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Morphological and chemical study of recycled plastic materials by using scanning electron microscopy and energy dispersive analysis

The purpose of our research is the study of surface structures and chemistry of plastic recyclable materials. It comprises the microscopic structure description of polymers, separation of component phases and determination of chemical elements of additives that we use. For this purpose we have used scanning electronic microscope (SEM) JEOL6380LV equipped with the system of energy dispersion spectroscopy (EDS). The plastic materials were provided by companies operating in the Albanian market. They are used in the fabrication of plastic bags, of packaging materials for transportation of products, and also, as construction materials. So far, we have studied 6 different polyethylene samples, one industrially clean PE sample and 5 other recyclable PE samples. Plastic packaging materials are considered an important source of environmental waste mainly due to their large friction by waste in the waste stream. We used SEM to study the microstructure of our samples. EDX analysis was used to investigate additives in the recyclable materials. Raw material of polyethylene was provided in granular shape which we transformed to plastic pellets with a smooth surface. Pellets were formed using a specific temperature-time plan during molding. Uniform pellets with smooth surfaces were formed when the polymers passed the viscoelastic state, e.g. a temperature of 180^{o}C, higher than the melting temperature of polyethylene and lower than the temperature that damages many plastic materials and their dyers. Cleaning and drying of the pellet surfaces was a key parameter in order to acquire images of high quality and resolution.

***Key words:** plastic materials, scanning electron microscope SEM, X-ray energy dispersive system EDS, plastic additives.*

INTRODUCTION

During the last few decades the use of plastic materials rapidly increased. Their use in different fields of industry is due to their specific properties. Despite several advantages, these plastic materials have also some disadvantages, which are mainly related to the environment. Their slow degradation from one side and the scarce of natural resources are the most important factors that have motivated researchers to find alternative methods of treatment. One method that is commonly used is recycling, which is defined as the complex set of processes that require the treatment of the plastic materials before and during the recycling process, as many properties are lost[1]. Recycling of plastics materials, such as of the plastic bags for packaging, is an important sector of polymer industry due to the large amount of their everyday use. Additives play a key role during the recycling process; therefore it is important to identify the type and the quantity of those materials as a function of the required properties [2].

There are several types of additives influencing plastic materials, such as modifiers, chargers, aromatics, lubricants, pigments, stabilizers, and additives for faster biodegradation of plastic materials. The additives make plastic materials easier to work with.

Scanning Electron Microscopy is an important tool for polymer characterization, since it is extensively used to study fracture and failure mechanics, particle sizes and shapes, filler orientation and dispersion in polymer matrices [3, 4].

MATERIALS

Industrially clean polyethylene granules are used to fabricate plastic bags for transportation purposes. Recycled polyethylene granules, are used to analyze four different types of recycled polyethylene which are extensively used in packaging. They are distinguished by color in the respective PE colors: PE red, PE blue, PE grey, and PE semi-transparent. The fifth sample was white and it is used to fabricate distribution boxes in electrical installations. Table 1 lists the plastic materials investigated in this study. Their usual color, the related products and their uses are also given.

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Table 1 **-** *List of the analyzed PE samples, described for their color, form and uses*

No	Sample	Color	Form	Uses
1	PE industrially clean	White	Plastic bags	Packaging
2	PE recycled	Red	Plastic bags	Packaging
3	PE recycled	Grey	Plastic bags	Packaging
4	PE recycled	Blue	Plastic bags	Packaging
5	PE recycled	White –semi transparent	Plastic bags	Packaging
6	PE recycled	White- opaque	Distribution box	Electrical installation

METHODS

For the morphological study of the surface of the plastic materials a SEM JEOL6380LV scanning electron microscope was used (National Technical University of Athens, Greece). High resolution images were acquired, either in the secondary electron mode (SEM) for topography, or the backscattered electron mode (BSE) to reveal possible compositional variations of additives.

This SEM is also equipped with an X-ray microanalysis system (EDS of Oxford Instruments). EDS stands for "Energy Dispersive Spectroscopy" and it is based on X-rays emitted from a sample during electron irradiation[5]. With this instrument chemical analysis, either qualitative or quantitative, can be acquired. In our case, only qualitative analyses are given because additives are impregnated in the polymeric material and mixed analyses cannot be avoided.

