on values for mechanical resistance parameters for several plastics and elastomers subjected to radiation under different conditions. When irradiation is carried out in the absence of oxygen (vacuum or inert atmosphere), the effect of radiation on the mechanical resistance parameters is independent of dose rate. On the other hand, in the presence of air, the relationship between effect and dose rate is evident. In the absence of air, this dose is larger than the values for irradiation in the presence of air. Wündrich attributes this behavior to the influence of oxygen in the degradation of polymers (oxidative degradation). This effect increases with the reduction in dose rate because it is a time-related process due to two mechanisms: the diffusion of oxygen in the polymer and the disintegration reaction of the peroxides formed [5]. Singh (1999) also presented two phenomena occur as a consequence of the HDPE gamma irradiation process: the formation of cross-linking and oxidative degradation. In general, Eq. (1) shows the reaction between free radicals (PE ●) of HDPE, produced by the loss of a hydrogen atom of HDPE (represented as PE), forming cross-linking between polymer molecules. This recombination reaction is predominant in cases of irradiation in vacuum or inert atmospheres

$$PE. + PE. \rightarrow PE - PE \quad \ldots (1)$$

During irradiation in the presence of air, the formation of peroxide radical Eq. (2) and the reaction of the PE free radical and the peroxide radical Eq. (3) predominates.

$$PE. + O_2 \rightarrow PEO_2. \quad \ldots (2)$$

$$PE. + PEO_2. \rightarrow PEOOPE \quad \ldots (3)$$

This happens because the oxygen is quickly consumed and the formation of peroxide radical Eq. (2) becomes limited to the oxygen diffusion rate [6]. However, Ionizing radiation induces chemical reactions in polymers, which result in change in both molecular structure and macroscopic properties. The energy transfer from the radiation to the polymer does not take place selectively relative to the mixed components in a blend. The probability of the generation of free radicals depends on the strength of the inter atomic bonds [7].

In this paper, we report on gamma-ray irradiation in modifying the mechanical properties of HDPE and their blends. Varieties of techniques have been used to identify and quantify the behavior of blends i.e. SEM, modulus elasticity, hardness testing and tensile testing. Finally, we obtained a good estimate of the proper blend ratio and the proper irradiation dose reasonable for desired properties.

EXPERIMENTAL MATERIALS

High Density Polyethylene

HDPE (Exxon Mobil HDPE HMA 035 provided by General Company of Chemical Industries) is used as a grain with specific gravity (0.9363 g/cm^3) and molecular structure CH_2=CH_2 [8].

High Impact Polystyrene

HIPS is a crystal-like with specific gravity of (1.031 g/cm^3), provided by general company of chemical industries.

Preparing of Polymer Blends

Thermal – mechanical mixing was used to prepare binary polymeric blends from (HDPE / HIPS) with different compositional ratios, i.e., (100/0, 90/10, and 80/20) of high-density PE with high impact PS by using Single Screw Extruder (DIS) element. This type is used in the current work to produce sheets from polymeric mixture (HDPE/HIPS) at speed of screw (38 cycle per min) (L / D= 25) the motor and Gars bocks and die produce (1.5 –2 mm) thick sheet, at temperatures used according to the polymer used (HIPS or HDPE).Table (1). gives the conditions of preparing blends for different percentages.

Table (1) the conditions of preparing blends.

Polymeric blends	Temperature ^oC		Screw speed Cycle per min.
	zone 1	zone 2	
HDPE	180	160	42
HIPS	190	170	42
HDPE/HIPS	200	180	37

Gamma-ray irradiation

The samples were irradiated at room temperature in present of oxygen by using (C_s-137) which emits gamma and beta rays. We are stopping beta ray by using Al oils. The operating dose rate was (4.18 μsv/hr) and the set of samples was exposed to (0.2kGy) of gamma ray under oxygen atmosphere.

