

ESTIMATION OF PLASTIC RECYCLING MATERIALS BY THE USE OF VIBRATION SPECTROSCOPIC METHODS

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ABSTRACT

The increase in use of plastic materials during last decades and their short time of degradation has caused a lot of environmental problems. The processes of selection, separation, processing and reuse of plastic materials in useful products is a actual challenge for our society and for the recycling industry. Based on their different physical-chemical properties, the operations of processing and reusing them as raw materials are different. During last years the recycling industry in Albania has grown up, increasing the capacities and types of plastic materials processed. The purpose of our study is to distinguish the plastic materials and to estimate the recycling grade by the use of Fourier Transform Infrared and Raman Spectroscopy. This analysis methods provide information about the polar and non-polar molecular bonds or molecular structure, and are complementary to each-other. The materials for this study provided by the Albania market are packaging bags and plastic bottles in virgin and recycled form. From FT-IR dhe Raman spectra are investigated the molecular bonds, the degradation of plastic materials during recycling process and the possibility of determination of plastic additives in recycled materials.

Keywords: *Plastic recycling, vibration spectroscopy, additives.*

INTRODUCTION

The development of technology and the increasing demand for goods has brought a rapid increase in production and uses of plastics in recent decades. Plastic materials, along with new products, have replaced a number of products made of paper, glass and various metals. Their physic-chemical properties have enabled the production of a variety of products, making our everyday lives easier. Above 78wt% of plastic materials (Plastics 2009) corresponding to the category of thermoplastic (mainly polyolefins, LDPE, HDPE, PP and PET) and the remainder thermosets (epoxy oleoresins and polyurethanes). Besides material goods and facilities, increased use of plastic materials has led to many problems related to the environment due to the very slow degradation of their (J.H.Khan et al., 2003). So solid waste plastics are a serious problem for any society nowadays and more effective management of them is a challenge that requires cooperation between society, governing institutions and the chemical industry. Their management policies focus on three main areas: reduction, recycling and reuse. Besides recycling, bulk plastic waste are buried in landfills (although undesirable) or used for energy production. Considering their waste problems, recent years many strategies have been designed for the production of plastic materials with high biodegradation as is the production of bio-based plastics or of fossil materials (Kokiwa Y. et al, 2009). Most of products are plastic bags of low-density polyethylene-LDPE used for packaging purposes and plastic bottles from polyethylene- terephthalate, PET. Although in recent years the use of plastic bags is conditional on more packages, they still constitute the main source of plastic waste. Also the addition of antioxidants in the structure of PET has enabled increased lifelength products (especially carbonated) increasing the use of PET bottles. Bags and plastic bottles can be collected and recycled by different methods, producing useful products from them. But during recycling, as a result of their oxidative processes in the presence of air, plastic materials lose many of their properties. Recovery of properties carried out by the addition of additives in polymeric structures, mainly during the recycling process (F.P. La Mantia et al., 1998). A large number of additive used as a dyestuff, plastic bags to give the desired colors. Also the analysis of plastic bags and bottles should consider the different dyes in their templates added after production.

The purpose of our paper was the study of clean and recycled plastic materials in Albanian market, their identification with spectroscopic methods, the study of the degree of recycling and determination of additives in their structures.

MATERIALS AND METHODS

Materials that were studied were obtained with low-density polyethylene and polyethylene LDPE polyethylene terephthalate PET. Materials were provided in the form of granules as raw material, as well as products: bags and plastic bottles from companies operating in the Albanian market. In the table below are materials specified by color, shape and their uses.

Tabela 1: Plastic samples classified from colour, form and uses.

| No | Sample | Color | Form | Uses |
|----|-----------------------|-------|--------------|-----------|
| 1 | PE industrially clean | White | Plastic bags | Packaging |

| | | | | |
|---|------------------------|-------------------------|-----------------|-----------|
| 2 | PET industrially clean | White | Plastic bottles | Packaging |
| 3 | PE recycled | Red | Plastic bags | Packaging |
| 4 | PE recycled | Grey | Plastic bags | Packaging |
| 5 | PE recycled | Blue | Plastic bags | Packaging |
| 6 | PE recycled | White –semi transparent | Plastic bags | Packaging |

Chemical structure of plastic materials were initially evaluated by studying their spectra in the infrared region. The instrument used was the spectrometer Perkin Elmer Spectrum GX1 with appropriate software for processing data and calculating the corresponding spectra. The instrument resolution was 4cm^{-1} . The frequency of the wavenumber was measured from 400 to 4000cm^{-1} . The number of accumulations to reduce the noise was 10.

To further study of the chemical structure of polyethylene was used Raman spectroscopy equipped with an electronic microscope and the corresponding software. The instrument used was the micro Raman spectrometer - Renishaw RM1000 RamaScope the wavelength of laser radiation at 633nm (red), optical microscope equipped with Leica DMLM.

