



5th International Conference
"Advanced Composite Materials Engineering "
COMAT 2014
16-17 October 2014, Braşov, Romania

SYNTHESIS AND CHARACTERIZATION OF SOME COMPOSITE MATERIALS OBTAINED FROM ELECTRONIC RECYCLING WASTE, WITH INTERSECTORIAL APPLICATIONS

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Abstract: The main goal of the paper was to obtain and characterize from physical - mechanical, chemical and thermal point of view some new polymer matrix based composites. These composites consist in re-granulated low density polyethylene (LDPE), re-granulated polypropylene (PP) and high density polyethylene (HDPE) grinding, obtained by the recycling from electronic waste and Nano-conductive (NC) powder used as reinforcement material, in order to obtain new composites for inter-sectorial applications (automotive, electrical, etc.). Were been prepared and characterized different samples of composites by varying the percentage of the NC powder relative to the polymer matrix. (3%, 7% and 10%).

Keywords: composite materials, physical-mechanical and thermal characteristics.

1. INTRODUCTION

The recent studies show that Polyethylene (PE), especially high density Polyethylene (HDPE), is the second most widely used material in civil constructions after Polyvinyl chloride (PVC). More, the trend is to diminish (up to complete replacement) the PVC in this sector (due mainly to the high degree of flammability and toxicity of combustion product). HDPE is also very convenient for automotive applications.

The same trend can be observed in the case of Polypropylene (PP), the interest being maxim in the filed of automotive applications.

Therefore, recycling of materials such as PE and PP from electronic waste and their use in construction/ automotive industry (like custom composites) represents a real interest because they can be easily identified and recovered (generally are not mixed with other thermoplastic compounds or contaminants).

2. TECHNICAL REQUIREMENTS

2.1. Materials

The raw materials used to obtain the composite materials are based on: low density Polyethylene (LDPE), high density Polyethylene (HDPE) and Polypropylene (PP), recycled from electronic waste. They were classified as follows: re-granulated LDPE from electronic waste, re-granulated PP from electronic waste and HDPE flakes from electronic waste. These materials were been mixed with different percents of NC powder (3%, 7% and 10%), obtained also from electronic waste

The samples were codified as follows: re-granulated LDPE from electronic waste- M₁; re-granulated LDPE from electronic waste/3NC- M₂; re-granulated LDPE from electronic waste/7NC- M₃; re-granulated LDPE from electronic waste/10NC- M₄; HDPE flakes from electronic waste- M₅; HDPE flakes from electronic waste/3NC- M₆; HDPE flakes from electronic waste/7NC- M₇; HDPE flakes from electronic waste/10NC- M₈; re-granulated PP from electronic waste-M₉; re-granulated PP from electronic waste/3NC- M₁₀; re-granulated PP from electronic waste/7NC- M₁₁; re-granulated PP from electronic waste/10NC- M₁₂.

2.2. Equipments, methods and procedures

2.2.1. *Obtaining raw materials.* Grinding was performed with a SPEX mill type, 8000M series. The milling time was 4 hours, with rotation speed of 875 cycles / min. Grinding was done in metallic or ceramic (tungsten carbide, alumina, zirconia, silicon nitride) mills. Dry milling was the simplest and successfully to use.

2.2.2. *Obtaining composite materials.* In order to obtain a uniform distribution of the components of the mixtures in the whole structure, the reinforcing material (NC powder) and polymers were mixed for one hour in a cylindrical type TURBULA T2F mixer. After homogenization, the mixture was placed in a Dr. Boy 35A injection machine (Germany) where were obtained specimens according to the necessary types of tests to perform.

2.2.3. *Identification of the crystalline phases by X-ray diffraction method* were carried out on a X-ray diffractometer D8 Advance type.

2.2.4. *Determination of mechanical properties (tensile strength and three points bending strength)* was performed on the equipment for mechanical strength in static regime, LFM model 30kN, Walter & Sai AG Switzerland. Shore hardness was determined using a Shore A hardness tester (with measurement uncertainty of 0.6%).

2.2.5. *Qualitative, semi quantitative and quantitative elemental chemical analyzes* were performed on wave length X-ray fluorescence spectrometer S8 Tiger, having wide limits of quantification (from 10 ppm up to 100%).

