ESTIMATION OF POLYPROPYLENE DEGRADATION DURING RECYCLING PROCESS BY USING VIBRATION SPECTROSCOPY METHODS

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ABSTRACT

The purpose of this work was the study of degradation of polypropylene (PP) during recycling process using vibration spectroscopic methods (FT-IR and Raman) and the possibility of estimation the grade of its degradation. Polypropylene, as one of the main ingredients of plastic materials, has found an extended use and application. The large amount used have generated large quantities of solid waste as well, which because of their high persistence are characterized of a very low degradation rate in the environment. So it would be of a great interest regarding environmental protection and raw materials saving at the same time, to find and optimize the technological parameters to increase its recycling rate. This paper aims just at this topic, not only optimize the recycling process but even studying the eventual structural changes by using contemporary instrumental analysis as an indispensable and reliable tool in performing such studies. As part of thermoplastics polymers, polypropylene can easily be recycled mechanically. As mechanical recycling method was used an industrial extruder with four temperature controller sections at a capacity about 2 kg per cycle. The grinding of polypropylene was done by using a knife plastic grinder. For obtaining FT-IR and Raman Spectra 20 mg polymer pellets were formed. The instruments used were Infrared Spectrometer with Fourier Transformation - Perkin Elmer GX1 and Raman Micro spectrometer – Rama Scope Renishaw RM1000. From the spectra analysis and data processing, the characteristic vibration peaks of chemical bonds of polypropylene were identified, and quantified as well based on the changes in the intensities of vibration peaks and the displacement of spectra background as a result of polypropylene degradation. After each recycling cycle the surface of polypropylene pellets was investigated by using optical microscopy method for the identification of any foreign element in polypropylene structure. Results obtained showed that this synthetic material offers good qualities even after considerable recycling cycles thus extending the number of materials highly recycled.

Keywords: Mechanical Recycling, Polypropylene, FT-IR and Raman Spectroscopy, Optical Microscopy

INTRODUCTION

The increase in use of plastic materials during recent decades has caused many environmental problems. Plastic waste, due to very slow degradation process in environmental conditions, are an actual problem for every society. A more efficient management is mandatory, but this requires the collaboration among the individuals and the local and central governments. Moreover this is a great challenge also for the chemical industry. There are three main pillars of their management: deposition in landfills, energy recovery and recycling. EU Directives require the reduction of the plastic wastes deposited in landfills and the increase of those recycled and used for energy recovery (EU 2013).

The global production of plastic materials in 2012 is 288 million tones, where in Europe their production is 57 million tones. China is the main producer of plastic materials and accounts for 23,9% of global production. In Europe, due to the directives, can be observed a slight decline of 2,5% in their production in 2012. Besides, there exists also many large differences related to their consumption, where in developed European countries there is a decline of 3%, while in the Central-Eastern Europe an increase of 0,6%. They are mainly used in packaging, constructions and buildings. Furthermore they are also used in automobiles, agriculture, in electricity filed electronics etc. Most common materials used are polyethylene, polypropylene, polystyrene, polyvinyl chloride etc. Polypropylene, which is studied in our experiment, accounts for 18,8% of the European market of plastic materials (Plastic Europe 2013).

Polypropylene is a very versatile material. It offers a great combination of properties such as lightweight, strong, high heat resistance, as well as stiffness and flexural retention. Among these and many other great properties, polypropylene is easily fabricated. Polypropylene can be subjected to a wide range of fabrication methods and applications. The common uses of these different polypropylene forms, broke down into percentages, is 26.5% packaging, 15.6% fabrics, 13.9% carpets & rugs, 11.0% housewares, 9.3% motor vehicles, and 23.7% other (J.Spaniol *et al*, 2007).

The consumption needs of plastic materials in EU 27+N+CH reached 45,9 million tones. 25,2 million tones of plastics ended up in the waste stream in 2012. From this quantity 26,3% was recycled. 35,6% was used for energy recovery, while the rest was deposited in landfills.