In infrared vibration spectroscopy affects to a large scale, shape and size of the material. FT-IR spectra were taken from polymeric pellets formed with the help of a Perkin Elmer press in temperature 180°C for LDPE and 290°C for PET. These temperatures were taken from literature and are at least 20°C above the melting temperature of LDPE and PET (D.S. Achilias et al, 2007). In the formation of LDPE pellets were put in time and change their mitigation, dedicated to various additives present in their structures. FT-IR spectra also were taken directly from the plastic bags because they were thin thickness, which enable obtaining clear spectra. To obtain the Raman spectra polymer pellets were used only for back-scattering method used, where the thickness does not affect the reception of information. The amount of plastic granules used to form pellets was ranked 20-30 mgr. The diameter of the pellets was 13mm.

Both these spectroscopic methods are non-destructive methods and formed pellets can be used for further studies. They are complementary to each other, and the analysis of their spectra can obtain information on polar and non-polar chemical bonds and in the structure of materials (D.W. Mayo et al, 2004).

For our study LDPE pellets were prepared industrially clean pellets and of four different types of recycled LDPE, used as packing bags. Also the pellets were prepared from the PET plastic bottles used to.

RESULTS

In the figures below are FT-IR and Raman spectra for clean and recycled materials. Spectra are located in such a way as to distinguish whether differences between methods and between different materials.

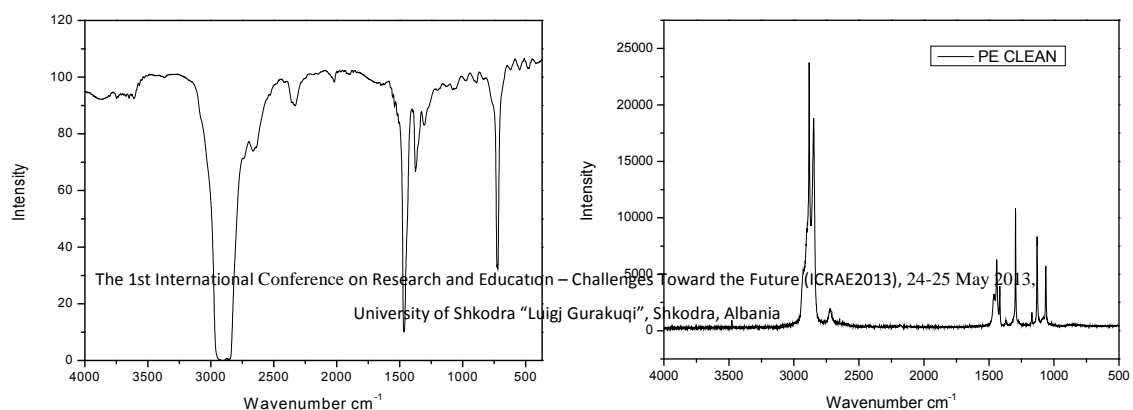


Figure 1: FT-IR and Raman spectra of clean LDPE

In FT-IR spectrum can be distinguished the presence of polyethylene. Three groups of spectra peaks, respectively, for the wavelength 2916.5 , 2855.3cm^{-1} (CH_2 asymmetrical stretching) ; 1492.2 - 1466.1cm^{-1} (bending) and 749.5 - 723.33cm^{-1} (CH_2 rocking) resulting from the absorptions of C-H bonds of polyethylene in the infrared area (D.W. Mayo et al., 2004, 2001 G. Socrates, WW Daniels et al., 1938). As shown in Raman spectrum in Figure 1 far right identify polyethylene as the main material, showing also the peaks of non-polar bonds (1300 , 1061 and 1127cm^{-1}).

In the region of the C-H Raman spectra of polyethylene 2700 - 3000cm^{-1} (Peter Ladkin, 2011) are observed two predominant vibrations of the methyl group $>\text{CH}_2$, non-symmetric and symmetric stretch (two protons hit each of two carbon atoms in each repeating unit). Since polyethylene solidify in high degree of center-symmetric crystalline phase, it contains two molecular chains. By movement of protons that will interact, vibration energies will unfold and reveal additional peak in the infrared spectra and Raman. This is an additional complication due to the interaction between C-H bonds, and combinations deformations $>\text{CH}_2$ (1410 - 1480cm^{-1}). For vibrating of structural chain of polyethylene, twisting occurs at approximately 1300cm^{-1} and Raman spectra observed only. This is evident in the form of crystalline and amorphous structures expanded peak. Stretch of bonds $>\text{C}-\text{C}<$ divided and displayed in two areas at wavelength 1061 and 1127cm^{-1} and differs only in Raman spectra. Raman spectra, just as well as infrared spectra, showed a weak peak at approximately wavelength 1375cm^{-1} attributed to the way the recent overlapping methyl groups even though the numbers are very small. This feature is very important in cases where groups of finite control important properties of materials.