In order to perform the morphologic and chemical analysis of PE granules, plastics were formed in thin pellets. The device used for this purpose was a hydraulic press (Perkin Elmer). Pellets were formed in vacuum and at a temperature of 20°C over the melting temperature of PE[6], similarly to the conditions suggested in the literature (melting temperature of PE~120°C)[7]. The temperature used was 180°C. Processing usually results in temperature well above 180°C, which without the addition of heat stabilizers would result in the plastic material literally falling apart [8]. The processing of plastic materials in this temperature can unfortunately sometimes spoil the color and weaken or embrittle the plastic. Due to its viscoelastic state, the pressure applied on the PE pellets was lower than one ton for one minute. The quantity of polyethylene used to form the pellets was in the range of 0.02-0.03gr. Thickness of pellets changed depending on the quantity of PE used but during our research we observed that this factor did not influence our work, as we study the surface of pellets with a diameter 13 mm. Before the analysis, the samples were cleaned with adequate solvent and were completely dried.

RESULTS

In the following set pictures (Figures 1 to 7) micrographs are shown (left), combined with their qualitative chemical analysis (energy dispersive X-ray spectra). As already noted, quantitative analyses are of no interest at this stage and in many cases difficult due to the preparation procedures of the samples, which would result in mixed analyses. Consequently, the provided chemical analyses are shown in the form of spectra. The provided images are shadow backscatter electron images to reveal compositional variations along with some topographical information. The spectra are used to show elements with atomic number higher than twelve, that is, from carbon and higher.

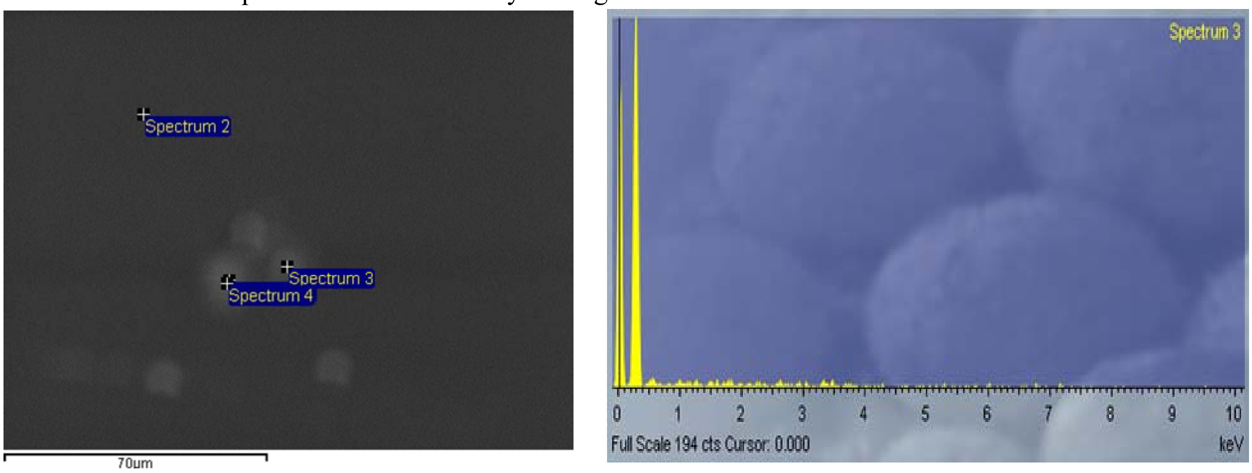

Figure 1 - (left) Micrograph of clean industrial polyethylene, (right) X-ray spectrum of PE, which, apart from carbon (second peak on the left), no other heavier elements are observed.

In Figure 1, stains with a lighter color are easily noticed in the BSE image on the surface of the pellet. These stains witness the presence of foreign elements in the matrix of polyethylene. Chemical analysis over a number of such stains reveals minor quantities of other elements, such as calcium, sodium, oxygen, silicon, iron, chlorine and potassium(Figure 2).