2.2.6. *Thermal analyzes were:* termogavrimetric analysis and analysis for determining conductivity and thermal diffusivity (measured between 25°C and 95°C). The analyzes were performed on a TG-DSC simultaneous thermal analyzer type STA 449 F3 Jupiter, and respectively a LFA-type device 447 NanoFlash – both from Netzsch (Germany).

2.3. Obtaining composite materials specimens by injection

In order to perform the proposed test program, was necessary to realize some dedicated specimens, using the injection method.

According to each composite material, were chosen the temperatures of the five heating zones of the injection machine cylinder, as follows:

- for re-granulated LDPE from electronic waste recipes : 190/190/200/210/220 (°C)
- for re-granulated PP from electronic waste recipes: 190/195/205/215/225(°C)
- for HDPE flakes from electronic waste recipes: 210/210/210/220/230(°C)

The specimens, having dedicated design, have been subjected to full program of tests, measurements and analyzes to determine the physico-mechanical, thermal and chemical properties, for possible intersectorial applications.

2.4. Identification of the crystalline phases by X-Ray diffraction method

In the Figures 1, 2 and 3 below, are presented the XRD spectra of the composite materials based on LDPE, HDE and PP (with different percents of NC powder). The XRD analyses were performed according to SR EN 13925-1, 2/2003 [1, 2], analysis identifying the network type of crystalline compounds and determining the unit cell parameters and crystallite size.

The XRD spectra of the samples have shown the follows:

- **in the case of re-granulated LDPE from electronic waste recipes** (figure 1): was identified and emphasized the specific structure of LDPE and the basic components of NC powder (Calcium/silicon/titanium oxides);
- **in the case of HDPE flakes from electronic waste recipes** (figure 2): was identified and emphasized the specific structure of a mix between HDPE and PP and also the basic components of NC powder (Calcium/silicon/titanium oxides);
- **in the case of re-granulated PP from electronic waste recipes** (figure 3): was identified and emphasized the specific structure of PP and the basic components of NC powder (Calcium/silicon/titanium oxides);

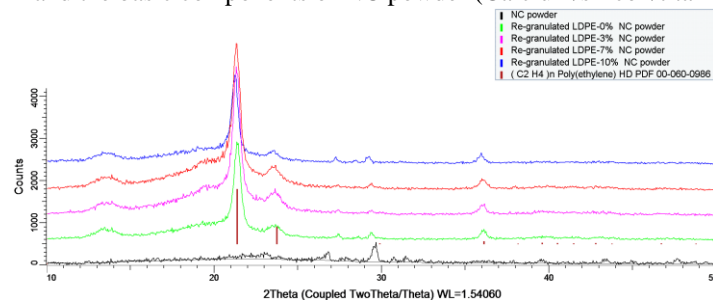


Figure 1 XRD spectra of re-granulated LDPE from electronic waste recipes

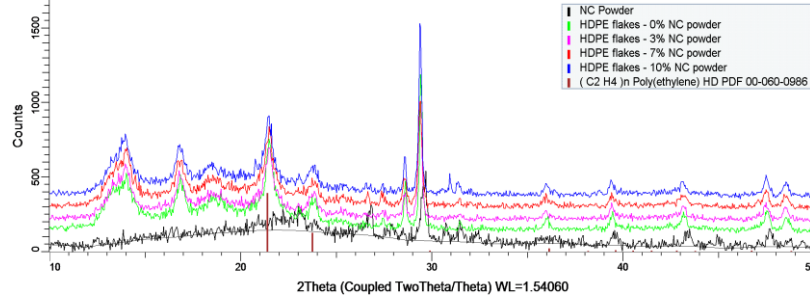


Figure 2 XRD spectra of HDPE flakes from electronic waste recipes

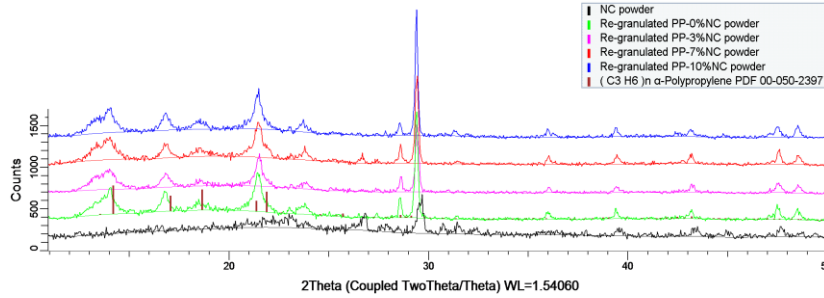


Figure 3: XRD spectra of re-granulated PP from electronic waste recipes

2.5. Determination of mechanical properties

The mechanical properties (tensile strength and three points bending strength) were determined according to the SR EN ISO: 527-2:2000 standard. [3]

