

MÖSSBAUER ANALYSIS OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE SUBJECT TO DIFFERENT MILLING TIMES

ANÁLISE MÖSSBAUER DE POLIETILENO DE ULTRA ALTO PESO MOLECULAR SUBMETIDO A DIFERENTES TEMPOS DE MOAGEM

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ABSTRACT

In this study ultra-high molecular weight polyethylene (UHMWPE) was subject to high energy mechanical milling at different milling times (5, 10 and 15 hours). Mössbauer spectroscopy analysis revealed that iron particles, coming from the milling container, were incorporated into the polymeric matrix. It is important to study the effects that such iron contaminating particles promote in polymeric cells because the contaminated polymer may present new properties. Mössbauer spectra demonstrated clearly the formation of two paramagnetic phases, indicating that the contaminating atoms were inserted in the polymer matrix, either in a replacing or in an interstitial form in two distinct regions of the polymer.

Keywords: Mössbauer spectroscopy. UHMWPE. High energy mechanical milling.

RESUMO

Neste trabalho, polietilenos de ultra alto peso molecular foram submetidos à moagem mecânica de altas energias sob diferentes tempos de moagem (5, 10 e 15 horas). Medidas de Espectroscopia Mössbauer mostram que partículas de ferro, proveniente do container de moagem, incorporaram-se na matriz polimérica. É importante estudar os efeitos que as partículas contaminantes de ferro promovem nas células poliméricas, uma vez que o polímero contaminado pode apresentar novas propriedades. Os espectros Mössbauer mostraram claramente a formação de duas fases paramagnéticas, indicando que os átomos contaminantes estão inseridos na matriz polimérica, ou de forma substitucional ou de forma intersticial em duas regiões distintas do polímero.

Palavras-chave: Espectroscopia Mössbauer. UHMWPE. Moagem Mecânica de Altas Energias.

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Introduction

Amongst synthetically produced materials, polymers are those with the highest industrial application, due to their low production cost, reduced weight and the possibility of using them in manufacturing in a variety of forms, sizes and colors. One of the main types of polymers is polyethylene. There are several kinds of polyethylene, which are classified according to their molecular weight (COUTINHO, 2003). In our work, we focused on ultra high molecular weight polyethylene ($> 3 \times 10^6$ g/mol) (UHMWPE) because it has excellent properties such as mechanical and physical resistance, high sound absorption, high chemical resistance, dielectric properties, and it is also a biocompatible material (MARCONDES, 2004). This particular type of polyethylene has a higher resistance to abrasion and impact than the majority of thermoplastics, and its friction coefficient is significantly low when compared to other materials used in industry (XIONG, 2001; RUDNIK, 1997). The structure of polyethylene is composed of amorphous and crystalline regions. Generally, the crystal structure of polyethylene is orthorhombic at room temperature and low pressure; this is the most stable structure. The dimensions of a unit cell of orthorhombic polyethylene are $a = 7.42 \text{ \AA}$, $b = 4.95 \text{ \AA}$ and $c = 2.55 \text{ \AA}$, with angles of 90° . Although the orthorhombic form is the most stable, certain factors such as mechanical deformation can take the form metastable growth, of the monoclinic structure with cell dimensions $a = 8.09 \text{ \AA}$, $b = 4.79 \text{ \AA}$, $c = 2.55 \text{ \AA}$, and $\beta = 107.9$ (Russell, 1997, Hendra, 1985). Through x-ray diffraction one can identify peaks relating to the crystalline phases of polyethylene, both orthorhombic and monoclinic. As JCPDS (International Centre for Diffraction Data) No. 11-0834 on a PE diffractogram one can identify two peaks relating to the orthorhombic phase, one at approximately $2\theta = 21^\circ$, relative to the plane (110), and another at approximately $2\theta = 24^\circ$, corresponding to the plane (200). The diffractogram peak at about $2\theta = 19^\circ$ corresponds to the plane (110) of the monoclinic phase (Castricum, 1997). Treatments using milling show that iron particles are occasionally taken from the milling container and contaminate the polymer (due to its high abrasion

coefficient). Initially, it is necessary to know where the iron is placed and whether there is any structural modification due to this contamination. This fact probably alters the physical characteristics of the polymer. The microstructures of the material without grinding are similar to those found in the literature (JAUFFRÈS, 2007; WU, 2002) where, depending on the manufacturing process, particles are obtained with very irregular surfaces, made up of agglomerations of smaller particles, some joined by tiny fibrils. Other authors have observed changes in the crystal structure of orthorhombic polyethylene for the metastable monoclinic structure (ISHIDA, 1994; Castricum, 1997; Barbosa, 2009). Therefore, it is necessary to know to what extent the intrinsic properties of the material are modified due to the presence of iron particles. In addition, this study has great interest for the magnetic media industry and is linked with research involving short-range coupling among magnetic particles separated by a non-magnetic matrix (Borges, 1993). In this present study, X-ray diffraction was employed for structural characterization and Mössbauer spectroscopy with iron probe was used to investigate the kind of structure the iron forms inside the material. Being a nuclear technique, Mössbauer spectroscopy is highly sensitive to iron atoms and has the capacity to reveal details of how these atoms are arranged in matrix.