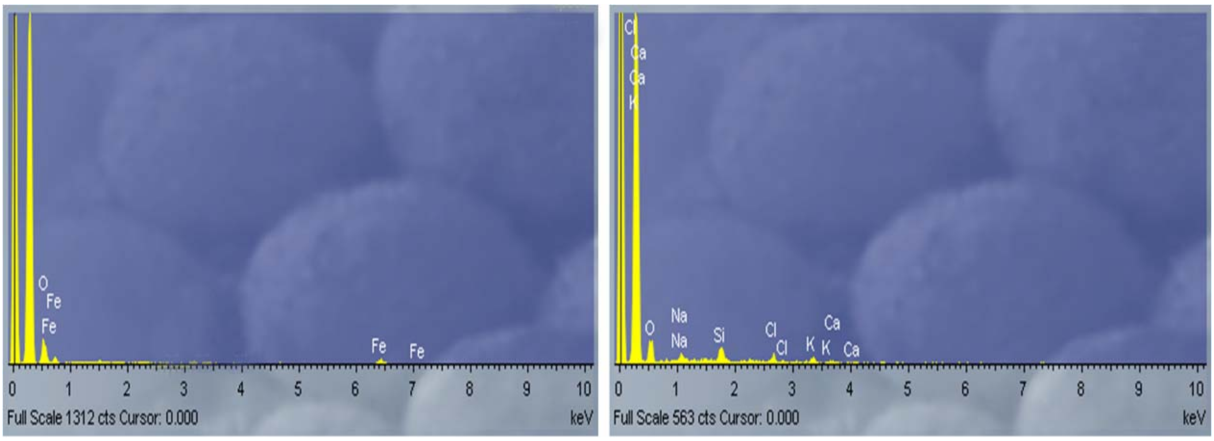

Figure 2 - X-ray spectrums that show the presence of foreign materials in the matrix of industrially clean polyethylene

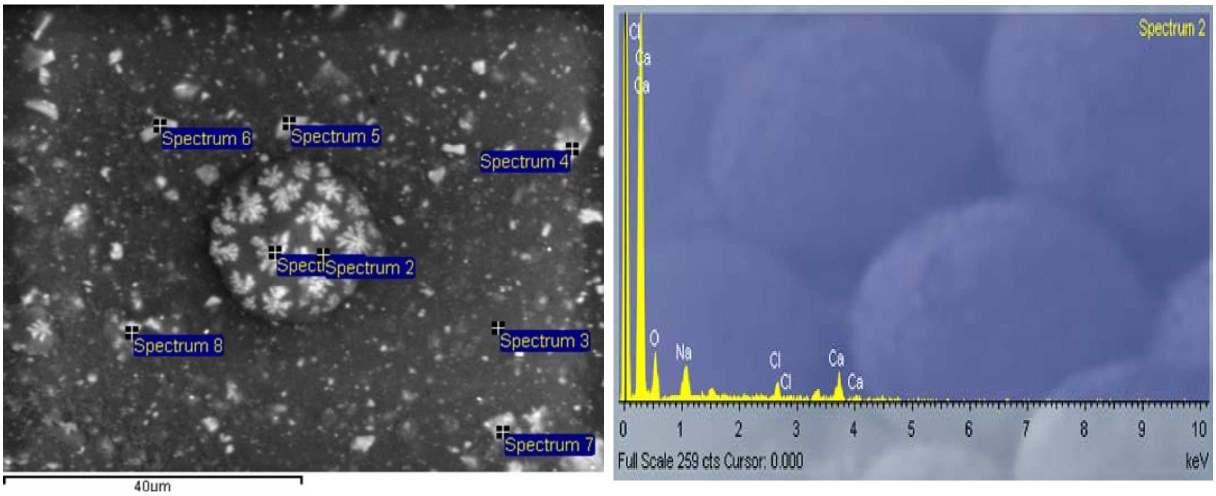

Figure 3 - (left) Micrograph of recycled red polyethylene, (right) X-ray spectrum of recycled red polyethylene.

