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The Study of Phase Compound and the Degree of Crystallinity of Recycled LDPE by X-ray Diffractometer and Optical Microscope

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Abstract: In this paper we study the phase compound of semi crystalline structures of recycled LDPE (Low Density Polyethylene) by Optical Microscopy and X-ray Diffraction techniques. Measurements of optical microscopy were made using the technique of polarized light microscopy in transmission mode (POM). The micrographs taken for all recycled LDPE samples indicate the presence of additives. XRD method is non destructive nature with in-depth crystallographic analysis and for this reason XRD techniques are used in this paper to study the phase compound and to calculate the degree of crystallinity of pure and recycled LDPE. By diffractgrams analyses were identified rutile's and calcite's peak, as additives added in the recycled LDPE. It was analyzed the influence of additives on the degree of crystallinity.

Keywords: phase compound, crystallinity, X-Ray diffraction, Optical Microscope.

1. Introduction

Polyethylene is the most widely used thermoplastic material and is composed of ethylene [1]. Polyethylene (PE) materials can be applied in many fields of life. Two important classes of PE materials are low density (LDPE) and high density polyethylene (HDPE). LDPE is manufactured by polymerization of ethylene under high pressures (103-345 MPa) and elevated temperatures (200-350°C) in the presence of oxygen (0.03-0.1%) as free-radical initiator. LDPE is characterized by a relatively low rigidity and low degree of crystallinity. LDPE offers excellent clarity and easy processing. Therefore it can be used as packaging material, e.g. foil, and as cover sheeting in many fields of daily and industrial life [1], [7]. Recycling is one the main ways processing plastic materials, constitutes one of the main problems of society including two important issues: solid waste management and environmental protection. Plastic recycling is both an economic and an environmental activity. Plastics recycling present numerous technical, economical, and marketing challenges. One such technical issue is the variability of product composition and color, because discarded products are made from a wide array of resins and additives [3], [8].

A polymer can be considered partly crystalline and partly amorphous [2]. The crystalline domains act as a reinforcing grid, like a composite material, and improve the performance over a wide range of temperature. The X-Ray Diffractometer (XRD) techniques are used successfully for the crystallographic study of polymers. It is used for analyzing crystalline phases, determining the extent of crystallinity and identifying crystalline structure [2]. X-rays are electromagnetic waves with a wavelength between 0.01 and 1 nm, which, when incident on a material, interact with electrons in the material and are scattered. X-ray waves scatter from different electrons and interfere with each other. This interference gives the resulting diffraction pattern, the positions of diffraction peaks and their relative heights, in which the intensities vary with scattering angle. X-rays scattered from the periodic repeating electron density of a perfectly crystalline material give sharp diffraction peaks at angles that satisfy the Bragg relation, whether the crystal consists of atoms, ions, small molecules, or large molecules. Amorphous materials will also diffract X-rays and electron, but the diffraction is a much more diffuse, low frequency halo (the so called "amorphous halo") [4]. Bragg derived Bragg's law for the distance d between consecutive identical planes of atoms in the crystal:

$$n\lambda = 2d\sin\Theta \qquad (1)$$

Where λ is the x-ray wavelength, Θ is the angle between the x-ray beam and these atomic planes and n corresponds to the order of diffraction .



Figure 1: Principle of diffraction. [5]

A general polymer x-ray spectrum will have a broad amorphous peak, and if the polymer has crystallinity, it will show up as sharp peaks on the top of large amorphous peak, as in the following figure



The percentage of the polymer that is crystalline can be determined from equation:

$$%Crystallinity = \frac{Area \ under \ crystallin \ e \ peaks}{Total \ Area \ under \ all \ peaks} \times 100\%$$
(2)

2. Materials and methods.

The study of phase compound and the determination of the degree of crystallinity of recycled LDPE samples was done using two apparatus. X-Ray Diffractometer and Optical Microscope. X-ray diffraction patterns were measured at, Institute of Ceramics, Glass and Construction Materials, Freiberg, Germany with a X'PERT Pro MPDPW 3040/60 diffractometer from PANALYTICAL in transmission geometry. The qualitative phase analysis procedure involved the identification of major and minor phases using the X'Pert High Score Plus Software. The measurement conditions were as follows, angular range, 7.5 < 2θ < 80 ° step size 0.013⁰, step time 30s, Copper radiation Cu (wavelength 1.540598 Å), tube power 40kV / 40 mA. Optical measurements were obtained by Optical Polarized Light microscope XJP 304 with transmission and reflection mode. Microscope is equipped with digital cameras TCC 800, type C and software TS Wiew. Polyethylene recycled materials as granules and plastic bags were obtained by recycling factory "Everest" Kashar. Samples for XRD measurements were prepared using different colors polyethylene granules. For XRD analysis the samples were prepared in this way: on different microscope slides it was put small amount of granules of recycled LDPE at different colors and each of them it was melted in room conditions at LDPE melting point $T_m =$ 110°C. For transmission measurement each melted sample was placed between two Kapton foils. The Kapton foil (the yellow one) doesn't affect the measurements. On a metal ring was fixed a thin of plastic foil on which was placed the sample. Above sample was placed another plastic foil. The sample was fixed with a second metal ring with larger diameter than the first ring. For optical measurements on different microscope slides it was put a piece of plastic bags of different colors. Optical microscope measurements were made under cross- polarization and without retardation plate.

The images were registered from digital camera with recording of 1 photo /s.

3. Results and Discussions

The micrographs taken by optical microscope for all recycled LDPE samples are presented below.



Figure 3: Optical micrographs of recycled LDPE with polarized light microscope under cross- polarization and without retardation plate (x100).