Materials and methods

The UHMWPE, supplied by Braskem S/A (Camaçari-BA), was subjected to high energy mechanical milling in an Attritor mill (Union Process model 01HD) for 5, 10 and 15 hours in an ambient atmosphere. Millings were carried out at the High Energy Milling Laboratory in the Metallurgy and Materials Engineering Department of the Polytechnic School at São Paulo University (USP). The material mass used in the Attritor mill was 50g and the milling power 40:1. The X-ray diffraction data were carried out in the Materials Engineering Department of Ponta Grossa State University (UEPG), using a Shimadzu (model RXD 6000) with Cu radiation. The database of the JCPDS file was used to identify the phases. Mössbauer spectroscopy measuring was carried out in the Physics Department of Maringá State

University (UEM), in the transmission geometry, at room temperature and free of external magnetic field, using a ^{57}Co radiation source dissolved in a Rh matrix. The hyperfine analysis data were interpreted in the Mössbauer Spectroscopy Laboratory of the Physics Department of Ponta Grossa State University (UEPG). The equipment calibration was made using sheets of pure metallic iron and the data were fitted with an adjustment program which was developed at the Institute of Physics of the Federal University of Rio Grande do Sul (UFRGS) using discrete Gaussian lines.

Results and discussion

When submitting the UHMWPE to high energy mechanical milling, changes in the polymer color were noticed, as can be seen in Fig. 1.

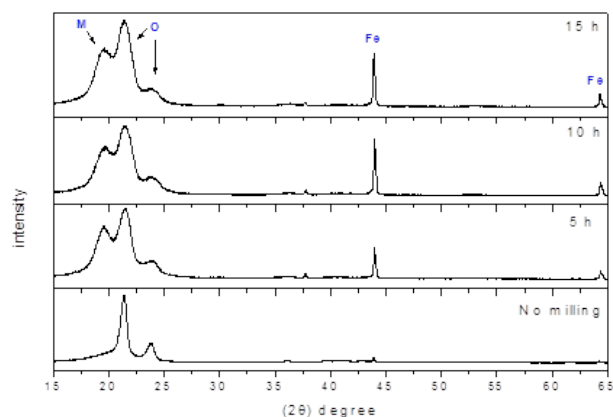
Figure 1 - From left to right, unmilled UHMWPE (white) and milled for 5, 10 and 15 hours (colorfull)



The X-ray diffractograms (Fig. 2) previously carried out, clearly show the appearance of the polymer in the monoclinical phase (M) after a few hours of milling. Studies have verified that the appearance of such phase occurs at the expense of the original orthorhombic phase (O) and is a consequence of the net deformation, due to the impact caused by the milling balls (GABRIEL, 2008). After some time the quantity of each referred phase stabilizes and no significant differences regarding increase in one or other are observed, as can be seen in the three diffractograms of the milled samples. However, these two phases are overlapped by an amorphous phase, which increases with the milling time. The appearance of two other significant

peaks was also observed, clearly indexed to the pure metallic iron, after 5 hours of milling (JCPDS 06-0696). Mössbauer spectra of the milled samples only showed contributions in the form of doublets in the middle of the spectra, revealing that there is iron contamination, and it presented two different configurations in the polymeric matrix, as shown in Figs. 3, 4 and 5. In these figures, the two blue lines are the theoretical sub-spectra, regarding each distinct site in which iron is inserted in the matrix.

Figure 2 - X-ray diffraction for the UHMWPE samples milled at three different times and the original.



The parameters used in the Mössbauer adjustments can be seen in Table 1. It was observed that the lines widths (Γ) are narrow enough to indicate an only site for each sub-spectrum. Regarding the isomeric displacement (IS) and quadruple unfolding (ΔE_q), there is no regular variation clearly defined in relation to the milling time. One of the possibilities for the interpretation of the iron doublets which appear in the spectrum could be hydroxylation of this element, forming lepidocrocite, wustite and goethite (BORGES, 1997) since hydrogen can be extracted from some carbon leaving it with free radicals and oxygen comes from the milling atmosphere. Despite the possibility of interpreting the parameters found for site B as a lepidocrocite, such interpretation is not accurate due to a lack of iron oxide characteristic peaks in the diffractogram. Another possible interpretation could be due to the iron finding some vacancies in the polymer net with sufficient distance for a quadruple interaction, but not close enough for magnetic coupling. However, considering the distance and format of polymeric

chains it would be too difficult for the iron to find interstitial sites with regular periodicity. There are two remaining possibilities: either amorphous iron, or in the form of nanometric grains, and therefore, super paramagnetic. The X-ray diffractogram suggests that the latter is more accurate due to the small width of the peaks for this element, clearly

indicating a high degree of cristallinity. It would be necessary to obtain a Mössbauer spectrum at low temperature in order to confirm such particles inside the polymeric sample, but unfortunately it is not possible to do this in our laboratory. The possibility of adjusting the spectrum with two sub-spectra, leads to the existence of grains with different sizes.