In figure 3, the BSE image shows the presence of many foreign elements inside the matrix of the red recyclable polyethylene. Especially in the middle of the picture a volume of dissolved and quickly quenched plastic material crystallized dendrites of additive materials. From the spectrum analysis in the PE structure we can identify the presence of chemical elements such as calcium, sodium and oxygen. Thus, the main additives are sodium chloride (NaCl) and calcium carbonate ($CaCO_3$). These substances are frequently used as additives in plastic materials. Calcium carbonate is one of the most used fillers in polyolefin [9]. Producers of commodity HDPE bottles and packaging rely on these fillers for minimizing raw resin costs. Fine particles of $CaCO_3$ loaded at 10%-60% and using the proper surface treatment increase stiffness, hardness and dimensional stability, while normally lowering tensile and impact strength properties, depending on the grade of $CaCO_3$ and the coating. Treating carbonate calcium particles allows maximum dispersion of the filler, easier processing of highly fillers compounds and higher impact strengths. In textiles and dyeing, sodium chloride is used as a brine rinse to separate organic contaminants, to promote "salting out" of dyestuff precipitates, and to blend with concentrated dyes to standardize them. One of its main roles is to provide the positive ion charge to promote the absorption of negatively charged ions of dyes [10].

From the SEM images we can notice the dense distribution of additives in the whole surface of the pellet. In others spectrum analyses it is also observed that other foreign elements such as aluminum are present in small amounts.

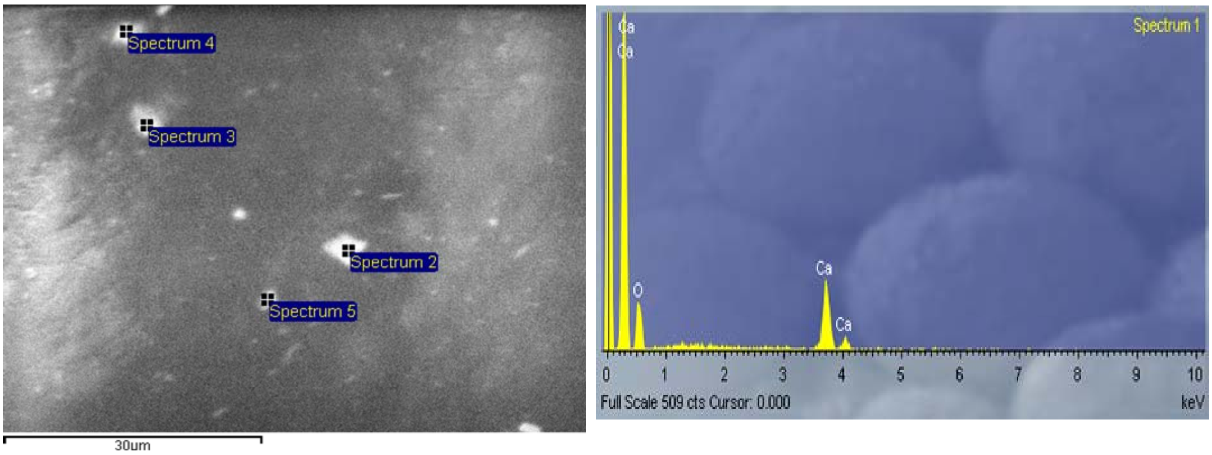

Figure 4 - (left) Micrograph of recycled grey polyethylene, (right) X-ray spectrum of recycled grey polyethylene.

The SEM image (Figure 4) shows the spread of additives in grey polyethylene. As we can see from the X-ray spectrum, calcium and oxygen are identified. Thus we can understand that in the bags of grey polyethylene $CaCO_3$ is used as additive and affects the properties of polyethylene itself. More spectrum analyses additionally show the presence of elements such as silicon and aluminum in considerable quantities. SiO_2 is used mainly as an additive in plastic materials and it has a low coefficient of thermal expansion and high stiffness. However silica particles are not flake and typically have low aspect ratio [9]. Silicon is also analyzed, present with calcium in the form of wollastonite mineral with a chemical formula $CaSiO_3$. This mineral is often used in loadings of 10% - 20% as reinforcing filler, which increases the polyolefin compound's tensile and flexural strength, and offers higher-dimensional stability and less mold shrinkage than talc or calcium carbonate compounds [9].