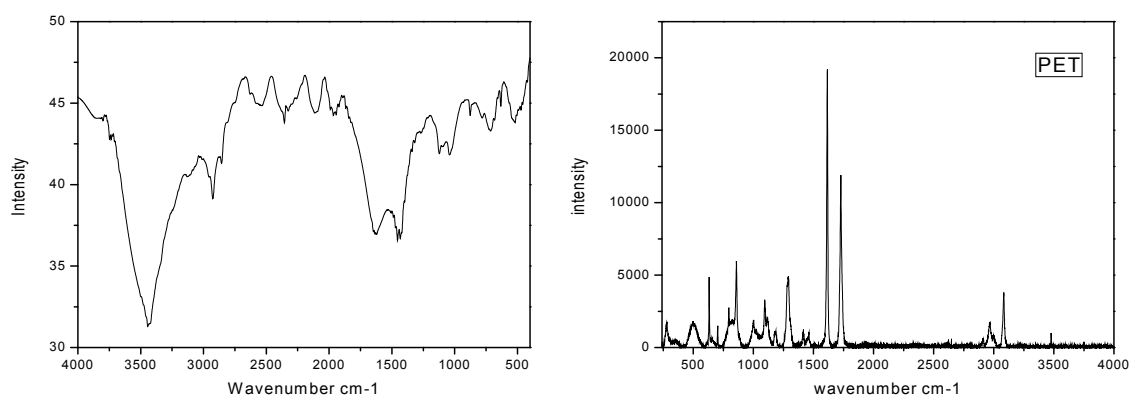


Figure 2: FT-IR and Raman spectra of clean PET

Figure 2 shows FT-IR and Raman spectra for polyethylene terephthalate PET. Wavenumber peak at 1730 cm^{-1} corresponds to C = O stretching bonds (ester), and wavenumber peak at 1615 cm^{-1} refers to the aromatic ring to form 8a vibration. (Peter R. Griffiths et al., 1995). Peak at the wavelength of 1295 cm^{-1} refer to C (O)-O asymmetric stretching. Asymmetric stretching O-C- C and stretching of ethylene glycol C-C bonds shown in peak at 1119 cm^{-1} wavenumber. At wavenumber 1096 cm^{-1} influence also the C-C rings. Wavenumber peak at 857 cm^{-1} refers to C-C ring and the wavenumber peak at 626 cm^{-1} refers to the vibration form 8b of the aromatic ring.

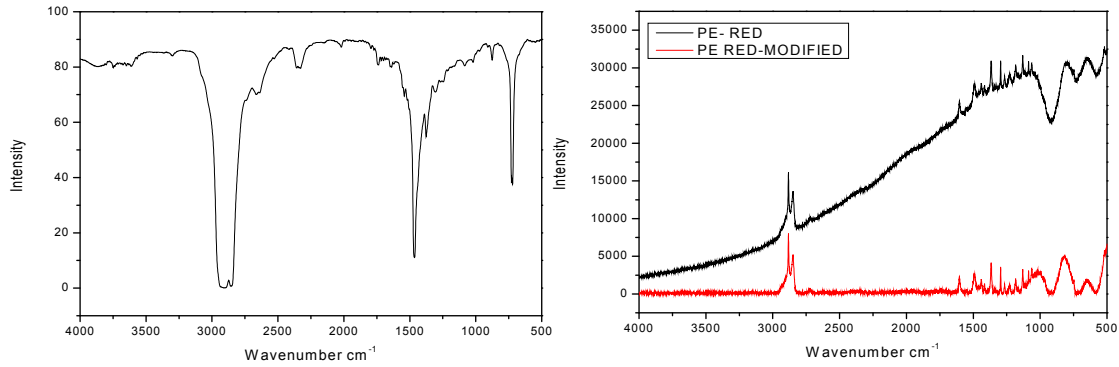


Figure 3: FT-IR and Raman spectra of red recycled LDPE

In FT-IR spectra can be identified exactly LDPE. In this Raman spectrum is shown the peak of LDPE, the appearance of others peaks besides those of LDPE and the movement of the background of the spectrum. All these indicate the presence of additives in LDPE structure and its recycling.

