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THE STUDY OF THE INFLUENCE OF ADDITIVES IN THE CRYSTALLINITY OF RECYCLED LDPE BY IR AND XRD ANALYSIS

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Abstract. *In this study, the influence of additives used during the recycling process, to the crystallinity of LDPE was analyzed. The usage of LDPE recycled is growing, as well as other types of recycled plastics, due to its flexibility and other properties. The spectroscopic method of infrared vibration is used for microstructure analysis of the samples. The presence of low-intensity peaks to infrared spectrum at 1300-800 cm^{-1} for all samples indicates the presence of additives. The additives used in the recycled polymers influence their degree of crystallinity that is closely linked with their physical and mechanical properties. Due to the different rates of crystallinity the samples show different intensities of peak at 726 cm^{-1}. XRD techniques are used to calculate the degree of crystallinity and to study the phase compound of recycled LDPE. Rutile's and calcite's peak were identified by diffractgrams analyses as the additives added in the recycled LDPE.*

Key words: *Crystallinity, microscopy, phase compound, polarized light, spectroscopic methods, X-Ray diffraction*

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 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]. Recycling is one the main ways processing plastic materials, it 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 presents 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 [2]. Infra Red spectroscopy is probably the most used spectroscopic methods in polymer science as is appropriate both in qualitative analysis as well as quantitative analysis of polymeric materials. Modern IR spectroscopy is a simple analysis method, and gives direct results. Using IR can identify unknown materials, to determine the quality or stability of a sample, monitor their production and processing, e.g. cross-link or cross-sectional degree as well as determine the composition of a compound mixture [3].

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an "unknown" with previously recorded reference spectra. In the most basic terms, the infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds from within a molecule [4].

Infrared Spectroscopy utilizes the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation complies with the transition energy of the bond or the group vibrating [4]. A polymer can be considered partly crystalline and partly amorphous. 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 [5]. X-rays are electromagnetic waves with a wavelength between 0.01 and 1 nm, which, when incident on a

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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") [5], [6].

Bragg derived Bragg's law for the distance d between consecutive identical planes of atoms in the crystal:

$$n\lambda = 2d \sin\theta \quad (1)$$

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.

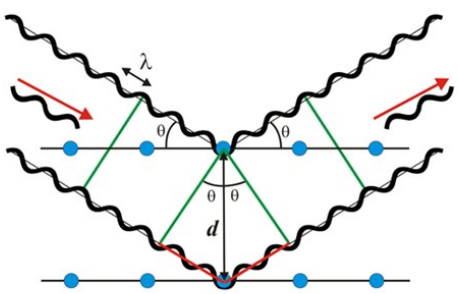

Figure 1. Principle of diffraction [6]

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.

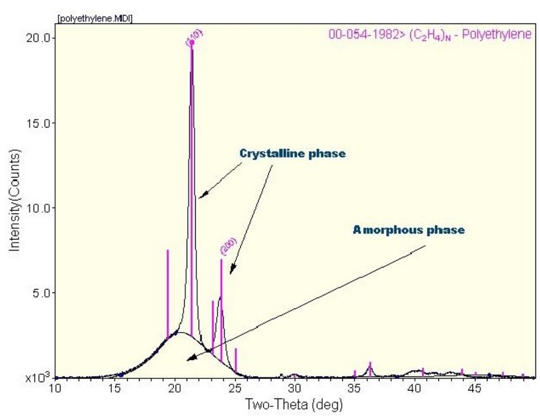

Figure 2. XRD pattern of Polyethylene [6]

The percentage of the polymer crystallinity can be determined from equation:

$$\%\text{crystallinity} = \frac{\text{Area under crystalline peaks}}{\text{Total area underall peaks}} \times 100\% \quad (2)$$

2. Materials and methods

Samples used for this study are pure and recycled LDPE as granules and plastic bags. Pure LDPE is provided by Alfa Aesar GmbH & Co KG. Recycled materials are provided by "Everest" Albanian company.

Table 1. List of samples

No	Sample	Color	Shape	Usage
1	Pure LDPE	white	microgranule	
2	Recycled LDPE	white	bag, granule	package
3	Recycled LDPE	Opaque	bag, granule	package
4	Recycled LDPE	green	bag, granule	package
5	Recycled LDPE	yellow	bag, granule	package
6	Recycled LDPE	red	bag, granule	package
7	Recycled LDPE	black	bag, granule	package

2.1. Infra Red Spectroscopy

The apparatus used is TJ270-30A Dualbeam Infrared Spectrophotometer. For the IR measurements are used, pure polyethylene and a wide range of recycled plastic bags LDPE, like thin films. The sizes of all samples are 4 x 4 (cm), enough to cover the circular hole that allows infrared radiation to pass between the metal holder. The measurements of infrared spectra are optimized using the corresponding software of the apparatus and the results are processed on the Origin program.