2.5.1. Tensile strength

The experimental results are summarized for each type of composite, in the Figure 4, below:

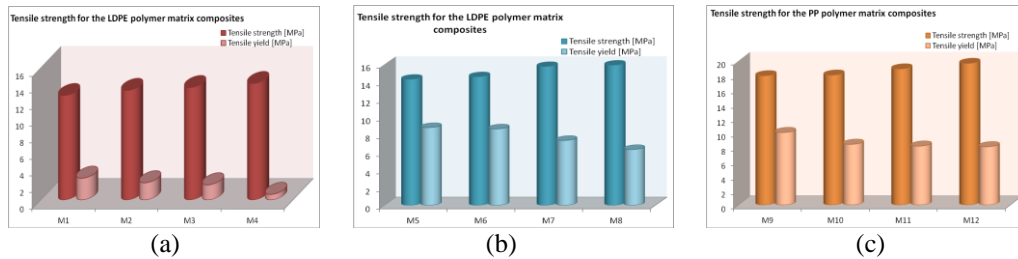


Figure 4: Compared tensile strength for (a) re-granulated LDPE from electronic waste recipes, (b) HDPE flakes from electronic waste recipes and (c) re-granulated PP from electronic waste recipes

The experimental results revealed the following:

- **in the case of re-granulated LDPE from electronic waste recipes:** the best values of the tensile strength were obtained for the sample M4- re-granulated LDPE from electronic waste/10NC. Increasing percentage addition of NC powder, leads to improved tensile strength as follows: $R_m M_2 > 5\% R_m M_1$; $R_m M_3 > 7\% R_m M_1$ and $R_m M_4 > 10\% R_m M_1$

- **in the case of HDPE flakes from electronic waste recipes:** the best values of the tensile strength were obtained for the sample HDPE flakes from electronic waste/10NC- M₈. Increasing percentage addition of NC powder, leads to improved tensile strength as follows: $R_m M_6 > 2\% R_m M_5$; $R_m M_7 > 9\% R_m M_5$ and $R_m M_8 > 10\% R_m M_5$

- **in the case of re-granulated PP from electronic waste recipes:** the best values of the tensile strength were obtained for the sample M12- re-granulated PP from electronic waste/10NC. Increasing percentage addition of NC powder, leads to improved tensile strength as follows: $R_m M_{10} > 0,5\% R_m M_9$; $R_m M_{11} > 5\% R_m M_9$ and $R_m M_{12} > 9\% R_m M_9$.

2.5.2. Three points bending strength

The experimental results are summarized for each type of composite, in the Figure 5, below:

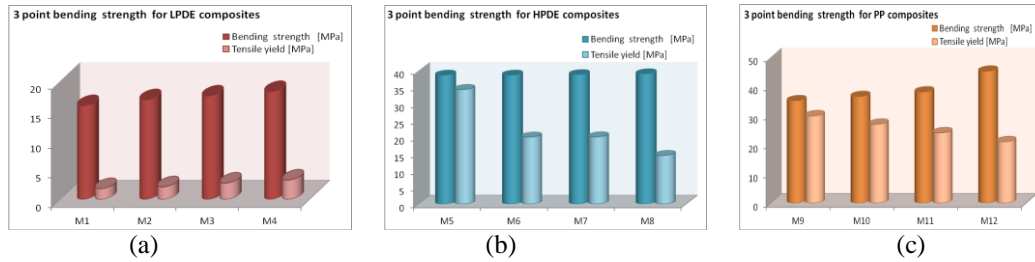


Figure 5: Compared three points bending strength for (a) re-granulated LDPE from electronic waste recipes, (b) HDPE flakes from electronic waste recipes and (c) re-granulated PP from electronic waste recipes