In Albania, a research conducted by IFC estimates that the composition of Municipal Solid Waste is as follows: 7% Metallic Scrap, Paper & Cardboard 17%, 10.5% Plastic, Glass 4.5%, the rest are other solid materials. From approximately 40.756 tones / year of solid plastic waste is estimated that approximately 11% of them are recycled (IFC 2006).

The low recycled quantity is related to the inefficient management system. The recycling industry imports large quantities of plastic waste, while the majority of plastic waste in Albania is deposited in landfills or is left to degrade in open environment. The local bodies and different organizations have carried out many initiatives for its collection, selection and the separation for recycling, but are still in the initial stage.

Mechanical Recycling is a method by which waste materials are recycled into “new” (secondary) raw materials without changing the basic structure of the material. It is also known as material recycling, material recovery or, related to plastics, back-to-plastics recycling (EUROPEAN BIOPLASTIC 2010) Post consumer plastic waste can be a very inhomogeneous and potentially contaminated waste fraction. It can consist of a huge range of material types, the shape and size of the material ranges widely, and in many cases the input material is composed of different material types. Besides these problems, related to the preliminary stages of plastic waste preparation for recycling, during the mechanical recycling process plastic materials lose some of their properties due to oxidation processes in presence of air (Javaid H. Khan *et al* 2003). Their reclamation is mainly carried out with the addition of additives in the structure of plastic materials, thus ensuring desired properties (J. C. J. Bart 2005).

The aim of our experiment was the study of degradation of polypropylene with the methods of vibration spectroscopy during mechanical recycling with extrusion method. During four consecutive recycling stages used, additives were added in the structure of PP.

MATERIALS AND METHODS

As raw material was used polypropylene industrially clean. Initially, industrially clean polypropylene was identified with infrared vibration spectroscopy method with Fourier transformation FT-IR and Raman. The FT-IR instrument that was used was the Perkin-Elmer spectrometer GX1, equipped with Spectrum spectra processing software. To further study of the chemical structure of polypropylene was used Raman spectroscopy equipped with an electronic microscope and the corresponding software. The instrument used was the micro Raman spectrometer - Renishaw RM1000 Rama Scope in the wavelength of laser radiation at 633nm (red), optical microscope equipped with Leica DMLM. Polymeric materials were analyzed in the medium infrared frequencies from 4000-400cm^{-1}. After, melt flow index was determined, which affects the processing conditions in extruder. Melt flow index was determined with RayRAN 6MPA Series instrument. The measurements were performed according to ASTM D 1238 standard. The temperature used for polyethylene was 230^{0}C and the weight applied was 2.16 kg. The MFI value affects the temperature and the processing velocity. As recycling method was used a single screw industrial extruder with a capacity approximately 2kg. Extruder had 4 temperature control zones as shown in figure 1. The single screw velocity was determined to the minimum 18 rpm.