Mechanical Testing

Mechanical properties were measured at room temperature (18- 25) ºC Using different types of mechanical testing instruments as shown below:

Modulus of Elasticity and Tensile Test

Tensile specimens of a dog-bone shape were formed following the procedure of reference [9] as shown in Figure (1).Young's modulus and Tensile testing were carried out using Instron instruments. The material testing machine is connected to a remote microcomputer for data acquisition and analysis. The load was measured by a load cell (0.5KN) capacity, while the displacement was measured using an internal extensometer. The speed of testing was (5 mm/min). Three samples with different rate blend were tested before and after radiation.

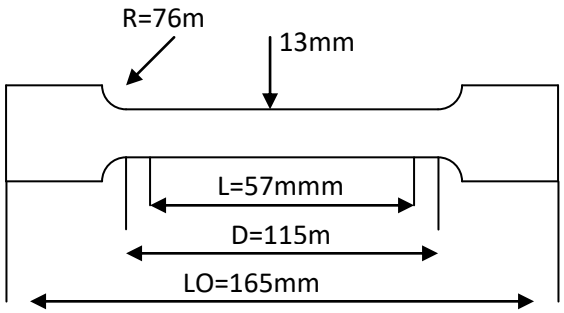
Test	Standard dimensions of specimen	Standards
Tensile strength		ASTM –D638M

Figure (1) Sample dimensions and standard specifications for the testing specimens [9].

The ultimate tensile strength (UTS) was calculated by applying the relationships [10]:

$$\sigma_{ult} = (F_{ult} / A) \qquad \ldots (4)$$

Where:

σ_{ult} is the Ultimate Tensile Strength (MPa), F_{ult} is the Maximum tensile force (N) and A is the Sample cross sectional area (mm^2) .

Modulus of Elasticity of tensile E (Mpa) was calculated from slope of (stress – strain) curve for each sample as show in Figure (2). which subjected to tensile test:

$$E = \frac{\Delta\sigma}{\Delta\in} \qquad \ldots (5)$$

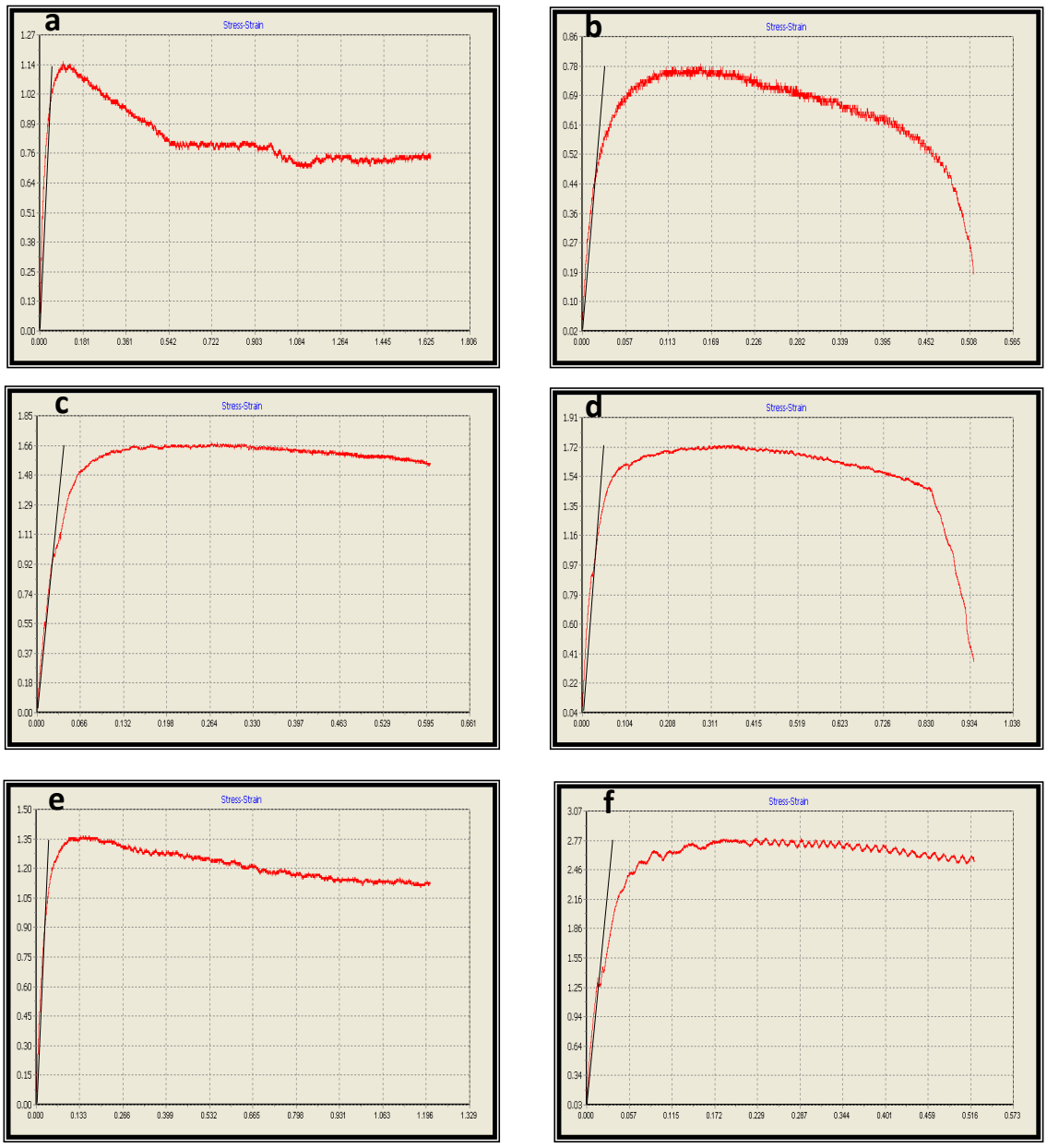


Figure (2) stress-strain curve of: (a) HDPE before irradiation, (b) HDPE after irradiation,(c) (90%HDPE/10% HIPS) blend before irradiation,(d) (90%HDPE/10% HIPS) blend after irradiation,(e) (80%HDPE/20% HIPS) blend before irradiation, (f) (80%HDPE/20% HIPS) blend after irradiation.

Shore D Hardness Test

Hardness of the surface of hard rubber and plastic. This tester (manufactured by TIME GROUP INC Company), was used to carry out the hardness test by using pointed dibbing tool. The pointed dibbing tool penetrates the material surface by the pressure applied on the instrument where the dibbing tool head touching the surface of the samples .The hardness values for the samples are then calculated.

Scanning Electron Microscope (Sem)

Tescan VEGA SEM was used to study the morphology of the fracture surface. Before measurements, the fracture surfaces (obtained after immersing the sample in liquid nitrogen) were sputter coated with a thin layer of gold in a vacuum chamber (specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface) .

RESULTS AND DISCUSSION

The tensile strength of (HDPE/HIPS) and their blends at 80/20 and 90/10 composition ,with and without irradiation Figure (4) shows an increase in tensile strength after irradiation for all blends ratio of (HDPE/HIPS). Possible explanation for this behavior could be that, at lower dose rates, oxidative degradation was predominant due to the slower consumption of the oxygen present in the samples. The oxygen was more rapidly consumed. After the oxygen in the sample was used up, the free radicals formed by irradiation began to improve cross-linking between (HDPE/HIPS) molecules. Similar result had been reached by Miller, Geymen and Chapiro [11]. It is concluded that irradiated (HDPE/HIPS) exhibits a 1.6 scission ratio for every crosslinking formed, whereas Slovaoktotava [12] reported that the consumption of unsaturated groups during low dose irradiation is related to slight crosslinking. Results similar to those presented in this research were reported by Mishra et al. [13].They determined that when (HDPE/HIPS) is irradiated at low doses, crosslinking reactions occur. The overall structure of the typical molecular chain of (HDPE/HIPS) after irradiation can be shown in the Figure (3). [14]:

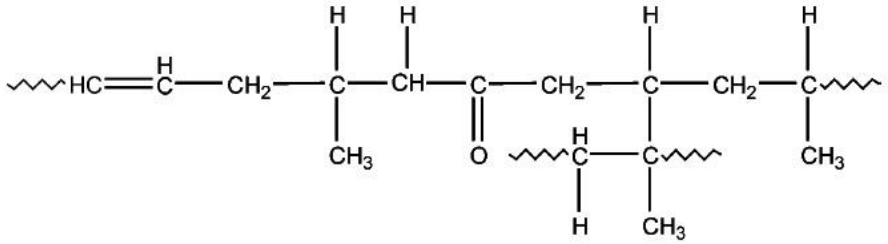


Figure (3) The overall structure of the typical molecular chain of (HDPE/HIPS) after irradiation.

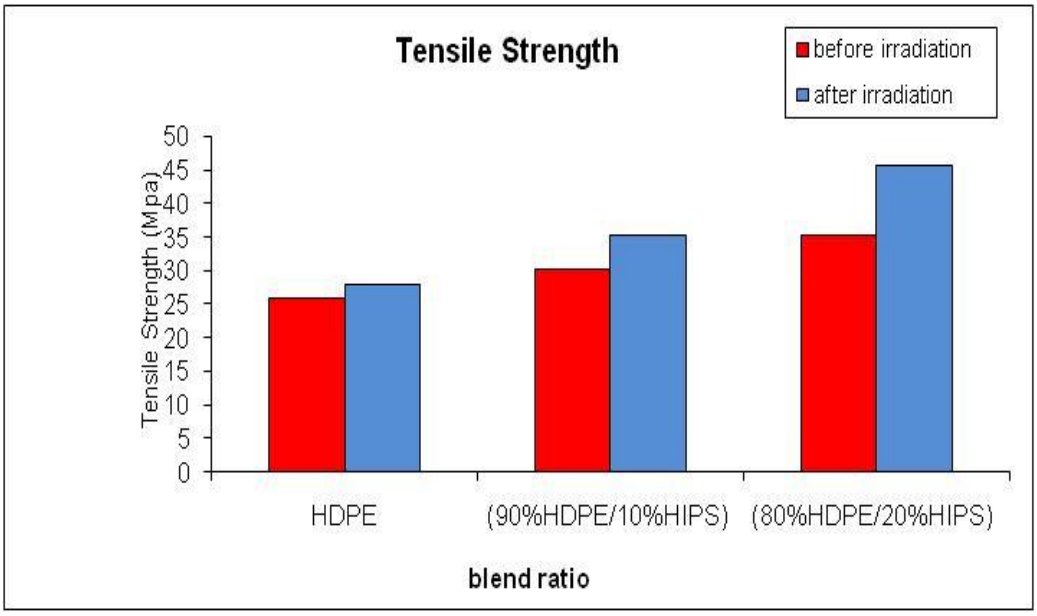


Figure (4) Tensile strength of (HDPE /HIPS) blends with and without irradiation.

The modulus of elasticity shown in Figure (5) was found to increase after the irradiation with gamma dose (0.2kGy).

Despite the fact that irradiation was carried out in the presence of air, the improvement in HDPE and their blends mechanical strength properties for certain conditions shows the predominance of cross-linking over oxidative degradation. A probable reason for these results could be a sample thickness. With a thickness of nearly (1.5-2) mm, the samples seem thick enough to prevent a significant part of the material from contact with oxygen. McKellop (1996) mentions a maximum oxidation at a depth of 0.5 to 2 mm [15]. These results are supported by Premnath et al. (1999) who suggest a maximum thickness of 1.6 mm as a way of assuring the complete oxygenation of irradiated samples [16]. In addition to the oxidation near the sample surface caused by diffusion processes and some oxidations can also occur due to the dissolved oxygen in the sample core.