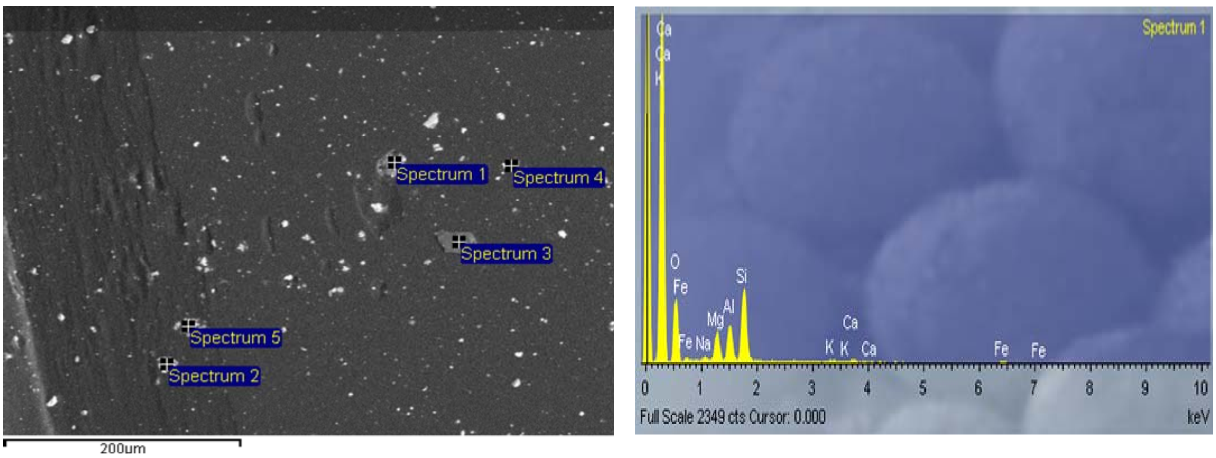

Figure 5 - (left) Micrograph of recycled blue polyethylene, (right) X-ray spectrum of recycled blue polyethylene.

In figure 5 the microstructure of blue recyclable polyethylene is shown. We can see the spread of additives in the whole structure of polyethylene (bright fragments). From the X-ray spectrum we can identify the presence of many chemical elements such as: silicon, aluminum, magnesium, iron, calcium, potassium and sodium. From the chemical analysis we can conclude that beside additives such as NaCl, $CaCO_3$ and $CaSiO_3$, is also used the talc mineral with a chemical formula $Mg_3Si_4O_{10}(OH)_2$ and magnetite Fe_3O_4, which are widely used as additives in plastic materials. Talc is the other most usable mineral as a filler of plastic materials. Relatively soft and slippery, talc has similar effects as calcium carbonate in polyolefin matrix, although talc typically increases modulus and reduces impact strength. Its mechanical effects are enhanced by its plate-like particles of high aspect ratio. Talc greatly affects certain properties in polyethylene and polypropylene. In PE films it provides anti-blocking properties. Magnetite adds density and magnetic properties of the resin for sound dampening or anti-static/low resistively applications. The filler also absorbs microwave energy and resists visible scratches. From the X-ray spectrum analysis we can also notice other elements in low quantities that do not have any influence on the properties of polyethylene, such as sulfur, potassium and sodium. The presence of minerals is the PE structures are related also to the presence of metal hydrated silicates (mica) with plate-like particles having aspect ratios of 50-100. As a platy filler, mica provides similar enhancements as talc [9]. Metal fillers such as aluminum flakes slightly reduce tensile strength. They are reported to reduce elongation substantially, by 20%-80%. Also the BSE micrograph shows structural defects during the formation of pellet that result to non-flat surfaces.