The experimental results revealed the following:

- **in the case of re-granulated LDPE from electronic waste recipes:** the best values of the bending strength were obtained for the sample M4- re-granulated LDPE from electronic waste/10NC. Increasing percentage addition of NC powder, leads to improved the bending strength as follows: $Rm M_2 > 6\% Rm M_1$; $Rm M_3 > 9\% Rm M_1$ and $Rm M_4 > 13\% Rm M_1$
- **in the case of HDPE flakes from electronic waste recipes:** the best values of the bending strength were obtained for the sample HDPE flakes from electronic waste/10NC- M₈. Increasing percentage addition of NC powder, leads to a very slight improved the bending strength as follows: $Rm M_6 > 0.03\% Rm M_5$; $Rm M_7 > 0.4\% Rm M_5$ and $Rm M_8 > 1\% Rm M_5$
- **in the case of re-granulated PP from electronic waste recipes:** the best values of the bending strength were obtained for the sample M12- re-granulated PP from electronic waste/10NC. Increasing percentage addition of NC powder, leads to improved the bending strength as follows: $Rm M_{10} > 4\% Rm M_9$; $Rm M_{11} > 8\% Rm M_9$ and $Rm M_{12} > 22\% Rm M_9$.

2.5.3. Shore hardness

Shore hardness was determined using a Shore A hardness tester (with measurement uncertainty of 0.6%), according to ASTM D 785 standard [4]. The values are represented as average of three measurements on each sample.

The statistical analysis leads to very closed values in terms of Shore hardness for all samples, whatever the nature of the composite (LPDE, HDPE or PP). More than, increasing percent of the NC powder, does not lead to modify the values of Shore hardness.

2.6. Chemical elemental analysis using X-Ray fluorescence spectrometry technique

Due the fact that the intermediate percents of NC powder (3% and respectively 7%) do not lead to supplementary information in the case of such type of analysis, the chemical elemental analysis was performed only on the samples prepared without NC powder (M₅ and M₉) and with 10% NC powder (M₄ and M₁₂).

The analysis were been perform according to the internal procedure PI-18/2013 and the Operating Manual of the S8 TIGER device [5].

The figures 6-9 below, show the chemical composition identified for each composite analyzed:

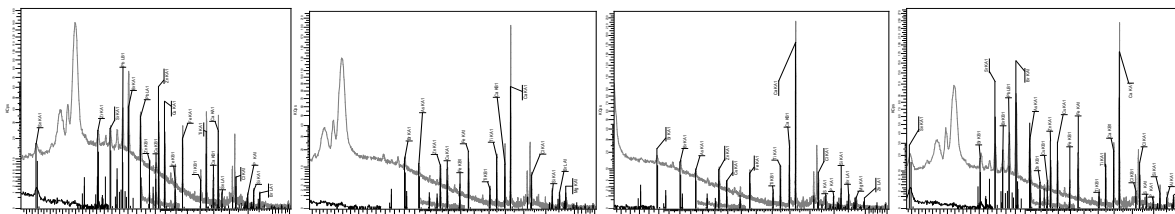


Figure 6: chemical elemental composition of sample M₄

Figure 7: chemical elemental composition of sample M₅

Figure 8: chemical elemental composition of sample M₉

Figure 9: chemical elemental composition of sample M₁₂

The results indicate the following:

- The NC powder used as reinforcing material, contains mainly elements: Si, Ca, Fe, Al, Cu, Pb, Ti, Sn, P, Sr (like oxides);
- The reference polymeric materials (LDPE, HDPE and PP) are chemically pure and is only emphasized organic matrix without any inclusions, impurities or additives

- The LDPE based composites have in composition additionally to polymeric matrix, elements such Ca, Ti, Si, and Fe (like oxides);
- The HDPE based composites have in composition additionally to polymeric matrix, the elements Ca, Ti and Si (like oxides);
- The PP based composites, have in composition additionally to polymeric matrix, the elements Ca, Ti, Si and Mg (like oxides);
- In all cases, the NC powder added in 10 percent into the polymeric matrix, leads both to the increasing of the common elements concentration and the appearance in the chemical composition of specific items only for NC powder (such as. Sn and Zr). This indicates an appropriate degree of mixing of polymers with NC powder during injection process to realize the testing samples.