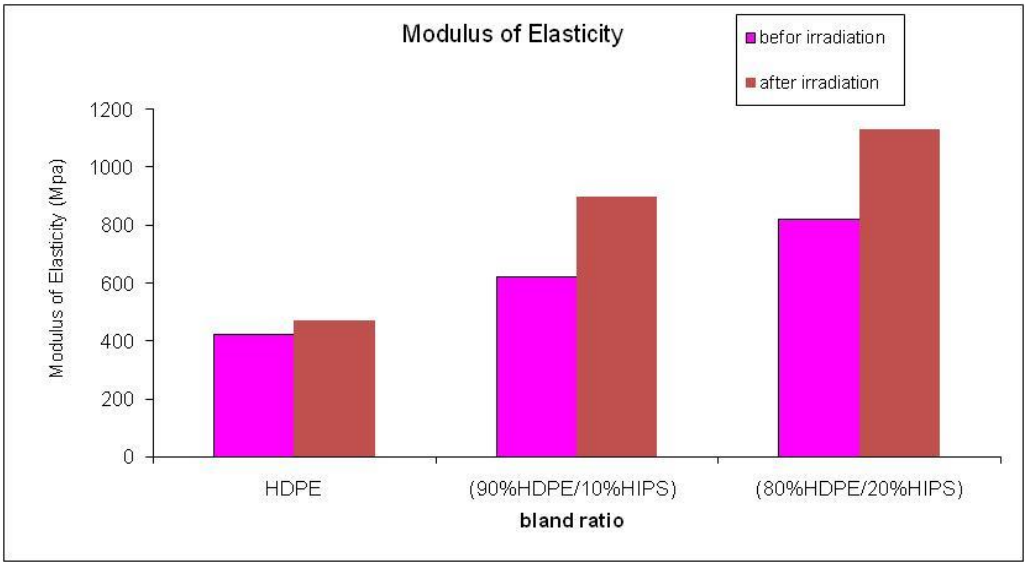


Figure (5) modulus of elasticity of (HDPE /HIPS) blends with and without irradiation.

The results of the hardness tests for irradiated and non-irradiated HDPE/HIPS blends are presented in Figure (6). At low dose exposure the hardness increases. That means there is an interactions are introduced by covalent cross linking, this can be easily established by observing the appreciable increase in the crystalinity of HDPE/HIPS blends , particularly at low levels of irradiation.

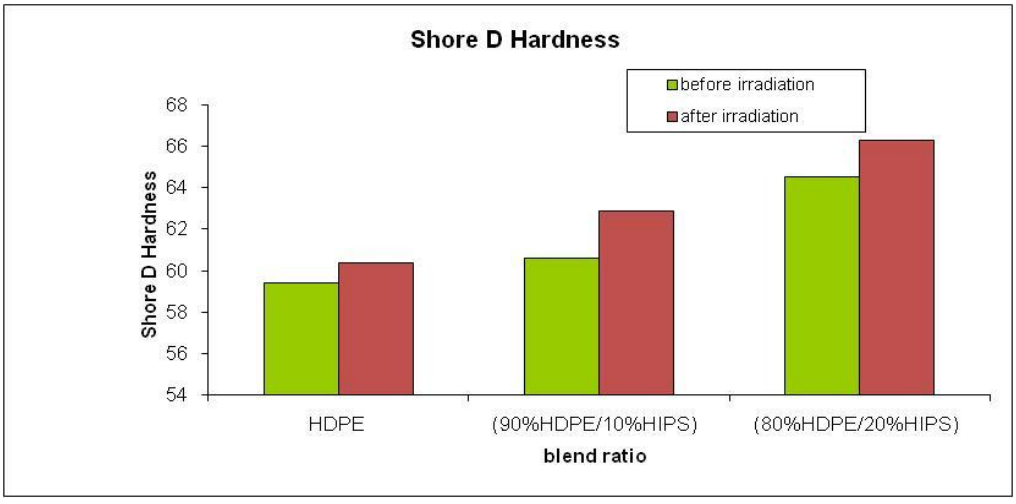


Figure (6) Shore D hardness of (HDPE /HIPS) blends with and Without irradiation.

