Structure studding of recycling rubber materials through Infrared with ATR, DSC and Scanning electron Microscopy and energy dispersive analysis (SEM)

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Abstract: *Tires are complex objects that consist of many different parts, each with a specific formulation, and include natural or synthetic polymers, carbon black, steel, dispersed oils, dispersed oils, sulfur for the vulcanization or bonding process, organic additives and inorganic, and even glass fibers. Their investigation poses a difficulty in identifying them, due to their complex structure. In the Tire Recycling Industry we encounter the problem of quality control, which is difficult due to the lack of solubility of rubber particles, as well as the limited technical means of these industries. The study aimed to investigate the structure and composition of recycled tires, used in artificial turf / grass as fillers.*

*The study focused on the development of standard investigation methods using three instrumental and analytical techniques, as well as the study of morphological changes they have undergone during the recycling process and the impact of additives on them. The aim of this scientific search is studying the structure rubber these materials are recycled, that is one of the most important issues, especially in Albani. **T**hrough FT-IR **with ATR** Analysis, is a analysis technique that provides information about the chemical bonding or molecular structure of materials**,** Differential Calorimetry DSC and Scanning Electronic microscope (SEM) equipped with the system of dispersive of energy spectroscopy (EDS).*

Keywords*: Recycled rubber, FTIR-ATR, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy and energy dispersive analysis (SEM), Synthetic a artificial grass, heating and cooling*

1. Introduction

Polymeric materials have reached a vital position in all branches of science and technology. Because the development of new polymeric materials is expensive, polymers are often mixed to meet the industry need for high-performance materials. Natural rubber can be mixed with styrene-butadiene rubber (SBR) to get an improved performance. Every year, thousands of tires disappear in landfills and landfills, in EU countries today approximately one tire / year is thrown away for every inhabitant, they are a free source from which can be produced crushed tires [1-2-3]. This resilient material provides enhanced durability and safety. Recycling of tire scrap until the 1960s in the US can be taken as an example; about half of manufactured automobile tires were used for recycling and only during the production of tires were synthetic tires used and the tires could be used directly without any major processing. [4] Recycling of used tires was also encouraged by the fact that these materials were also expensive. The increasing use of synthetic rubber, however, reduced production costs and reduced the need for recycling. [5]

Rubber is produced from natural or synthetic sources. Natural gum is obtained from the milky white fluid called latex, found in many plants; synthetic tires are produced from unsaturated hydrocarbons. Recycled tire material, or "rubber crumb", is used as a component of many recreational areas, including artificial turf fields. These crumbs make up up to 90% (by weight) of the fields. Tire crumbs are approximately the size of coarse sand grains and are created from the shredding of used tires. Rubber particle materials are spread two to three inches thick over the terrain surface and packed between strips of green plastic used to simulate green grass [3]. Synthetic tires are classified into general purpose tires and special purpose tires.

Over 16 million of old tires are re-used as coated, i.e., where new tire is formed into an old tire. Tire recycling uses much less oil and other resources than were used to create a new tire. About 56 million tires are used in civil engineering projects such as road slabs and other engineering uses. Vulcanized rubber, like elastomer, is difficult to recycle. Therefore, there is a need to develop direct, rapid and accurate methods to evaluate the composition of such mixtures when the composition is not known. [6].

Eight different types of rubber particles were taken for the study from the fields with artificial grass, which are distinguished by their color and size. The study is to investigate the components of granular tire particles used in the field with artificial grass in Albania. Due to the content of additives in recycled tires, their identification by classical methods, such as flotation or incineration, is inaccurate. Thus, for the identification of crushed tires if they are recycled, the spectroscopic methods of vibration and Fourier transform: infrared (FT-IR with ATR) were initially used, as well as the study of the crystalline structure by means of thermal analysis, differential calorimetry by scanning (DSC). Study of microstructural defects and chemical content of additives by scanning electron microscopy, equipped with SEM-EDX power distribution system.

2. Materials

The present investigation involved eight granulated rubbers from different football fields being used as fillers in artificial grass football fields, received by Albanian and foreign market. Information about color, shape and size of the samples are reposted in Fig1

Fig :1 *Studying rubber sample*

3. Methods

The paper includes the description of the micrographic structure of the tires, the separation of the constituent phases and the determination of the chemical elements of the additives used. And determining if these rubber particles are from recycled wheels. Rubber itself is different from other polymeric materials, since it is a thermoset material has difficulty in recycling, this lies in the fact that to recycle it in a way similar to plastic often lead to undesirable results. One of the most important issues, not every tire can be recycled and, this poses a serious problem to investigate in proving that these are materials that come from recycled tires.