2.7. Determination of thermal properties

2.7.1. Thermal gravimetry and dynamic scanning calorimetry analysis (TG-DSC)

The analysis was performed according to the ASTM E831-2006 standard [6].

In the Figure 10 below, are presented the thermograms of the analyzed samples:

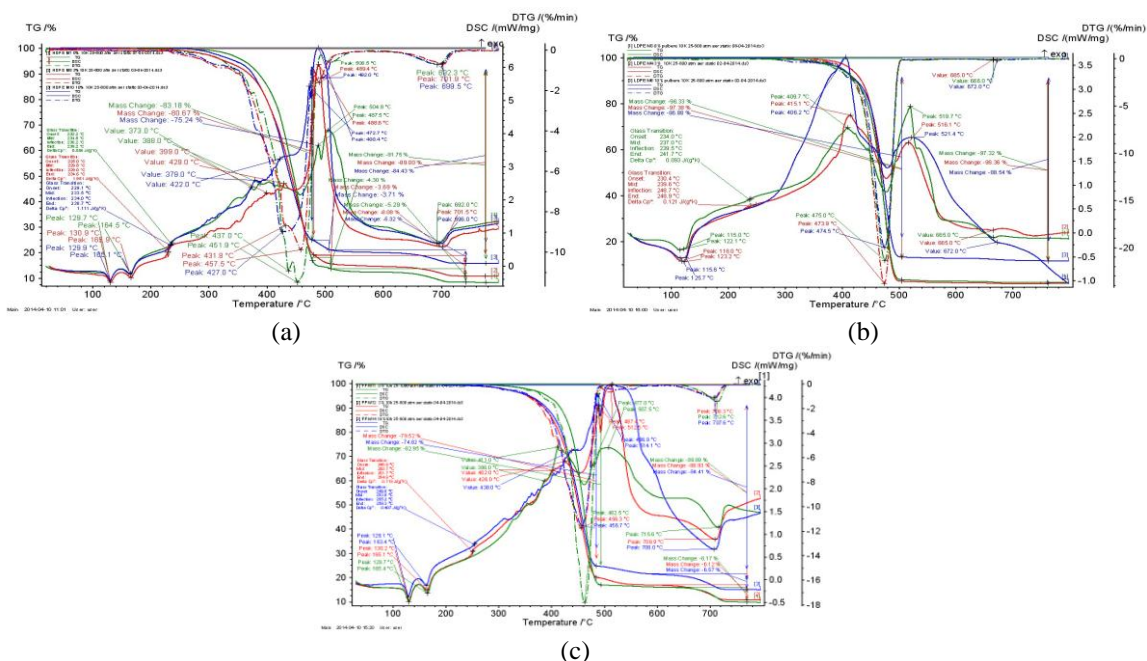


Figure10: TG- DSC curves for (a) HDPE flakes from electronic waste recipes, (b) re-granulated LDPE from electronic waste recipes and (c) re-granulated PP from electronic waste recipes

The thermograms represent an average result of determinations on three different samples, with a confidence level of 95% .

The materials present a similar behavior due the polymeric matrix. This behavior is limited to a series of phenomena, clearly identified in TG-thermal mass loss and their related derivative- DTG. DSC curves shows the absorbed or given heat by such materials in dynamic regime (differential scanning calorimetry).

- ♦ **Process I – Melting.** In all cases is distinguished the melting point (a glass transition of second kind).
 - In the case of HDPE flakes from electronic waste recipes and re-granulated PP from electronic waste recipes , it shows a split of melting phenomenon, which may be due to re-granulation of polymeric material and to the addition of reinforcing powder.
 - In the case of re-granulated LDPE from electronic waste recipes, it appears only the tendency to split the melting process, but without area widening.
- **Process II Oxidation .** In all cases can be observed the beginning of the oxidation around 300°C. It is distinguished also the related mass loss TG-DTG.
- **Process III Thermo-oxidation.** This process is outlines in the TG – DTG curves.
- **Process IV Decomposition.** In the case of pure polymeric materials it observes a behavior consisting of a melting process, a glass transition (only for LDPE) and an oxidation-thermo-oxidation process. Compared to the pure polymeric materials, the analyzed composites shows a trend of translation of thermal phenomena to higher temperatures. This phenomenon is confirmed by the temperature differences found during glass transition

process, where is observed increasing of starting process temperature, which may be due both to material re-granulation and NC powder addition.