2.2. XRD Diffractometry

X-ray diffraction patterns are measured at the 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 are as follows: angular range, 7.5< 2θ < 80 ° step size 0.013°, step time 30s, Copper radiation Cu (wavelength 1.540598 Å), tube power 40kV / 40 mA. XRD measurements are performed using recycled LDPE as granules. Small amount of granules of recycled LDPE in different colors is put on different microscope slides and each of them is melted in room conditions at LDPE melting point T_m = 110°C. For transmission measurement each melted sample is placed between two Kapton foils. The Kapton foil (the yellow one) does not affect the measurements. Thin plastic foil is fixed on a metal ring on which the sample is placed. Another plastic foil is placed above the sample. A second metal ring with a larger diameter than the first ring is used to fix the sample.

3. Results and discussion

3.1. IR characterization

IR spectroscopic measurements are performed for all plastic bag recycled LDPE samples.

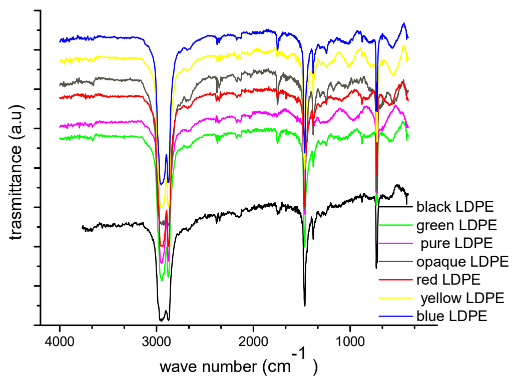

Figure 3. IR spectra of
all plastic bag samples vertically shifted

The transmittance of black recycled LDPE is significantly lower than other samples. All recycled plastic bags LDPE samples display three characteristic groups of pure LDPE peaks respectively to the wave numbers: 2920-2850 cm $^{-1}$, 1490-1420 cm^{-1}, 750 to 720 cm^{-1} [3]. All recycled samples are composed of pure LDPE. Peaks displayed wavelengths to above bands are the absorption peaks of C-H and C-C connections belonging to the main chain of polyethylene at infrared area. [4],[7]. The peak at the 2920-2850 cm^{-1} band, is attributed to CH_2 groups. The peak shown at the wave number 1460 cm^{-1}, is dedicated to the scissors bending of CH_2 groups and the peak at 1303 cm^{-1} belongs to amorphous area polymer. Low-intensity peaks in the area of 1300-800cm^{-1}, indicate the presence of additives for all recycled LDPE samples [4], [7], [8]. The peak at 726 cm^{-1}, represents a rocking frequency of the CH_2 group in planar zigzag chain and is indicative of the crystals' existence. In the zone of 726cm^{-1} all samples exhibit different intensities peak, which indicate different percentages of their crystallinity.

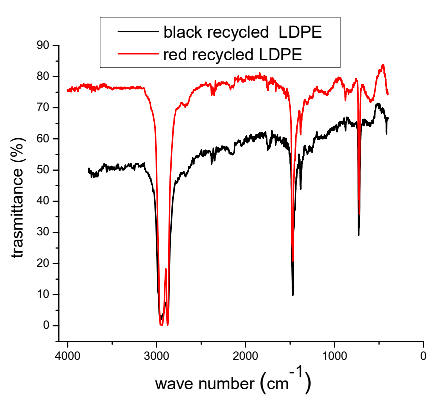

Figure 4. IR spectra for black and
red plastic bags recycled LDPE

From Figure 4, red plastic bag recycled LDPE sample has the highest intensity of peak and black sample has the lowest one compared to other samples.

3.2. XRD characterization

In Figure 6, diffractograms of red and black granule recycled LDPE as representatives of highest and lowest crystallinity are presented. The diffractogram of pure LDPE in Figure 5 is presented to be compared with recycled material.