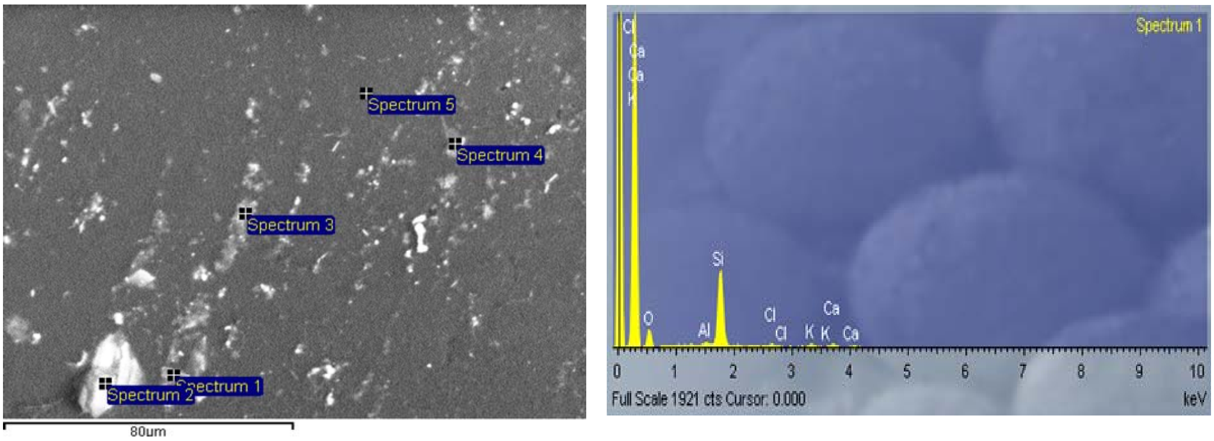

Figure 6 - (left) Micrograph of recycled white semi-transparent PE, (right) X-ray spectrum of recycled white semi-transparent PE.

BSE image in figure 6 shows a clear view of the spread of the additives inside the structure of polyethylene. EDX spectrum analysis identifies the presence of elements such as silicon, calcium, oxygen and in low quantities that of potassium, aluminum and chlorine. The presence of chlorine is possible from low quantity of PVC in polyethylene due to non effective separation of plastic materials. Detailed analyses on different areas of the sample's surface does not show the presence of any other phase. This proves the presence in a very low quantity of chlorine.

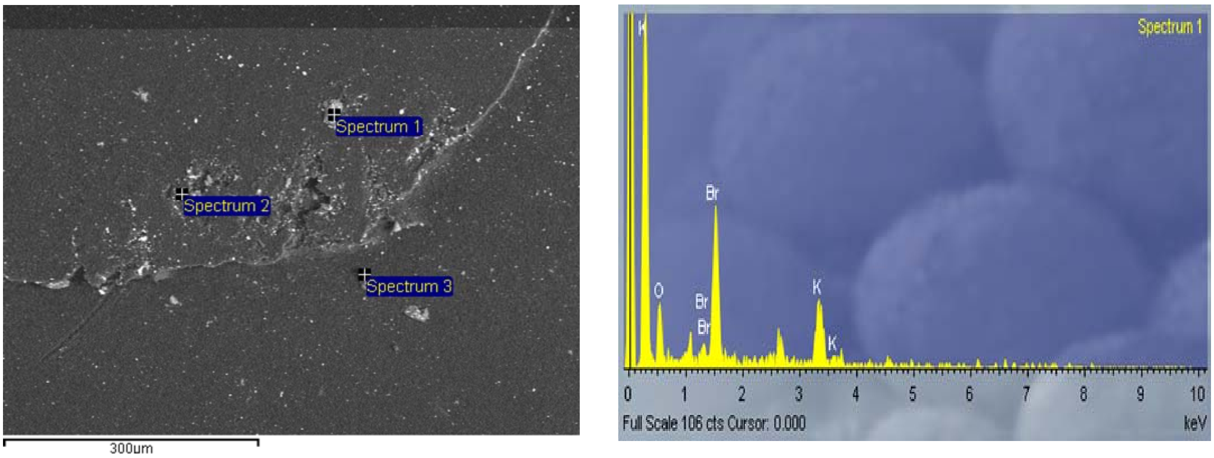

Figure 7 - (left) Micrograph of recycled white opaque PE, (right) X-ray spectrum of recycled white opaque PE.