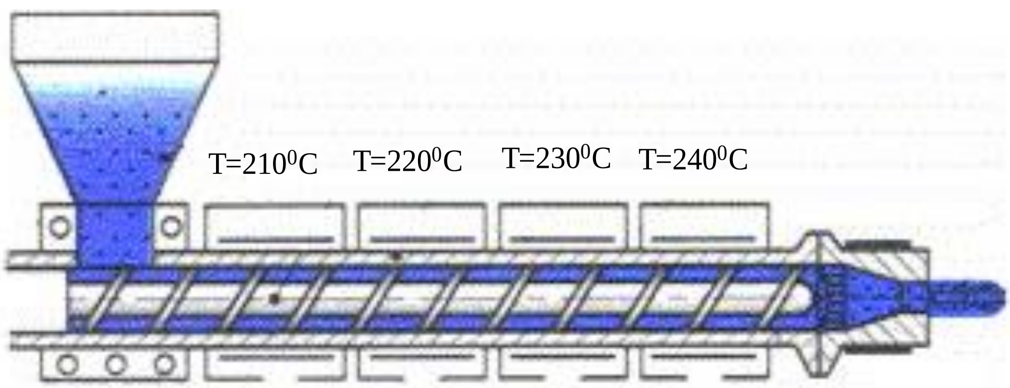


Figure 1: *Temperature control in extruder*

After each recycling cycle were derived polymeric rods with diameter 4-6mm. These rods were left to grow cool in the environmental temperature. After they were grinded with a knife plastic grinder. The ground material was recycled again. 4 recycling stages were applied in this way. After each recycling cycle ground material was taken with a Perkin Elmer hydraulic press at the temperature 180 ^{0}C and 20mg polymeric pellets with 13mm diameter were formed (Achilias *et al* 2007). The study of degradation with FT-IR and Raman methods was carried out from specters derived by those pellets. Furthermore 6mm rods after each stage were taken, which after being polished, were cleaned and were studied by the optical microscopy method. Polarized microscope XJP 300 with the TS View Version 1.0.0.1 program and Sony TCC-8.1 camera were used. Micro photos were taken with reflection and polarization in 0 degree angle for each clean and recycled sample.

RESULTS AND DISCUSSION

In figure 2 are shown FT-IR and Raman spectra for industrially clean polypropylene. From the peaks analysis which is also represented below is made the correct identification with both methods of vibration spectroscopy.

The addition of a methyl side group on every other carbon atom in polyethylene gives us polypropylene and quickly complicates the infrared spectrum. In addition to the methylene, we now have methyl and methine groups present. The methyl peaks appear at 2,962/2,952 (split peak), 2,868 and 1,377 [cm.sup.-1]. A methyl deformation is also overlapped with the methylene deformation, and this peak has shifted slightly to 1,458 [cm.sup.-1]. The methine peaks are weak and of no analytical value (D.W. Mayo *et al*, 2004)

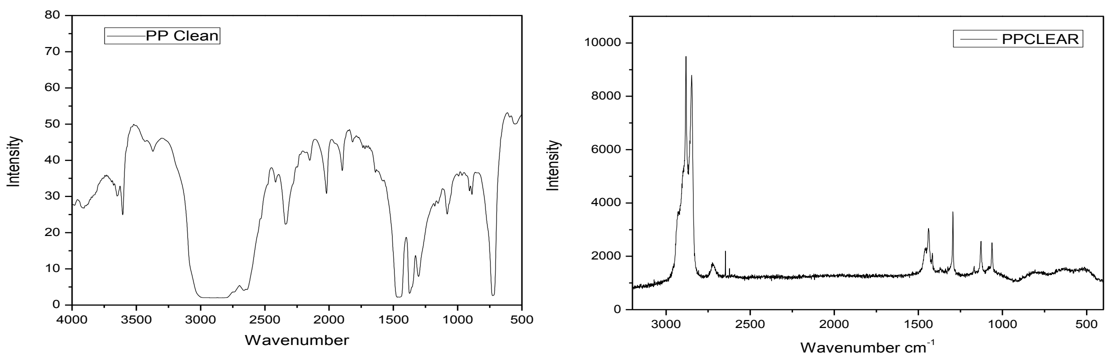


Figure 2 *Representation of FT-IR and Raman spectra of clean Polypropylene*

As observed also from the figure Raman specter show the peaks of vibrations of non polar C-C linkages. In table 1 are given IR characteristics vibration frequencies of polypropylene (James E. Mark 1999).

Table 1: IR characteristic frequencies of propylene

IR (characteristic absorption frequencies) cm-1	CH_3 , CH_2 , CH stretching	2956 (s), 2951 (s), 2925 (sh), 2907 (sh), 2880 (s), 2868 (s), 2843 (s)
	CH_3 asymmetric bending, CH_2 bending	1459 (sh), 1454 (s)
	Various CH_3 , CH_2 , and CH bending, wagging, twisting, C±C stretching	1377 (s), 1359 (m), 1329 (w), 1305 (w), 1297 (w), 1257 (w), 1219 (w)
	Various CH_3 , CH_2 , and CH bending, wagging, twisting, and rocking, C-C stretching	1167 (s), 1153 (sh), 997 (s), 973 (s), 841 (s), 809 (m)

The melt flow index was determined in 25g/10min, according to ASTM 1238 Standard. This value guided us in deciding the temperatures in extruder respectively from 210-240^{0}C. The recycling process in these conditions did not display any problem.