The first stage of the research involves the study of rubber gills by the method of vibrating infrared spectroscopy and the Fourier FTIR transformation equipped with the ATR system, a method that enables the analysis of thick surface samples without any prior preparation.

Sampling of samples was performed in the wavelength range from 4000-400 cm-1. The research of the structure was then carried out by the method of thermal analysis, by means of calorimetry with DSC scanning that will provide information about the composition in the rubber granules. Thermal analysis is an essential technique for measuring temperature or response depending on the time of physical and chemical changes that occur in materials. The second stage of the work is the research of the structure from the micrographic point of view of the granular tires, the separation of the component phases and the determination of the chemical elements of the additives used. For this purpose we used the electron scanning microscope (SEM).

The information obtained from the FT-IR-ATR spectra identified low-intensity rubber in all eight samples, while the determination of additives was difficult due to the overlap of peaks and their low intensity in the FT-IR-ATR spectrum. and due to the high fluorescence in the recycled materials in the spectra, which indicates the presence of fillers in them. Accurate identification of fillers indicates difficulty due to their low intensity.

Having encountered difficulties in determining the additives with the above method, then we applied two other methods for their determination. To determine the thermal properties, we use differential scan calorimetry (DSC). The temperature range chosen for rubber testing is from -80 0C to +200 0C with a hot heat step of 10 0C / min. The equipment used is the DSC 200 F3Maia rate (Customs laboratory) of 10 0C / min in a nitrogen photo environment.

The technique provides valuable information on softening temperatures (or Tg), melting temperatures, melting heat, percentage crystallinity and recrystallization (temperatures and heat) [8].

An SEM scanning electron microscope was used for the morphological study of the surface of rubber materials. High-resolution images were obtained, either in secondary electronic mode (SEM) for topography, or in diffuse electron mode (BSE) mode to detect possible component variation.

4. Results

In Fourier transform infrared spectroscopy FTIR-ATR, it is a useful method for the study of polymers when we do not know its structure. Using infrared spectroscopy we can determine if the rubber particles are rubber or any other polymer.

The analysis of the peaks of the FT-IR spectrum revealed the basic material of the tires, as well as the presence of some other peaks with low intensity due to the presence of foreign matter.

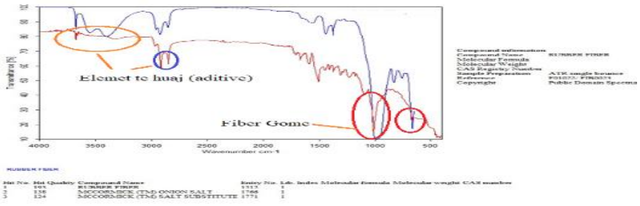


***Fig: 2** FT-IR spectra for G-1 rubber samples*

Fig 2 shows the presence of rubber as the base material was identified across the spectra. Groups of spectrum peaks in the wavelength range 2850 -3000 cm^{-1} resulting from the absorption of C-H3, C-H2 and C-H bonds during deformation. The group of peaks with wavelength 2300 - 2400 cm^{-1} is due to the nitrile group which seems to be present in all tested samples. In addition, the peak frequencies of the 1500-1600cm^{-1} wave number representing the carbon group and the 900-1000cm^{-1} wavelength representing the sulfoxide group are present in the tested samples. Different fillers in rubber can be the source of small changes in the wavelength of spectra. The greatest impact on fillers is the intensity of the peaks, as well as their doubling as shown in Fig 3. From the analysis of the FT-IR spectrum with ATR it is noticed the presence of a large number of curves those of the tires, also all the peaks have a low intensity from the base material, this is due to the large amount of fillers.

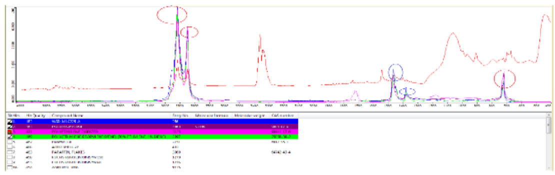


***Fig: 3** FT-IR spectra for G-1 and G-6 rubber samples*

During the research of rubber particles we concluded and we can say that FT-IR infrared spectroscopy with ATR gives us accurate information for the identification of recycled polymers, but it is not a good method for determining the recycling rate. This is also seen in Fig 4, which shows the FT-IR spectra with ATR for the eight tire samples. Differences in peak intensities for all samples, gives us an overlap from the content of additives in tires, this problematic initially requires a morphological analysis of the elements or substances found in the tire structures.