Figure 3 - UHMWPE milled for 5 hours.

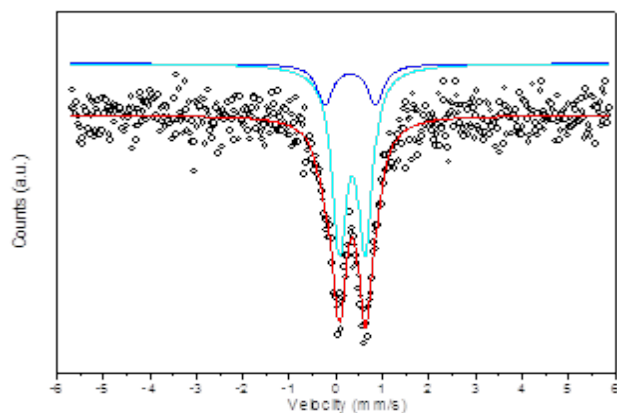


Figure 4 - UHMWPE milled for 10 hours.

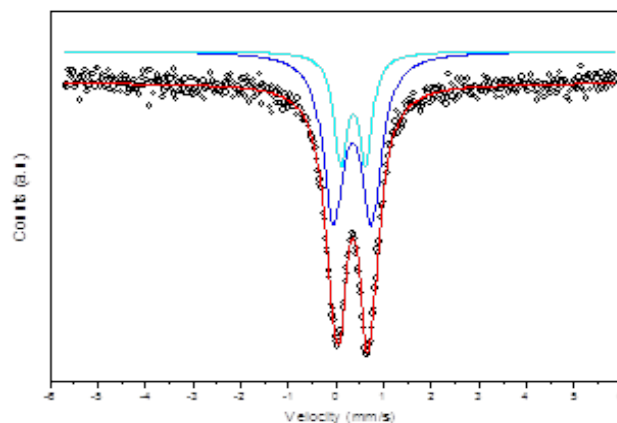


Figure 5 - UHMWPE milled for 15 hours.

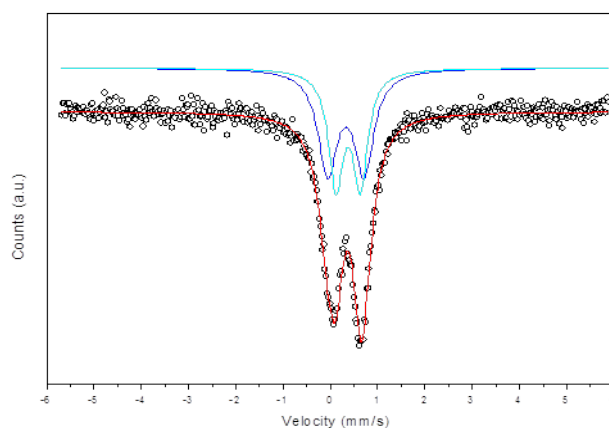


Table 1 - Parameters used in the Mössbauer adjustments

Time (h)	Site	Γ (mm/s)	IS (mm/s)	ΔE_q (mm/s)	A (%)
15	A	0.49	0.33	0.77	53.9
	B	0.38	0.38	0.52	46.1
10	A	0.51	0.34	0.80	69.6
	B	0.34	0.36	0.52	30.4
05	A	0.41	0.31	1.08	20.0
	B	0.38	0.35	0.55	80.0

Where: Γ is the line width half way in the curves; IS is the isomeric displacement; ΔE_q is the quadruple unfolding; A is the relative area of each sub-spectrum.

Conclusions

The polymer color changed according to the milling time which was due to the diffusion of iron, coming from the milling container. This occurred due to the high abrasion coefficient of the UHMWPE. The interpretations of diffractometry associated with the Mössbauer spectroscopy suggest the existence of two distinct sites, probably resulting from super paramagnetic particles of different sizes. Iron diffusion in the polymeric matrix might alter the UHMWPE properties, increasing the range of its applications as well as opening up a new line of studies of polymeric materials with magnetic potential.

Acknowledgements

The authors are grateful to Fundação Araucária for their support for this research.

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