In the BSE image of figure 7 besides the presence of fillers (high contrast, white grains), apparent are also the defects of the plastic film caused by the formation of the pellets from granules. From this figure we can reach conclusions about the influence of the time interval of the formation of pellets. Since the melting temperature has been the same for all the granules we can conclude that the residence time in this case was not sufficient for the recyclable polyethylene to pass in the viscoelastic state, where we could easily form pellets. From the EDX spectrum analyses we can notice the presence of elements such as potassium, bromine and oxygen. The white color of the reference pellet is possible thanks to the potassium bromide additive, which is a white crystalline powder. From the analysis of the other spectra there is a very low content of elements such as titanium, sulfur and chlorine. Titanium carbide is widely used in plastic materials because it can increase the abrasive resistance of polymers[11]. Using TiC as an additive, the plastic materials get lighter and we can work easily on them and at the same time have a higher corrosive resistance. The carbide of titanium particles can be injected easily in the matrix of polyethylene.

CONCLUSIONS

Using the scanning electron microscope (SEM) with EDS system, we studied the surface structure of polyethylene and identified the additives used in them. From the analysis of BSE images we highlighted the basic matrix of polyethylene. We did not observe any other polymeric matrix, which demonstrates a good pre-treatment process of recyclable plastic materials. In the industrially clean polyethylene we identified low quantities of some other chemical elements, which do not affect its use as packaging bags for transportation purposes. We easily observed the presence of additives in recyclable materials. Different shapes and sizes of particles of additives were spread on the whole surface (and therefore volume) of polyethylene.

Analyzing the EDX spectra, we identified the main additives. Thus, additives which influence the mechanical properties, such as calcium carbonate, talc, potassium chloride, silicon dioxide, magnetite, mica and wollastonite mineral, were easily identified in a qualitative way. In the polyethylene sample, which is used as a box in electrical installations, we identified the presence of additives as titanium carbide, which affect the abrasive properties of the plastic materials.

A lot of attention was focused on the influence of temperature and time in the formation process of pellets. The melting temperature was kept at least 20^0C above the melting temperature of clean polyethylene [6]. The additives that were used in plastic materials decreased in a low range the melting temperature of plastic materials. The influence of the melting time can be seen in figure 7 (on the left), where we can notice the boundaries of granules. So the polymeric chains did not have the sufficient time to pass the polyethylene in viscoelastic state. Also figure 5 shows the structural defects in the surface of polyethylene during the processing of pellet formation.

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IZVOD

MORFOLOŠKA I HEMIJSKA ANALIZA RECIKLIRANIH PLASTIČNIH MATERIJALA KORIŠĆENJEM SEM I EDS

Cilj istraživanja je proučavanje strukture površine i hemije plastičnih sekundarnih sirovina. Ovo istraživanje se sastoji od opisa mikroskopskih struktura polimera, razdvajanje komponenti faza i određivanje hemijskih slemenata koji se koriste kao aditivi. U tu svrhu je korišćen skenirajući elektronski mikroskop (SEM) JEOL6380LV opremljen sistemom disperzione spektroskopije (EDS). Plastične materije je obezbedila kompanija koja posluje na albanskom tržištu.Ovi materijali se koriste u izradi plastičnih kesa, ambalaže za prevoz proizvoda a, takođe, i kao građevinski materijali. Do sada je proučeno šest različitih uzoraka polietilena, jedan industrijski čist PE i pet uzoraka drugih recikliranih PE uzoraka. Plastične ambalaže se smatraju izvorom otpada u okolini, uglavnom zbog svojeg velikog trenja. Korišćen je SEM za proučavanje mikrostrukture navedenih uzoraka. EDS analiza je korišćena da bi se istražili aditivi u sekundarnim sirovinama.Sirovine polietilena su bile u obliku granula koje su transformisane u pelete sa glatkom površinom.Pelete su formirane livenjem pri određenoj temperaturi. Uniformne pelete sa glatkim površinama su formirane kada je polimer prošao određenu viskoznost, na primer, na temperaturi od 180^0C, koja je veća od temperature topljenja polietilena i niža od temperature koja šteti mnogim plastičnim materijalima. Čišćenje i sušenje površina pelete je ključni parametar radi dobijanja slike visokog kvaliteta i rezolucije.

Ključne reči: *plastični materijali, SEM,X-ray EDS, plastični aditivi*

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