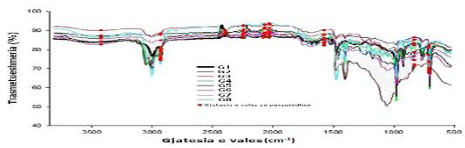


***Fig:4** FT-IR spectra for all samples*

The DSC results generated from the test are shown in Fig 5. Using the program it was possible to calculate the characteristics of each curve for the second heating and the second cooling. Curves measured from tire particles with heating speed 10˚C / min. This curve shows a glass transition transition occurring at 127 ˚C, an exothermic crystallization peak at about 102 ˚C, and an endothermic peak melting at about -40 ˚C. The results of the glass transition temperatures are very small between samples, which may be associated with limitations due to the interaction between the filler and the rubber matrix.

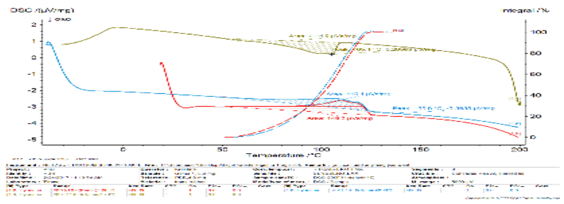
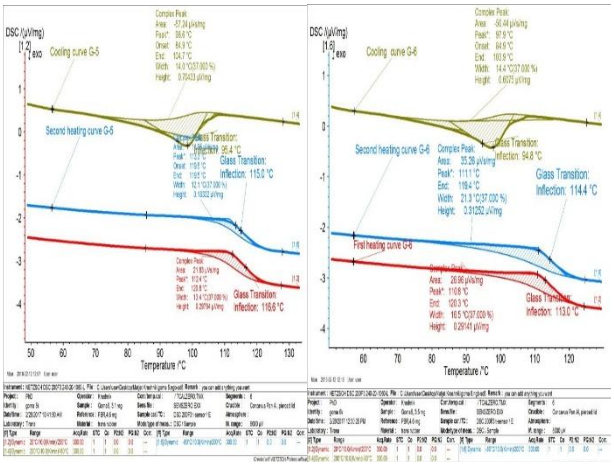


Figure. 5: *First, second DSC heating and cooling curves, for example G-1. (a), first, second DSC heating and cooling turns,*

For sample G-3 and G-4, the first and the second heating are almost identical, as the curves overlap on top of each other. The same behavior is noticed also on the samples G-5 and G-6, G-7 and G-8, as presented in the following figures.



. (a) (b)

Fig 6: *DSC curves of first, second heating and cooling down, for sample G-5. (a), DSC curves of first, second heating and cooling down, for sample G-6*

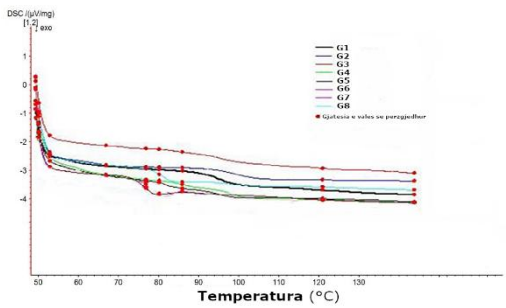


Fig:7 *DSC heating and cooling curves first, second, for all example||*

In the TG derivative (DTG) the rate of data analysis for weight loss is plotted against temperature or time. In a dynamic TGA, the temperature corresponding to the peak weight loss of a rubber derivative depends on the degree of temperature scanning, the average of the environment, the composition, and the thermal history. An increase in the degree of heating shifts the peak of DTG to a higher temperature.

Under nitrogen rubber degrades thermally, but in air or oxygen degradation is thermo-oxidizing in nature. The presence of filler, vulcanizing agent and antioxidant also affect the thermal degradation of rubber. The presence of filler, vulcanizing agent and antioxidant also affect the thermal degradation of rubber. Representative TGA thermograms of a chewing gum and SBR vulcanized carbon black are shown in Fig 7.

After performing the SEM analyses for all seven samples a spectrum was taken as show a figures. Consequently, the provided chemical analyses are shown in the form of spectra [7]. In Figure 7, stains with a lighter color are easily noticed in the BSE image on the surface of the crumb. These stains witness the presence of foreign elements in the matrix of rubber. Chemical analysis over a number of such stains reveals minor quantities of other elements, such as zinc, silicon, potassium, magnesium, iron, and sulfur. Zinc oxide, together with stearic acid, plays an important role in vulcanization chemistry, called activators. These compounds react together and with accelerators to form a zinc sulfurating compound, which in turn is the key intermediary in adding sulfur to a diene elastomer and creating sulfur interlinks.