Figure (7b) shows the deterioration of the (80%HDPE /20%HIPS) fracture surface as a result of irradiation as compared with Figure (7a) of the non-irradiated (80%HDPE /20%HIPS). A more lamellar-like morphology can be observed in Figure (7b), which is responsible for the high toughness of the blends and coincides with the mechanical behavior which had been analyzed.

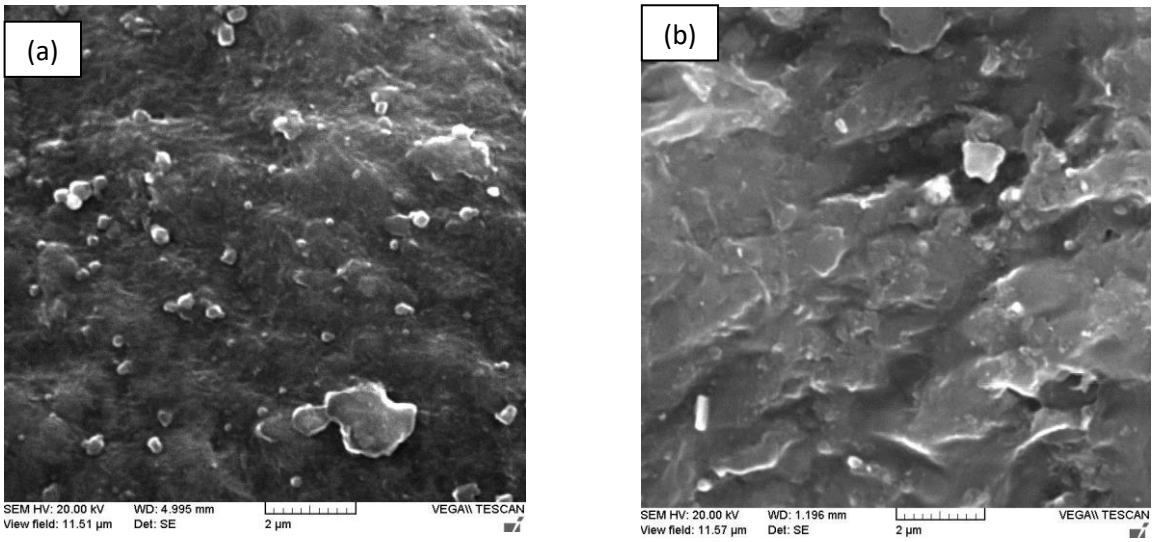


Figure (7) SEM micrograph of fracture surfaces from the irradiated 80%HDPE/20% HIPS blend: (a) at 0 kGy, (b) at 0.2 kGy gamma ray.

CONCLUSIONS

1- Considering the experimental data from a comparative perspective, the results show an improvement in HDPE mechanical strength properties within irradiation. Indicating the predominance of cross-linking over oxidative degradation, despite the irradiation in air, which would theoretically ensure oxygen availability across the sample. These results indicate that sample thickness could be a very important parameter for the design of an irradiation test and should represent the real dimensions of the polymeric component to be submitted to radiation. The results also show that lower doses are necessary to obtain a similar change in mechanical strength parameters when radiation is applied at lower dose rates, showing that gamma radiation affects the HDPE in a more efficient way at lower dose rates.

2- A competing process of oxidative chain scission has been problematic with the gamma-ray irradiation approach. Fortunately, the oxidative degradation of (HDPE/HIPS) blends occurs in air at the gamma-ray dose at 0.2 kGy. This indicates that (HDPE/HIPS) blends are suitable for long-term technical applications in radiation environment.

3- The study of the irradiation chemistry of (HDPE/HIPS) is of particular interest since the molecular structure of this polymer contains large numbers of benzene rings, which are known to have protective actions in much radical chemical process.

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