2.7.2 Thermal conductivity

The thermal conductivity measurements were been conducted between 25°C si 95°C, according to the ASTM E-1461:2007 standard, using “flash” method [7].

In the figure 11 below, is presented compared the variation of the thermal conductivity for each type of samples:

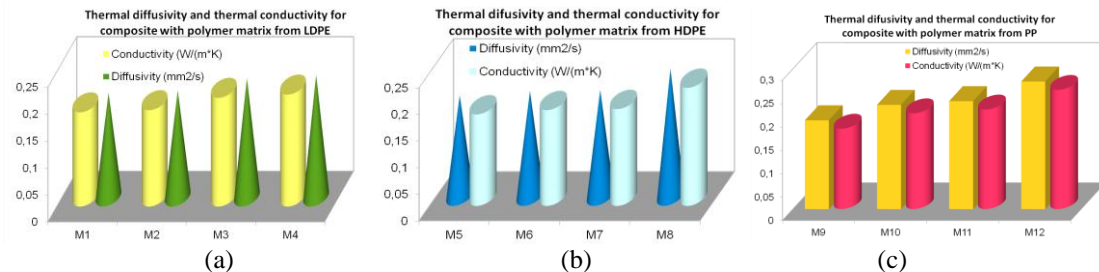


Figure 11: The variation of thermal conductivity for (a) re-granulated LDPE from electronic waste recipes, (b) HDPE flakes from electronic waste recipes and (c) re-granulated PP from electronic waste recipes

The experimental results show that the adding of increased percents of NC powder, has not important influence in terms of thermal conductivity. Anyway, the best values were obtained for the receipes containing the highest percent of NC powder (10%), respectively: re-granulated LDPE from electronic waste/10NC- M₄; HDPE flakes from electronic waste/10NC- M₈ and re-granulated PP from electronic waste/10NC- M₁₂. Of these, the best value was obtained for the re-granulated PP from electronic waste/10NC- M₁₂ composite.

3. CONCLUSIONS

The tests conducted on the composites based on some materials from electronic waste, were able to draw the following conclusions:

- The composites based on different polymers (LDPE, HDPE and PP) from electronic waste, have basic polymer composition. The adding of the NC powder like reinforcing material, leads in all cases to the appearance of specific peaks in the existing compounds (oxides of calcium, titanium, silicon and / or combinations thereof);
- Mechanical -tests have emerged as the best option composite the re-granulated PP from electronic waste/10NC- M₁₂;
- Chemical tests indicate that NC powder (used in all three types of composites) contains mainly elements Si, Ca, Fe, Al, Cu, Pb, Ti, Sn, P, Sr (like oxides). Reference materials (LDPE, HDPE and PP) are almost chemically pure and is only emphasized the organic matrix, without any inclusions, impurities or additives;
- The thermal analyses revealed the presence of melting, glass transition (only for LDPE) and oxidation-thermo-oxidation processes. Compared to the reference materials, the reinforced composites show a trend of translation of thermal phenomena to higher temperatures.
- Thermal conductivity highest value was found also for is the best option for re-granulated PP from electronic waste/10NC- M₁₂;

All the tests indicate the re-granulated PP from electronic waste/10NC receipt as the best option for intersectorial applications.

4. REFERENCES

- [1] SR EN 13925-1, 2/2003 Qualitative phase analysis
- [2] SR EN 13925/3 -2005 and PI - 04
- [3] SR EN ISO: 527-2:2000 – Plastic materials. Tensile strength. Part 2-Test conditions for injected and extruded plastic materials. Test Method for Rockwell Hardness of Plastics and Electrical Insulating Materials.
- [4] PI-18/2013 and Operating Manual of the S8 TIGER device
- [5] Workstation Auriga SmartSEM V05.04.
- [6] ASTM E831-2006 Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis.
- [7] ASTM E-1461:2007 Standard Test Method for Thermal Diffusivity by the Flash Method