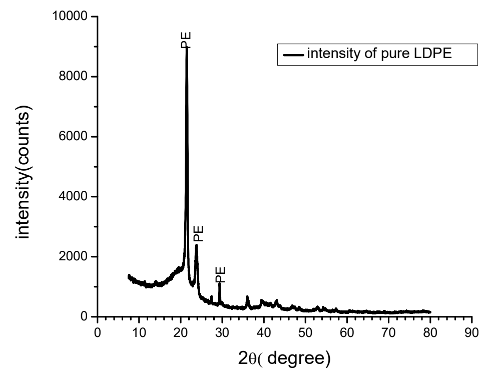

Figure 5. XRD pattern of pure LDPE

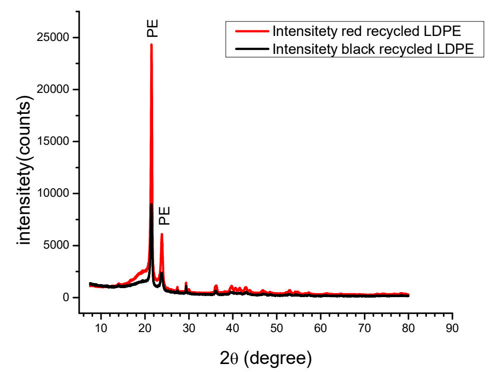

Figure 6. XRD pattern of red and
black recycled LDPE granules

Diffractograms obtained experimentally for all LDPE samples indicate that pure and granule recycled material is a semi crystalline polymer. The crystalline parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak. It is observed in all diffractograms of recycled LDPE the appearance of two characteristic peaks of polyethylene (C_2H_4), as the main compound, at 2θ angles of 21.73° and 24.18° respectively. By the analysis of phase compound using the X'Pert High Score Plus Software, is identified the presence of rutile (TiO_2) and calcite ($CaCO_3$) peaks to all recycled samples [9]. This presence is confirmed also with the calculation of the interplanar spacing (d-spacing) using experimental data and Bragg's law.

Table 2. Qualitative analysis of X-ray

Peak	2θ	d_{hkl} (Å)	I (impuls/s)	phase
1	21.73	4.090	9056	PE
2	24.18	3.681	2388	PE
3	27.41	3.25	1343	TiO_2
4	29.33	3.04	1548	$CaCO_3$

Finely powdered rutile (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 [9]. Calcite is a rock-forming mineral with a chemical formula of $CaCO_3$. Powdered calcite is often used as a white pigment or "whiting". $CaCO_3$ 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) [9]. There are observed by diffractograms, different intensity values of the main peak 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 the crystallinity degree [9], [10]. By processing raw experiment data for each sample, the dependence of intensity vs. 2θ angle data, in the range of 14° <2θ <26° angles and the fitted multiply peaks curve, is presented to determine the degree of crystallinity.

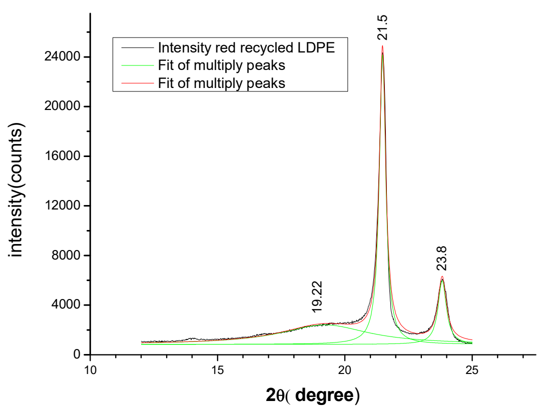

Figure 7. Intensity vs. 2θ angle data, in the range of 14° <2θ <26° and the fitted multiply peaks curves of recycled LDPE (red).

The degree of crystallinity for all granule recycled samples and for pure LDPE sample are calculated. The results are presented in Table 3.

As it is seen from Table 3, the LDPE samples have different degree of crystallinity. LDPE (black) has the lowest degree of crystallinity and the red one has the highest from the recycled polymers. The samples have different amounts of additives and thus represent varying degrees of crystallinity. Additives added during recycling process influence their crystallinity degree [10].

Table 3. The area under crystalline and amorphous peaks and the degree of crystallinity for all LDPE samples

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

4. Conclusion

XRD and IR methods used in this paper confirmed the existence of additives in all recycled LDPE samples as granules and plastic bags. The percentages of crystallinty in granule recycled of LDPE samples are calculated using XRD method because it measures long-range order or intermolecular order as a result of chain packing. IR measures short-range order, so it is a supporting method. All recycled LDPE samples display three characteristic groups of pure LDPE peaks. Recycled LDPE does not have fundamental structural changes from pure LDPE. All plastic bag recycled samples exhibit different intensities peak at 726cm^{-1}, which indicates a different percentages of their crystallinity.

Recycled LDPE is a semicrystalline material. By the qualitative analysis are identified the presence of rutile (TiO_2) and calcite ($CaCO_3$) peaks at all granule recycled samples. Additives added improve polymer crystallinity and its physical properties LDPE samples have different degrees of crystallinity due to different amounts of additives into them.

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