FT-IR and Raman specters, derived from formed pellets with material from each recycling cycle are presented in figures 3 and 4.

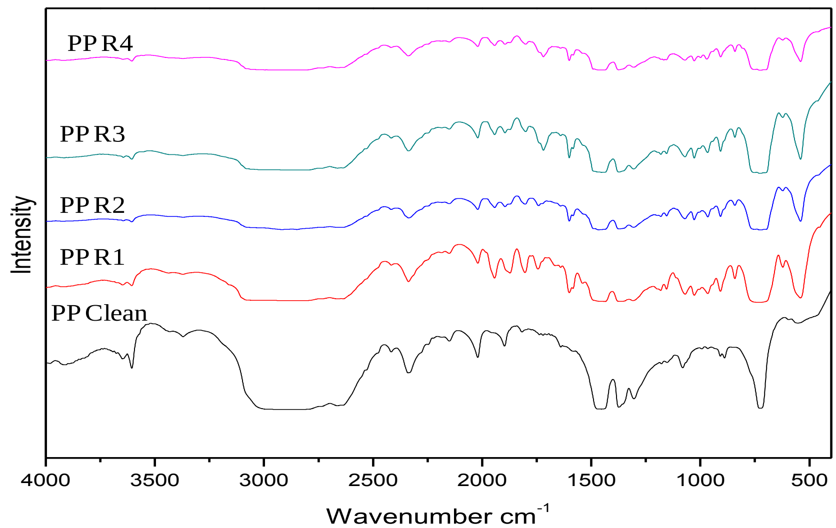


Figure 3 *Representation of all FT-IR spectra of Polypropylene*

Form the analysis of spectra polypropylene is identified as raw material. Respective peaks of polypropylene show the same vibration frequences of molecular bonds, with some changes in their intensity. The reduction of peaks intensity is an indicative factor of polypropylene degradation. Although the quantitative determination of degradation is difficult to be carried out with infrared spectroscopy.

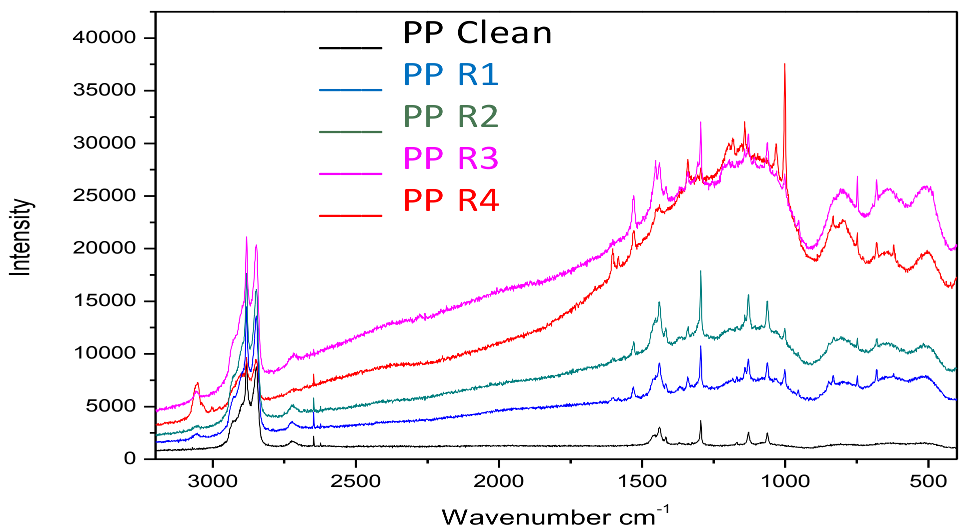
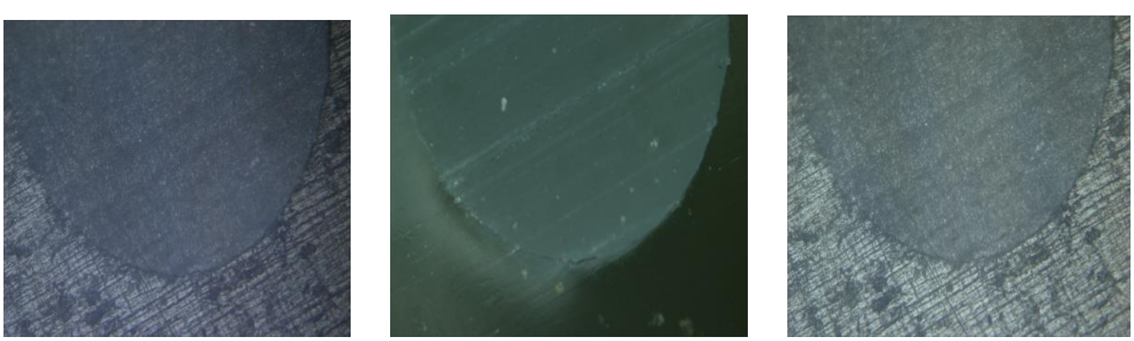