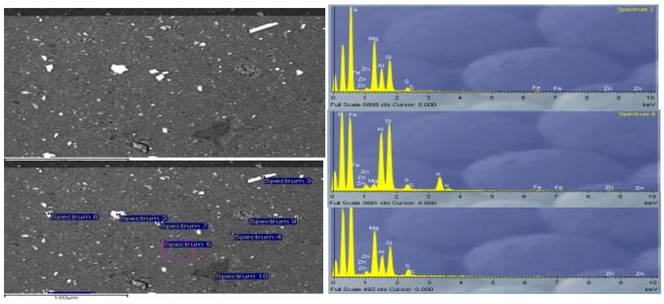


Fig 8. *(left) Micrographs of second rubber with crumb, (right) X-ray spectra of 2nd rubber*

Reinforcing fillers used in rubber with particles of similar shape and size are finely separated silica. Magnesium oxide is needed to give it resistance during vulcanization, mixed with zinc oxide. Magnesia is included in the formulation to act as a chlorine atom searcher. Iron oxides are active fillers which improve the mechanical and magnetic properties of elastomers. Aluminum silicates are good reinforcing fillers, they create relatively stronger vulcanization than other fillers, such as calcium silicates [8].

5. CONCLUSION

The FT-IR infrared vibration spectroscopy method with ATR enables the accurate identification of rubber particles, even in cases when there is a high content of additives in them and when the tires have a high degree of degradation. Determining the degree of degradation is difficult to determine because the intensities of the molecular bond peaks are almost the same for all the rubber particles analyzed.

The analysis of the peaks of the FT-IR spectrum with ATR revealed the basic material of the tires, as well as the presence of some other peaks with low intensity due to the presence of foreign matter. Due to the Tg glazing temperature of the tires, the mode of crystallization affected to a very large extent the obtaining of FT-IR spectra with ATR. Accurate identification of the diaries was difficult to accomplish due to the low intensity of the peaks and their overlap. Thus, for the accurate determination of additives, in addition to the FT-IR method with ATR, an additional method was required for the qualitative determination of chemical elements in tire structures,

• The DSC Differential Calorimetry Scanning method further confirmed the identification of the tires. Analyzing thermographs shows the differences between the samples as they show different values of heat capacity. Samples G-4 and G-7 show almost the same values of heat capacity for the first heating and for the second heating, unlike the other samples, due to the fact that there is no change in the thermal history. Samples G-6 and G-8 show higher values of heat capacity in the second heating compared to the first heating.

From the results of thermograms obtained from the thermal analysis of rubber particles, from recycling the material does not undergo changes in thermoplastic properties. The thermograms obtained in the thermal analysis of the isothermal kinetics of recycled rubber particles show that in all eight materials there is repetition in the general shape of the thermogram and displacement with the time of melting peaks of the two materials at different crystallization temperatures. This can be explained by the presence of various additives that can crystallize, however this needs a more detailed analysis which is in further research work. Different shapes and sizes of additive particles were spread all over the surface (and therefore the volume) of the rubber.

• SEM scanning electron microscopy equipped with EDS power distribution system identified different types of tires and identified the additives used in them, but in small quantities. From the analysis of optical images it was concluded that they were minerals. Their presence affects the physico-chemical-mechanical properties of rubber particles. In some cases the determination of additives was difficult to determine due to the small amount used (the apparatus identifies additives in quantities over 5% by mass), as well as the lack of crystallinity.

From the BSE image analysis the basic rubber matrix was highlighted. Different shapes and sizes of additive particles are spread over the entire surface (and volume) of the rubber. In addition to chemical analysis of additives, we can see defects of rubber microstructure presented as holes and microcumulations. From the XDS spectra was determined the chemical content of foreign elements in the structures of rubber particles, to the composition of chemical elements and literature concluded in the content of additives. Thus proved the use of the main additives in tires such as silicon, aluminum, zinc, magnesium, oxide and potassium. In this case the presence of chlorine may define the rubber as chlorinated. Chlorinated rubber is a type of thermoplastic resin in the form of high hardness powder. It is considered as environmentally friendly resin. With perfect adhesion, it can be used for chemicals and abrasives. Due to its high chlorine content, it is non-combustible and thus used

for the production of fire-retardant paints. Her films exhibit excellent resistance to corrosive elements. Throughout the spread of additives in the particle the eight types of gum particles are identified as silicon, aluminum, zinc, magnesium, calcium and potassium. The presence of these elements is mainly due to the use of mineral fillers such as mica talc, which have been used as lubricants and anti-dust agents. We also see some microdefects in the rubber microstructure. Quantitative determination of these additives was impossible to accomplish due to chemical interactions between them, given that polymers are processed at temperatures above 200^0C.

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