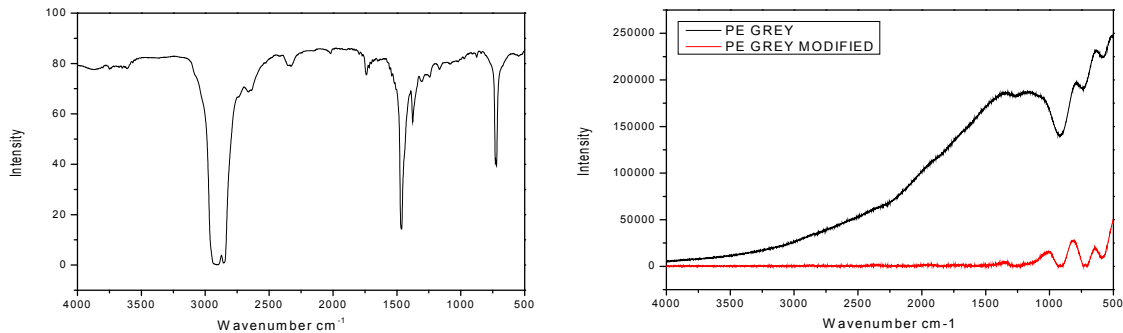


Figure 4: FT-IR and Raman spectra of gray recycled LDPE

In FT-IR spectra LDPE can be identified exactly, although recycled and with the presence additive in structure. In the case of gray recycled LDPE have no information from the Raman spectra due to the high fluorescence, due to the presence of additives in large quantities and high degree of recycling.

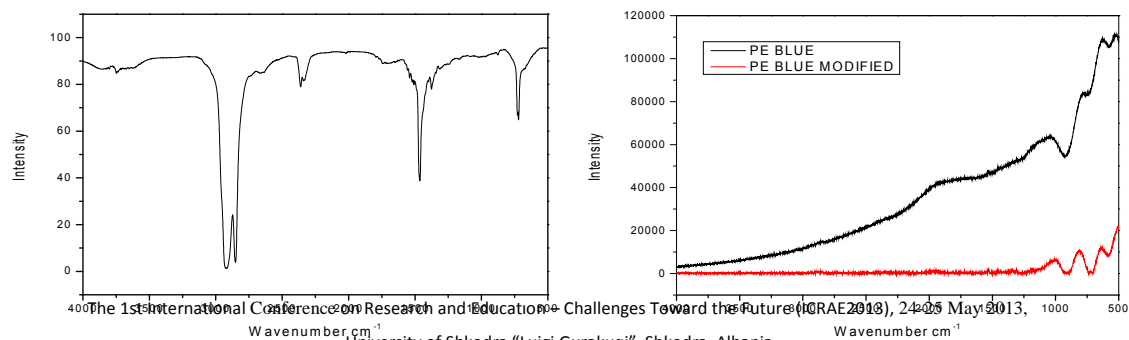


Figure 5: FT-IR and Raman spectra of blue recycled LDPE

Even in the case of blue recycled LDPE we correctly identify from the FT-IR spectra the main polymer and non-receipt of information from the Raman spectra due to the presence of additives and its recycling.

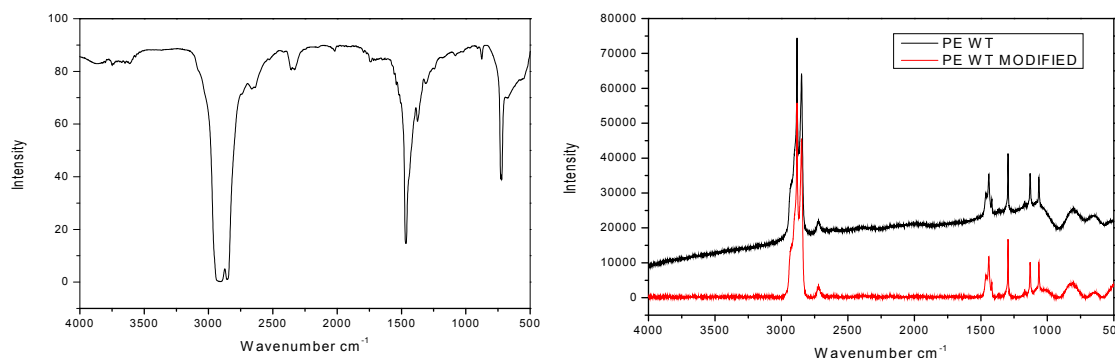


Figure 6: FT-IR and Raman spectra of white transparent recycled LDPE

In the spectra of Figure 6 are shown the characteristic peaks of LDPE. We can also observe other peaks in lower intensity that confirm the presence of additives. Background also has an upward displacement.

CONCLUSIONS

Using vibration Spectroscopic methods, FT-IR and Raman, were studied clean and recycled plastic materials LDPE and PET. FT-IR spectroscopy is more efficient in their identification, even when they have a high content of additive and have a high degree of recycling. While Raman spectroscopy is more effective in determining the presence of additives and identification of recycling, and when their high presence. In many cases, because of the high fluorescence, we have information loss from Raman spectra. In such cases required laser source with higher intensity. For more accurate analysis of the required additives other instrumental methods as GC, NMR or SEM-EDX.

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