As it seen from the figure above, there are dark areas and illuminated spots to all the images. This occurs because it has been worked under cross-polarization and there was no illumination. So the area of polymer molecules is dark while the additive's molecules area is illuminated. This is due to the fact that the additive's molecules are anisotropic and appear in micrographs in the form of illuminated spots. There are more illuminated spots in red recycled LDPE image, than in other samples, which indicates that the quantity of additives in this sample is greater than the others. There are a few illuminated spots in black recycled LDPE image. This fact indicates that this sample has lower degree of crystallinity than the others. The image of opaque recycled LDPE has more spots than the green one.

For a further study of situation the XRD technique were used. Diffractograms obtained by X ray diffractometer for each different sample of LDPE, both pure and recycled are presented as follows.



Figure 4: XRD pattern of Pure LDPE



Figure 5: XRD pattern of recycled LDPE (Black)



Figure 6: XRD pattern of recycled LDPE (Blue)







Figure 8: XRD pattern of recycled LDPE (Red)



Figure 9: XRD pattern of recycled LDPE(Green)



Figure 10: XRD pattern of recycled LDPE (yellow)

Diffractograms obtained experimentally indicate that pure and recycled LDPE is semi crystalline polymer. The crystalline parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak. The diffractogram of pure LDPE (figure.4) comply with standard spectrum of LDPE [8]. As it seen at figure 4-figure 10, it is observed the appearance of two characteristic peaks of polyethylene (C_2H_2)_n, as the main compound respectively at 20 angles: 21.5° and 23.8°, are apparent in all other diffractograms of recycled LDPE. By the analysis of phase compound using the X'Pert High Score Plus Software were identified the presence of rutile (TiO₂) and calcite (CaCO₃) peaks at all recycled samples. This presence was confirmed also with the calculation of the interplanar spacing (d-

Volume 4 Issue 2, February 2015 <u>www.ijsr.net</u> Licensed Under Creative Commons Attribution CC BY spacing) as in equation (1), using experimental data and Bragg's law.

 Table 1: The calculation of interplanar spacing (d-spacing for rutile and calcite peaks

2θ(°)	sinθ	Intensity	$\lambda_{Cu}(A^{\circ})$	$d = \lambda/2 sin\theta$	phase
27.41	0.23	1343	1.54	3.25	TiO ₂
29.33	0.25	1548	1.54	3.04	CaCO ₃

Finely powdered rutile is a brilliant white pigment and is used in paints, plastics, paper, foods, and other applications that call for a bright white color. Titanium dioxide is the most important white pigment used in the polymer industry thereby imparting whiteness, brightness, and opacity when incorporated into a plastic product. It is widely used, because it efficiently scatters visible light, thereby protecting the polymer from UV degradation [6].

Calcite is a rock-forming mineral with a chemical formula of CaCO₃. Powdered calcite is often used as a white pigment or "whiting. CaCO3 may be white or in different colors and can be used as coloring pigment in polymers. The presence of calcium carbonate provides the maintenance of transparency in polymer, keeps unchanged optical properties of the polymer, increases plastic resistance against light and high temperatures and enables no change of color of plastic under the influence of UV (Ultra Violet) [6].

By diffractograms above it was observed that the intensity of the main peak has different values at different samples. This indicates that samples have different amounts of additives and thus represent varying degrees of crystallinity. Additives added during recycling process influence to the degree crystallinity [8].

By processing raw experiment data for each sample it was presented the dependence of intensity vs. 2θ angle data, in the range of $14^{\circ} < 2\theta < 26^{\circ}$ angles and the fitted multiply peaks curve, to determine the degree of crystallinity



Figure 11: Intensity vs. 2θ angle data, in the range of $14^{\circ} < 2\theta < 26^{\circ}$ and the fitted multiply peaks curves of recycled LDPE (red).

Using equation (2) it was calculated the degree of crystallinity and all results are presented as follows.

 Table 2: The surfaces under crystalline peaks and

 amorphous peaks and the degree of crystallinity for all LDPE

 samples

samples										
LDPE	Pure	Black	Blue	Opaque	Green	Red	Yellow			
Area amorphs peaks	12033	20197	2020	13410	15748	10423	13684			
Area crystallin peaks	3165	6100	8000	10442	4543	11172	4913			
	771	1900	3008	3198	1279	3163	1403			
% crystallinity	25	28	40	50	35	58	32			

As it seen from the table 2, the LDPE samples have different degree of crystallinity. LDPE (Pure) has the lowest degree of crystallinity and the red one has highest. The conclusions obtained by calculations are visible also in the diffractograms above. The intensity of main peak of LDPE (pure) sample in fig.4. is the lowest. The intensity of the main peak of red sample in fig.8 is higher than all the others. It depends on the amount of additive they have respectively, because the additives play an important role in the crystallinity of polymers [9].

4. Conclusions

Optical microscopy and XRD diffraction techniques are very important to the study of phase compound and the degree of crystallinity of polymers.

Micrographs obtained by Polarized Light Microscope under cross-polarized, without retardation plate, indicated that samples of different colors of recycled LDPE display different images due to quantity of additives they possess. Micrograph of red color has more illuminated spots than the others and the micrograph of the black one has lowest spots. Samples of different amounts of additives represent varying degrees of crystallinity.

Diffractograms obtained experimentally indicated that recycled LDPE is a semi crystalline polymer. The crystalline parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak. From the analysis of the recycled LDPE diffractograms, it was confirmed the presence of rutile (TiO₂) and calcite (CaCO₃) as additives in all samples. From the calculations was concluded that recycled samples have different degree of crystallinity, because additives added during recycling process influence to the degree crystallinity

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