Figure 4 *Representation of all Raman spectra of Polypropylene*

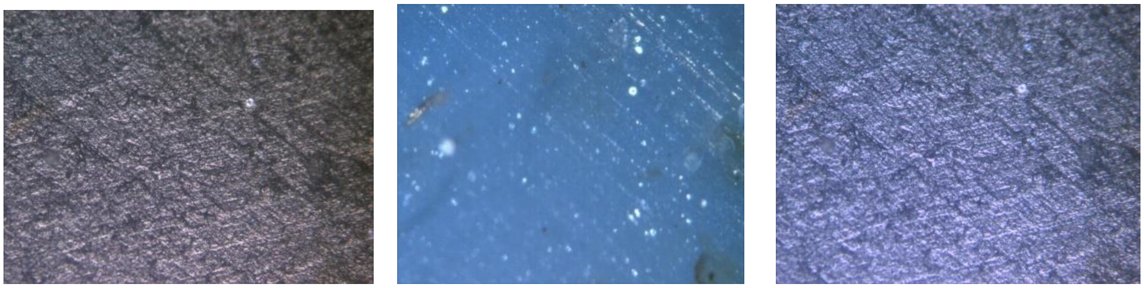
Raman spectra gives a clearer idea of polypropylene degradation during recycling process. In this way, the reduction of peaks intensity and upward displacement of backgrounds are indicative sings of its degradation. In the fourth stage a small visible reduction in the peaks intensity of PP is observed. Background displacement in a lower scale than that of third stage can be explained with the peaks low intensity, thus loosing the information as a result of degradation. Anyway, complementary explanation may be given based on the initial intensity of specters where can be observed (if we count on this occurence) that the background also in this case is displaced upward for the upcoming stage. In other stages one can observe a regular and gradual displacement of backgrounds in function of recycling stages.

Besides the analysis with FT-IR and Raman spectra was also studied the structure with optical microscopy. In the following pictures are shown micro-images for clean and recycled polypropylene after the fourth stage.



a) b) c)

Polypropylene-4th recycling stage



a) b) c)

Figure 5 *Representation of clean and recycled polypropylene in fourth stage in microscope view a) with reflecting light b) with polarized light and intercrossed Nikolete c) with polarized light with paralel Nikolet.*

In the figures above are shown optical images of recycled and clean polypropylene. Refering to the images above one can observe the display of white marks in small quantities for each stage (also for clean PP), which proves the presence of foreign elements in the structure of polypropylene, that from the color are identified as minerals. Anyway, we do not see the presence of any high intensity peak in FT-IR and Raman spectra, which shows that their presence is in low quantities.

CONCLUSION

The method of infrared spectroscopy with Fourier Transformation makes the correct identification of polypropylene possible, also in the case when it is recycled. Determination of degradation scale with this method presents difficulties, related mainly with the conditions of pellets formation. Raman method provides a more accurate information concerning degradation scale of PP, because of upward displacement of backgrounds and reduction of vibration peaks intensity. From the analysis with the optical microscopy is observed the presence of foreign elements in the structure of polypropylene, also in the case of industrially clean polypropylene.

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